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OF RESEARCHES IN ENGINEERING: C

# Chemical Engineering

Characterization of Biodiesel

Production of Biodegradable

Highlights

Biodegradable Equal Mixture

Polymer Blend of PVA and PVP

### **Discovering Thoughts, Inventing Future**

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## Natural Dyeing of Silk with Eucalyptus Leaves Extract

### By Nivea Taìs Vila

Federal University of Technology Owerri

*Abstract-* This study aimed to evaluate the process of silk dyeing with the extract of eucalyptus leaves. pH, temperature, initial extract concentration was investigated. The initial extract concentration of 20 g L-1, pH 3 and temperature of 90 °C were the conditions which yielded the best results from dyeing. The pseudo-second order model was the one that best represented the kinetic mechanism of dyeing, indicating that chemisorption was the main mechanism involved. The equilibrium data were adjusted to the Langmuir-Freundlich model indicating significant contribution from the chemisorption process. Dyeing with the extract of eucalyptus leaves is a spontaneous and endothermic process with a high degree of disorder. The notes washing fastness of dyed fabrics were 3-4 for the color change and 4 for staining on cotton and wool.

Keywords: adsorption, coloration, washing fastness, langmuir-freundlich model.

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## Natural Dyeing of Silk with Eucalyptus Leaves Extract

Nivea Taìs Vila

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#### I. INTRODUCTION

he art of applying color in fabrics has been known for a long time. Historical records of the use of natural dyesextracted from vegetables, fruits, flowers, insects and also fish date back to3500 BC. However, the importance of natural dyes disappeared since the advent of synthetic dyes, which have a wide range of colors and shades as their main advantages(Gurley, 1996; Kant, 2012).

The generation of liquid effluents is a significant environmental problem, since mostsynthetic dyesare complex aromatic molecular structures, which make them inert with difficulty inbiode grading when discharged into the environment(Khouni, Marrot, Moulin, & Ben Amar, 2011; Samanta & Agarwal, 2009).

In the last years, the dyestuffs in dustry has been increasingly forced to reducetoxic effluents and stop the production of potentially azardous dyes and pigments(Mirjalili, Nazarpoor, & Karimi, 2011).Moreover, due to the in creased perception of environmental and health risks associated with the synthesis, processing, and use of synthetic dyes, interest in natural dyes has in creased worldwide. Therefore, a new market that value sproducts originated from natural raw materials is growing, with huge advantages to the environment(Ali, 2007; Becht old & Mussak, 2009). Natural dyes are environmentally compatible, biodegradable, nontoxic, free of allergic effects, as well as available from a wide range of sources that includes coloring from plants, insects, fungi and minerals(Ibrahim, El-Gamal, Gouda, & Mahrous, 2010).

Among such a wide range of natural dyes, eucalyptus deserves special attention because this tree may be found in many countries. The main components of eucalyptus leaves that are responsible for the color given to textile materials are tannins (gallic acid and ellagic acid) and flavonoids (rutin and quercetin). These substances are considered very use fulduring the dyeing processdue to their ability to fix the dye within fabrics. Figure 1 shows the structures of the components responsible for color found in eucalyptus leaves(Mongkholrattanasit, Kryštůfek, & Wiener, 2011). In all molecules there are hydroxyl groups and oxygen atoms that may be related to hydrolysis or partial charges, which are probably responsible for attraction to the silk residual groups.



Figure 1: Color composition of eucalyptus leaves extract.

Author: e-mail: nivea980@hotmail.com

The silk is composed of a protein called fibroin surrounded by a gum called silk sericin, removed in the degumming process. Therefore, the silk fabric is basically fibroin. Fibroin consists of a long parallel chain containing about 400 amino acid residues with the structure of the general type as shown in Figure 2 (Iqbal, 2008).



Figure 2: General structure of the fibroin.

The residues are derived mainly from the amino acids glycine (R = H), alanine (R =  $CH_3$ ), serine (R =  $CH_2OH$ ) and tyrosine (R = -  $CH_2$  --- OH), but there are many others in small amounts (Iqbal, 2008; Needles, 1986).

In the dyeing process, the colorants in solutions hould adsorb, diffuse in to the fiber and finally, establish with it physicochemical linter actions (Alcântara & Dalt in, 1996; Salem, 2010). Unfortunately, such mechanisms are not well understood as the process is stillempirical. The dyeing procedure and mainly the adsorption mechanism have been scarcely reported.

In this context, the objective of this work was to study the ideal conditions for silk dyeing with eucalyptus leaves extract. Parameters such as initial concentration, pH and temperature were investigated. The amount of eucalyptus extract retained and color fastness to washing were the response parameters. The dyeing mechanism was investigated through kinetic and isotherm models. Thermodynamic parameters were also obtained.

#### II. MATERIAL AND METHODS

#### a) Materials

Eucalyptus leaves (Eucalyptusgrandis) were used in this work. Initially, the fresh eucalyptus leaves were dried in the open air for fifteen days and crumbled in a blender.

Solutions of the eucalyptus leaves extract were prepared adding 10, 15 or 20 g of crumbled leaves in 1000 mL of distilled water. Samples were then heated with stirring at90 °C for 60 min and then filtered. The filtrated solution was used in the dyeing process.

Concentration of the dyeing solutions was analyzed through spectro photometry. At first, the wavelength of maximum absorption ( $\lambda_{max}$ ) of the filtrated solution was obtained through the 1601DCS himadzue quipment. Biospectro SP 22 spectrophoto meter was calibrated with  $\lambda_{max}$  to obtain the extract concentration in solution.

Pure silk fabric ready for dyeing (70 gm-<sup>2</sup>) was used. The non-ionic detergent Nionlab CELM was

applied in the fastness to washing procedure. Concentration of 2 g  $L^{-1}$  was used.

#### b) Dyeing process

Influence of temperature, pH and initial concentration of extract solutions was studied through a2<sup>3</sup> complete factorial design composed of eleventrials, three trialsas the central point. Dyeing of each sample lasted 60 minin AT1-SW Kimak equipment with a liquor ratio 1:100.The response variable was the amount of extract adsorbed in the fabrics. Table 1 lists the variables and levels for dyeing. Design-Expert software version 7 was used.

Table 1: Factorial design for dyeing of silk fabrics

Numeric variables	Levels		Central
	-1	1	0
T (°C)	80	90	85
рН	3.0	4.0	3.5
Initial concentration of extract (gL <sup>-1</sup> )	10	20	15

After dyeing, the samples were subjected to washing with the non-ionic detergent solution at 60  $^\circ\mathrm{C}$  for 10 min., rinsed in cold water and dried at room temperature.

The amount of extract adsorbedper gram of silk (q) (mgg-<sup>1</sup>) was determined through a mass balance as described in Equation(1):

$$q = \left(C_0 - C_f\right) \frac{V}{W} \tag{1}$$

where Vis the volume of the solution(L), W is the weight of the silk (g), C0 is the initial concentration of extract(mgL- $^1$ ) and Cfis the extract concentration after dyeing(mgL- $^1$ ).

#### c) Kinetic of the dyeing process

Silk fabrics were put in contact with eucalyptus extract in AT1-SW Kimak equipment in the

experimentally optimized conditions given by the response variable of Table1.

The fabrics were fast removed after dyeing at different times. After cooling, all effluents were subjected to spectro photometric reading and extract concentrations determined.

The amount of extract adsorbed per gram of fabric (qt) (mg g-<sup>1</sup>), at any time t, was calculated using Equation (1), where Cf takes the value of the concentration at time t (Ct).

Experimental data was modeled through the pseudo-first order and pseudo-second order kinetic models. The pseudo-first order kinetic equation is the well-known Lagergren Equation(Lagergren, 1898). It may be expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{2}$$

where  $q_e$  (mg g<sup>-1</sup>) stands for the amount of eucalyptus extract when equilibrium is reached and k1 is the pseudo-first order rate constant (min<sup>-1</sup>).

For the integration of Equation (2) with boundary conditions at t = 0, qt = 0, and at t = t, qt = qt, the nonlinear form of the equation becomes:

$$q_t = q_e (1 - \frac{1}{e^{k_l t}})$$
 (3)

The pseudo-second order equation is:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{4}$$

where  $k_2$  is the pseudo-second order rate constant (g mg<sup>-1</sup>min<sup>-1</sup>) (Ho, 2006).

Integration of Equation (4) generate:

$$q_{t} = \frac{k_{2}q_{e}^{2}t}{1 + q_{e}k_{2}t}$$
(5)

The pseudo-second order rate expression is used to describe chemisorption involving valence forces through the sharing or exchange of electrons between the eucalyptus extract and the fabric as covalent forces (Ho, 2006).

#### d) Equilibrium of the dyeing process

The equilibrium data was carried out using solutions of extract with different concentrations at 70, 80 and 90 °C and the best pH given by results of the factorial design. Solutions were put in contact with the silk samples up to the equilibrium time obtained in the previous section.

The Langmuir adsorption isotherm has been successfully applied to a wide range of aqueous

adsorption processes, including dyeing(Arora, Gupta, Rastogi, & Gulrajani, 2012; Kong kachuichay, Shitangkoon, & Hirunkitmonkon, 2010; Lagergren, 1898). A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, a saturation value is reached when no further adsorption can take place. The saturated monolayer curve can be represented by the Equation (6):

$$q_e = \frac{q_{\max}bC_e}{1+bC_e} \tag{6}$$

where in the equation, qmax (mg g-1) is the maximum amount of the eucalyptus extract per unit weight of silk to form complete monolayer coverage of the surface. It represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules; b is the Langmuir constant related to the affinity of binding sites (L mg-1)(Arora et al., 2012; Lagergren, 1898; Langmuir, 1918).

The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. Besides being more applicable, the Freundlich isotherm provides no information on the monolayer adsorption capacity. It predicts a multilayer adsorption process and is written by Equation (7):

$$q_e = k_F C_e^n \tag{7}$$

where kF is the adsorption equilibrium constant of Freundlich (L g-1) and n is the heterogeneity. In general, as the kF value increases, the adsorption capacity increases. Values of n between 1 and 10 show favorable adsorption. If n < 1 and  $n \rightarrow 0$ , the silk fabric is saturated with the eucalyptus extract since adsorption energies decreases with surface density (Dávila-Jiménez, Elizalde-González, & Peláez-Cid, 2005; Freundlich, 1906).

The experimental data may be also fitted to the three-parameter model of Langmuir-Freundlich when the two-parameter models of Langmuir and Freundlich do not provide reasonable results. The Langmuir-Freundlich model is able to describe both the adsorptive behavior characteristic of the Langmuir type as the Freundlich. Normally this model fits better in cases where the adsorbent has heterogeneous surface, as it is the case of silk,(Iqbal, 2008; Needles, 1986) and is commonly expressed by the Equation (8):

$$q_{e} = \frac{[q_{m}(K_{LF}C_{e})^{n}]}{[1 + (K_{LF}C_{e})^{n}]}$$
(8)

Where KLF is the adsorption constant of Langmuir-Freundlich (L mg-1), qmaxis the maximum

adsorption capacity (mg g-1), and n is the parameter of heterogeneity (Chiou & Li, 2003).

#### Thermodynamic parameters e)

Gibbs free energy ( $\Delta G^{\circ}$ ), enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) were calculated by the Equations (9), (10) and (11) in 70, 80 and 90 °C.

$$K_c = \frac{C_{ad,e}}{C_e} \tag{9}$$

$$\Delta G^{\circ} = -RT \ln K_c \tag{10}$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(11)

where  $K_c$  is the equilibrium constant, and  $C_{ad,e}$  and Ce are the eucalyptus extract concentration adsorbed at equilibrium with the concentration in the fluid phase (mg L-<sup>1</sup>), respectively.

#### Color fastness to washing *f*)

Sample dyed in the experimental optimized conditions provided by results of Table 1 was submitted to color fastness to washing.

The wash fastness test followed the procedures of ISO 105-C06: 2006 A1S cycle - Tests for color fastness: Part C-06: Color fastness to domestic and commercial laundering(ISO, 2006). Evaluation of the transfer and change of color of the samples was performed using 550 Data color spectrophotometer.

#### **RESULTS AND DISCUSSION** III.

#### Wavelength of Maximum Absorption a)

The UV-Vis wavelength range is show in Figure 3. The extracts were able to absorb UV-C (wavelength below 280 nm), UV-B (280-315) and UV-A (315-400) regions (Feng et al., 2007). The highest absorbance was found at 197 nm



Figure 3: UV-Vis spectrum of eucalyptus leaf extract.

Although there has not been any kind of isolation of the substances responsible for dyeing with the aqueous extract of eucalyptus leaves, the absorption in the region 190-210 nm can be attributed to various chromophores, including the C = C bond of various compounds, carbonyl compound bonding (C = O) and the benzene ring, probably from aromatic compounds. Absorption in the region of 250-270 nm can be attributed to electronic transitions of benzene and its derivatives, which may include various aromatic compounds such as phenolics (Pretsch, Buhlmann, & Badertsscher, 2009). Absorption in the regions of 240-285 nm and 300-550 nm, in turn, are characteristic of flavonoid compounds(Lombard, Geoffriau, & Peffley, 2002).

The wavelength of 380 nm was used in all concentration analysis due to experimental limitations of the Biospectro SP22 UV-Visible spectrophotometer, with a range of 300-1000 nm.

#### Silk Dyeing with Eucalyptus Extract b)

All samples of the dyeing process showed different yellowish-brown coloration, according to the amount of extract adsorbed.

Results of the factorial design are shown in Table 2.

Test	Concentration (mg L <sup>-1</sup> )	Temperature (°C)	рН	<i>q</i> (mg g <sup>-1</sup> )	Color
1	-	-	-	149	
2	+	-	-	290	
3	-	+	-	197	
4	+	+	-	350	
5	-	-	+	86	
6	+	-	+	237	
7	-	+	+	102	
8	+	+	+	274	
9	0	0	0	210	
10	0	0	0	220	
11	0	0	0	207	

Table 2: Results of the 2<sup>3</sup> factorial design used in evaluating the influence of the variables on the response (q) for the silk dyeing with eucalyptus extract

It was seen that the initial concentration of extract had a huge influence in the amount of eucalyptus extract retained in the silk fabric. Actually, concentration of 20 g L-1 promoted higher values of q than the diluted concentration of 10 g L<sup>-1</sup>. It happened due to the increase of the concentration gradient. Then, it may be concluded that initial concentration of extract played an important role in the adsorption capacity of eucalyptus extract onto silk, which is in total agreement with results already reported (Chairat, Rattanaphani, Bremner, & Rattanaphani, 2005; Farizadeh, Montazer, Yazdanshenas, Rashidi, & Malek, 2009; Lagergren, 1898: Septhum. Rattanaphani, Bremner. ጲ Rattanaphani, 2009).

Increasing temperatures also favored the adsorption process. It may be seen that 90 oC originated higher values of q if compared to 80 oC. It emphasizes that chemisorption is very important in the dyeing process. The positive influence of temperature may reflect an increase in the mobility of large extract molecules. If so, an increase in the number of molecules interacting with the active sites at the silk fabric was expected(Lagergren, 1898).

Lower pH values provided higher q values. As the isoeletric point of silk filber varies between pH 3.6 and 5.2(Sashina, Bochek, Novoselov, & Kirichenko, 2006) at pH 3 the fiber was more positively charged. In this case, the acidic and, especially the protonated amino groups of the silk fiber are of prime importance in the uptake of anionic dyestuffs presented in the eucalyptus extract (Lagergren, 1898). In such a case, adsorption occurred as a result of electrostatic forces, such as ion-ion forces and H-bonding, with van der Waals forces and hydrophobic interaction. Although not knowing all molecular structures presented in the eucalyptus extract, probably  $\pi$  -  $\pi$  could not be neglected as well(Tang, Tang, & Yang, 2010).

Specifically. the attraction between the eucalyptus extract and the fiber may have occurred primarily by the large amount of tannins in the eucalyptus leaves, since tannins contain phenolic compounds that can form hydrogen bonds with the carboxyl groups of silk. There are two other possibilities of interaction involved: (a) anionically charged phenolic groups form an ionic bond with cationic (amino groups) in the silk, and (b) a covalent bond may also form through an interaction between any quinine or semiguinone groups present in the tannins and suitable reactive groups on the silk(Mongkholrattanasit. Kryštůfek, & Wiener, 2011). Such mechanism may emphasize the main contribution of chemisorption although physisorption could be also present (Tang et al., 2010).

Considering the dyeing parameters studied herein, the highest response value was found in test 4, in which the initial concentration of 20 g L-<sup>1</sup>, pH 3 and 90 <sup>o</sup>C promoted the highest amount of 350 mg of eucalyptus extract per g of silk. The effect and the contribution percentage on the response variable (q) are shown in Table 3.

Term	Effects	Contribution (%)
A – Initial Concentration of extract (mg L <sup>-1</sup> )	154.57	77.10
B – Temperature (°C)	39.75	5.10
C – pH	-71.76	16.62
Interaction AB	8.28	0.22
Interaction AC	7.18	0.17
Interaction BC	-13.80	0.61
Interaction ABC	2.21	0.02
Curvature	15.85	6.70.10 <sup>-3</sup>
Lack of fit	-	0.00
Pure error	-	0.15

Table 3: Main effect and interaction between variables and the percentage contribution of the effects on the response variable for silk dyeing with eucalyptus extract

It was seen that the initial concentration of eucalyptus extract had the greatest contribution in increasing the response variable (g), followed by pH and the temperature. Furthermore, the effect of pH on response variable was negative. It means that an increase in that variable decreased the value of q, which is in agreement with the experimental data.

#### c) Adsorption Kinetics

Figure 3a shows that the kinetic data carried out under the optimal conditions of 20 mg L-1, 90 oC and pH 3 given by test 4. It may be seen that adsorption was very fast in the early stages of contact time and gradually decreased with time until it remained constant in the optimum contact time of 60 min. The same behavior was observed in the work of Septhum et al. (2009) and Samanta & Konar (2011). Hence, subsequent equilibrium experiments took into account such contact time. The higher dyeing rate in the early stages is possibly due to a large number of available sites of adsorption in the silk. Decrease in the adsorption rate was a consequence of decrease in the concentration gradient due to the increased number of sites already occupied by the extract molecules.

The nonlinear fit of pseudo-first-order and pseudo-second-order models is shown in Figure 3b and c, respectively.



Figure 4: Dyeing kinetics a) Effect of contact time of the kinetic adsorption of the eucalyptus extract on silk. b) Graphic model of pseudo first-order. c) Graphic model of pseudo second-order.

It was observed experimental data was better described by the pseudo-second order model. Indeed, Table 4 presents the quantitative results of the adjustments. It can be seen that higher correlation factor  $R^2$  occurred in the pseudo-second-order model. Moreover, the amount of eucalyptus extract experimentally retained in the equilibrium was very similar to the value estimated through the model.

Table 4: Comparison of kinetic model	s pseudo-first and second-order
--------------------------------------	---------------------------------

<i>q<sub>e,exp</sub></i> (mg g⁻¹)	Pseudo first-order model				
	k <sub>1</sub> (min <sup>-1</sup> )	$q_{e,cal}~({ m mg~g}^{ extsf{-1}})$	R <sup>2</sup>		
	0.10091 ± 0.015	355 ± 12	0.946		
372	Pseudo second-order model				
	k <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	$q_{e,cal}~({ m mg~g}^{ extsf{-1}})$	R <sup>2</sup>		
	$0.00034 \pm 0.000r06$	399 ± 12	0.978		

These data suggested that pseudo-second order kinetics model was predominant and that the overall rate of adsorption of eucalyptus extract on silk was likely controlled by the chemisorption process(Lagergren, 1898). Adsorption of dyes in specific sites of silk was already reported(De Giorgi & Cerniani, 1991) and this is in agreement with the influence of temperature and the possible attraction of the molecules to the positively charged silk at pH 3.

#### d) Adsorption Isotherm

Equilibrium data and adjustments to Langmuir, Freundlich and Langmuir-Freundlich isotherm models are shown in Figure 4a, b and c, respectively. At first, it should be emphasized the favorable shape of the isotherms, mainly with increasing temperatures, which is characteristic of endothermic processes. This result may reflect an increase in the mobility of the dye ionic charges with temperature as already discussed. In the very beginning of the isotherm it was seen an induction period, which means that the dye molecules had nearly the same affinity for more dye molecules as the initial sites of the silk fabric, characteristic of cooperative adsorption. The rise and the pronounced plateau was attributed to the development of the monolayer as a new surface where chemisorption could also occur. Then, this plateau represented the saturation of such new surface. These isotherms may be classified as type S2 according to Giles, MacEwan, Nakhwa, & Smith(1960).



*Figure 5:* Adsorption isotherms models a) Langmuir. b) Freundlich. c) Langmuir-Freundlich.

It is well known that the Langmuir model may represent equilibrium data where chemisorption process is involved, forming a dye monolayer in the silk (Chairat et al., 2005; Vinod, Puttaswamy, Gowda, & Sudhakar, 2011; Wei, Chen, Chen, Tang, & Zhang, 2013).

Possibly, the monolayer occurred with the interaction between the hydroxyl groups of the dve and the amino groups of the silk protein, (Vinod et al., 2011) as already seen. On the other hand, the Freundlich model is related to a multilayer process and may represent some dyeing process as well(Chairat et al., 2005; Sawada & Ueda, 2003). Therefore, the Langmuir-Freundlich model that emphasizes the importance of both phenomena comes naturally as the model that may represent the equilibrium data of the eucalyptus extract in the silk fabric. In fact, experimental data obtained at

70, 80 and 90 °C were visually better adjusted to such model.

Regression parameters for the model of Langmuir, Freundlich and Langmuir-Freundlich are shown in Table 5. Actually, neither Langmuir nor Freundlich single models provided reasonable adjustments according to the low correlation factor R<sup>2</sup> and high deviations of the parameters. As already expected, equilibrium data was better fitted to the Langmuir-Freundlich model, which is in total agreement with the isotherm shape.

loothorm	Parameters	70 °C	80 °C	90 °C
Isotherm	$q_{maxexp.}$ (mgg <sup>-1</sup> )	376	402	428
	$q_{max}$ (mg g <sup>-1</sup> )	$640 \pm 77$	721 ± 102	$661 \pm 68$
Langmuir	В	$0.00008 \pm 0.00002$	$0.00008 \pm 0.00002$	$0.00012 \pm 0.00003$
	R <sup>2</sup>	0.974	0.971	0.972
	k <sub>F</sub>	$0.81 \pm 0.65$	$0.68 \pm 0.57$	1.68 ± 1.31
Freundlich	Ν	$1.58 \pm 0.22$	$1.52 \pm 0.21$	$1.74 \pm 0.26$
	R <sup>2</sup>	0.929	0.928	0.913
	$q_{max.}~(\mathrm{mgg}^{-1})$	$414 \pm 11$	440 ± 14	$458 \pm 8.7$
Lanamuir	k <sub>LF</sub>	$0.00019 \pm 8.22.10^{-6}$	$0.00019 \pm 9.17.10^{-1}$	$0.00024 \pm 7.48.10^{-6}$
Eanymui- Froundlich			6	
Treundlich	Ν	$1.87 \pm 0.12$	$1.96 \pm 0.15$	1.96 ± 0.11
	R <sup>2</sup>	0.998	0.997	0.998

Table 5: Model parameters of Langmuir, Freundlich and Langmuir-Freundlich isotherm

The Langmuir-Freundlich model may predict gmax close to the experimental value gmax.exp at 70, 80 and 90 °C. The heterogeneity parameter, n. assumes values slightly greater than unity, indicating an approximation to Langmuir isotherm, with the formation of a homogeneous monolayer. Similar results can be seen in Tang et al.(2010) where adjustments to Langmuir-Freundlich model were obtained. Such model

includes contribution physisorption of and chemisorption, with n equal to unity.

#### Thermodynamic parameters e)

The results of the thermodynamic parameters,  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  of eucalyptus extract adsorption are shown in Table 6.

Table 6: Thermodynamic parameters for the adsorption of eucalyptus extract onto silk

Temperature (°C)	K°	∆G° (J mol⁻¹)	ΔH° (J mol⁻¹)	∆S° (J mol⁻¹K⁻¹)
70	45.76	-10934		
80	49.78	-11283	10258	61.61
90	55.76	-12166		

The highest value of  $K_c$  was obtained at 90 °C, indicating the most favorable equilibrium among the temperatures studied herein. Such results were in agreement with isotherm experimental data and the factorial design.  $\Delta G^{\circ}$  values were all negative, indicating that the process was spontaneous. Moreover, the increase in the temperature provided a slightly decrease in the free energy. Such phenomenon may indicate that: firstly, it is possibly related to the contribution of the chemisorption in the process of retaining the eucalyptus extract in the fiber(Komboonchoo & Bechtold, 2010) and secondly, as the numerical values were very close to

each other, it confirmed the small and positive contribution of temperature (5.10%) in the dyeing process. In confirmed that the dyeing process was endothermic  $(\Delta H^{\circ} > 0)$ also as previously observed(Vinod et al., 2011).

The positive value of  $\Delta S^{\circ}$  suggests an increase of randomness at the solid-solution interface, originated of some structural changes in both adsorbent and adsorbate. These high values  $\Delta S^{\circ}$  are typical of endothermic processes(Hill Jr., 1977).

#### f) Color Fastness to Washing

The indices of wash fastness in the optimized conditions (initial concentration of extract of 20 g L-1, pH 3.0 at 90 °C) were considerable as acceptable. The color change was 3-4, while the staining on cotton and wool presented note 4.

The good fastness properties of dyed silk fabric can be a consequence of the covalent bonds of tannins with the fiber, as seen previously(Mongkholrattanasit, Kryštůfek, & Wiener, 2011).

#### IV. Conclusion

From this study it can be concluded that the silk fabrics can be easily dyed with eucalyptus extract yielding a yellowish-brown color. The best result was achieved using a dyeing temperature of 90  $^{\circ}$ C at pH 3 and 20 gL-1 as extract initial concentration.

By the way, concentration of the initial solution was the most relevant parameter of dyeing, followed by pH and temperature.

The pseudo-second order model best represented the kinetic data whereas equilibrium data was adequately modeled with Langmuir-Freundlich equation. This adjustment may indicate that chemisorption has a huge importance in the dyeing mechanism. Probably the first monolayer based on ionic bonds acted as another adsorption sites for a multilayer formed by hydrogen and covalent bonds.

The thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  showed that the silk dyeing is an endothermic and spontaneous process with increased randomness at the solid-solution interface.

The good fastness to washing probably occurred due to the presence of tannins in the eucalyptus extract that acted as mordant.

#### References Références Referencias

- 1. Alcântara, M. R., & Daltin, D. (1996). A Química do processamento têxtil. Química Nova, 19(3), 320–330.
- 2. Ali, S. (2007). Evaluation of Cotton Dyeing With Aqueous Extracts of Natural Dyes From Indigenous Chemistry Department of Chemistry University of Agriculture, University of Agriculture, Faisalabad.
- Arora, A., Gupta, D., Rastogi, D., & Gulrajani, M. L. (2012). Kinetics and thermodynamics of dye extracted from Arnebia nobilis Rech . f . on wool. Indian Journal of Fibre & Textile Research, 37(June), 178–182.
- Bechtold, T., & Mussak, R. A. M. (2009). Natural Colorants in Textile Dyeing. In T. Bechtold & R. A. M. Mussak (Eds.), Handbook of Natural Colorants (pp. 315–335). Cambridge: Woodhead Publishing Ltd.

- Chairat, M., Rattanaphani, S., Bremner, J. B., & Rattanaphani, V. (2005). An adsorption and kinetic study of lac dyeing on silk. Dyes and Pigments, 64(3), 231–241. https://doi.org/10.1016/j.dyepig. 2004.06.009
- Chiou, M. S., & Li, H. Y. (2003). Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. Chemosphere, 50(8), 1095–1105. https://doi.org/10.1016/S0045-6535 (02) 00636-7
- Dávila-Jiménez, M. M., Elizalde-González, M. P., & Peláez-Cid, a. a. (2005). Adsorption interaction between natural adsorbents and textile dyes in aqueous solution. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 254 (1–3), 107–114. https://doi.org/10.1016/j.colsurfa. 2004.11.022
- De Giorgi, M. R., & Cerniani, A. (1991). Thermodynamic affinity of acid dyes on silk. Dyes and Pigments, 15(1), 47–55. https://doi.org/ 10.1016/0143-7208(91)87006-9
- Farizadeh, K., Montazer, M., Yazdanshenas, M. E., Rashidi, A., & Malek, R. M. A. (2009). Extraction, identification and sorption studies of dyes from madder on wool. Journal of Applied Polymer Science, 113(6), 3799–3808. https://doi.org /10.1002/app.30051
- Freundlich, H. M. F. (1906). Over the adsorption in solution. The Journal of Physical Chemistry, 57, 385–471.
- Giles, C. H., MacEwan, T. H., Nakhwa, S. N., & Smith, D. (1960). Studies in adsorption. Part XI. A System of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. Journal of the Chemical Society, 3973–3993.
- 12. Gurley, S. (1996). Mordant composition for natural dye processes. US Patent 5,509,941. Retrieved from http://www.google.com/patents/US5509941
- 13. Hill Jr., C. G. (1977). An Introduction to Chemical Engineering Kinetics & Reactor Design.
- Ho, Y.-S. (2006). Review of second-order models for adsorption systems. Journal of Hazardous Materials, 136(3), 681–9. https://doi.org/10.1016/j. jhazmat.2005.12.043
- Ibrahim, N. a., El-Gamal, A. R., Gouda, M., & Mahrous, F. (2010). A new approach for natural dyeing and functional finishing of cotton cellulose. Carbohydrate Polymers, 82(4), 1205–1211. https://doi.org/10.1016/j.carbpol.2010.06.054 lqbal, M. (2008). Textile Dyes. Rahber Publishers.
- 16. ISO. (2006). ISO 105-C06: Tests for color fastness: Part C06: Color fastness to domestic and commercial laundering.

- 17. Kant, R. (2012). Textile dyeing industry an environmental hazard. Natural Science, 4(1), 22-26. https://doi.org/10.4236/ns.2012.41004
- 18. Khouni, I., Marrot, B., Moulin, P., & Ben Amar, R. (2011). Decolourization of the reconstituted textile effluent by different process treatments: Enzymatic catalysis, coagulation/flocculation and nanofiltration Desalination, 27–37. processes. 268(1-3),https://doi.org/10.1016/j.desal.2010.09.046
- 19. Komboonchoo, S., & Bechtold, T. (2010). Sorption Characteristics of Indigo Carmine as a Blue Colorant for Use in One-bath Natural Dyeing. Textile Research Journal, 80(8), 734-743. https://doi. org/10.1177/0040517509342319
- 20. Kongkachuichav. Ρ.. Shitangkoon, & Α.. Hirunkitmonkon, S. (2010). Thermodynamics Study of Natural Indigo Adsorption on Silk Yarn, 37(2), 363-367.
- 21. Lageraren, S. Y. (1898). Zur theorie der sogenannten adsorption gelöster stoffe. K Sven Vetenskapsakad Handl, 24, 1–39.
- 22. Langmuir, I. (1918). The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. Research Laboratory of The General Electric Co., 1361-1403.
- 23. Lombard, K. A., Geoffriau, E., & Peffley, E. (2002). Flavonoid quantification in onion by spectro photometric and high performance liauid chromatography analysis. Hort Science, 37(4), 682-685.
- 24. Mirjalili, M., Nazarpoor, K., & Karimi, L. (2011). Ecofriendly dyeing of wool using natural dye from weld as co-partner with synthetic dye. Journal of Cleaner Production, 19(9-10), 1045-1051. https://doi.org/ 10.1016/j.jclepro.2011.02.001
- 25. Mongkholrattanasit, R., Kryštůfek, J., & Wiener, J. (2011). Dyeing, Fastness, and UV Protection Properties of Silk and Wool Fabrics Dyed with Eucalyptus Leaf Extract by the Exhaustion Process. Fibres & Textiles in Eastern Europe, 19(3), 94–99.
- 26. Mongkholrattanasit, R., Kryštůfek, J., Wiener, J., & Studničková, J. (2011). Natural Dye from Eucalyptus Leaves and Application for Wool Fabric Dyeing by Using Padding Techniques. In Natural Dyes (pp. 57-79). InTech.
- 27. Needles, H. L. (1986). Textile Fibers, Dyes, Finishes, and Processes: A Concise Guide. Noves Publications.
- 28. Pretsch, E., Buhlmann, P., & Badertsscher, M. (2009).Structure Determination of Organic Compounds (Tables of Spectral Data) (Fourth, Re). Berlin, Germany: Springer.
- 29. Salem, V. (2010). Tingimen to Têxtil Fibras, Conceitos e Tecnologia. Edgard Blucher.

- 30. Samanta, A. K., & Agarwal, P. (2009). Application of natural dyes on textiles. Indian Journal of Fibre & Textile Research, 34(December), 384-399.
- 31. Samanta, A. K., & Konar, A. (2011). Dyeing of textiles with natural dyes. In E. P. A. Kumbasar (Ed.), Natural Dyes (pp. 29-57). Croácia: Intech.
- 32. Sashina, E. S., Bochek, A. M., Novoselov, N. P., & Kirichenko, D. A. (2006). Structure and solubility of natural silk fibroin. Russian Journal of Applied Chemistry, 79(6), 869-876. https://doi.org/10.1134/ S1070427206060012
- 33. Sawada, K., & Ueda, M. (2003). Dyeing of protein fiber in a reverse micellar system. Dyes and Pigments, 58(2), 99-103. https://doi.org/10.1016/ S0143-7208(03)00048-2
- 34. Septhum, C., Rattanaphani, S., Bremner, J. B., & Rattanaphani, V. (2009). An adsorption study of alum-morin dyeing onto silk yarn. Fibers and Polymers, 10(4), 481-487. https://doi.org/10.1007/s 12221-009-0481-2
- 35. Tang, R. C., Tang, H., & Yang, C. (2010). Adsorption isotherms and mordant dyeing properties of tea polyphenols on wool, silk, and nylon. Industrial and Engineering Chemistry Research, 49(19), 8894-8901. https://doi.org/10.1021/ie100052b
- 36. Vinod, K. N., Puttaswa my, Gowda, K. N. N., & Sudhakar, R. (2011). Isolation of colour components from flowers of Tabebuia argentea: kinetic and adsorption studies on silk yarn. Coloration Technology, 127(3), 205-209, https://doi.org/10, 1111/j.1478-4408.2011.00300.x
- 37. Wei, B., Chen, Q. Y., Chen, G., Tang, R. C., & Zhang, J. (2013). Adsorption properties of lac dyes on wool, silk, and nylon. Journal of Chemistry, (october 2013), 1-6. https://doi.org/10.1155/2013/ 546839



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## Production of Biodegradable Detergent from Castor Oil

By Ajayi P. R. & Momoh S. A.

Ahmadu Bello University Zaria

*Abstract-* This research work was carried out with the objective of extraction of oil from castor seeds and its utilization to produce a biodegradable detergent. Solvent extraction method was employed in extracting the oil and the total percent oil yield was found to be 23.8%. The experimentally determined saponification value of the oil was 183.7275mgKOH/g of oil. The detergent efficiency, determined as a measure of the foamability of the detergent was found to be 2.6cm. The pH tests revealed mildly basic properties. The color, scent and efficiency of the detergent were improved with the addition of bleaching agent, perfume and foaming agents respectively.

Keywords: castor seeds, castor oil, biodegradable detergent, saponification.

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## Production of Biodegradable Detergent from Castor Oil

Ajayi P. R.<sup>a</sup> & Momoh S. A.<sup>o</sup>

Abstract- This research work was carried out with the objective of extraction of oil from castor seeds and its utilization to produce a biodegradable detergent. Solvent extraction method was employed in extracting the oil and the total percent oil yield was found to be 23.8%. The experimentally determined saponification value of the oil was 183.7275mgKOH/g of oil. The detergent efficiency, determined as a measure of the foamability of the detergent was found to be 2.6cm. The pH tests revealed mildly basic properties. The color, scent and efficiency of the detergent were improved with the addition of bleaching agent, perfume and foaming agents respectively.

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#### I. INTRODUCTION

astor oil has long been used commercially as a highly renewable resource for the chemical industry. It is a vegetable oil obtained by pressing the seeds of the castor oil plant (Ricinus communis L.) that is mainly cultivated in Africa, South America, and India. Major castor oil-producing countries include Brazil, China, and India. Even though castor oil accounts for only 0.15% of the world production of vegetable oils, worldwide consumption of this commodity has increased more than 50% during the past 25 years, rising from approximately 400,000 tons in 1985 to 610,000 tons in 2010 (Scholz, 2008). On average, worldwide consumption of castor oil increased at a rate of 7.32 thousand tons per year. In general, the current rate of castor oil production is not considered sufficient to meet the anticipated increase in demand (Ogunniyi, 2006, Mutlu, 2010, Thomas, 2000).

Soap industry, has roots over 2000 years in past, a soap factory having been found in the Pompeii excavation. Soap itself was never actually "discovered", but instead gradually evolved from crude mixture of alkaline and fatty acid (George, 1984). Scientifically, the term detergent covers both soap and synthetic detergent, or "syndets" but it is widely used to indicate synthetic cleaning compounds as distinguished from soap. Detergent differs from soap in their action in hard water. Although soaps are excellent cleansers, they do have disadvantages. As salts of week acids, they are converted by mineral acids into free fatty acids. These fatty acids are less soluble than the sodium or potassium salts and form precipitate or soap scum. Because of this, soaps are ineffective in acidic water. Also soaps form insoluble salts in hard water such as water containing magnesium, calcium or iron. The insoluble salts from bath rub rings, leave film that reduce hair luster, and gray/roughen textiles after repeated washings. Synthetic detergents, however, may be soluble in both acid and alkaline solutions and don't form insoluble precipitate in hard water (Hong, 2015, McKeon, 2016, Shrirame *et al.*, 2011, Tewari, 2012).

All the activities of man, starting from the primitive farming techniques to today's high technology industrial activities have in small or large ways impacted negatively on man and his environment while the various products developed are highly desirable for the enhancement of the citizenry's well being and sustenance of nations' economy, the negative impacts precipitated by the introduction of its unwanted byproducts into the ecological systems may be catastrophic if allowed to build up and uncontrolled. Industrial revolution and evolution have been targeted principally at satisfying immediate changing demands rather than tailored towards a structured, wholesome and guided global program that will satisfy not only temporary human needs but are environmentally safe. The result of this is an increasing ecological degradation that has severely polluted water, land and air (Odigure, 1998).

The detergent and soap making industries are no exceptions to the above trends, for while they provide us with cleansing agents, their processing and byproducts are also a cause of public nuisance. For instance, detergents, unlike soaps, have proved very effective cleansing agents in hard and cool water whereas soap is often wholly ineffective under such condition. It was observed, however that many of these detergents were neither soluble nor biodegradable, that is they were so stable that when they flow into the soil in laundry sewage water, they remain unchanged, resisting conversion into less complex and more soluble substances. They thus, create suds and foams in fresh tap water, naturally occurring ground and surface waters (Severino et al., 2012).

This paper is aimed at producing a biodegradable detergent from castor oil with the objectives of replacing the non-biodegradable

Author α: Department of Chemical Engineering, Ahmadu Bello University Zaria. e-mail: polamajayi@gmail.com

detergents. Production of environmentally friendly biodegradable detergents (soft detergents) from castor oil has the dual advantage of using locally sourced raw material that can be grown and generating wastes that are appetizing to micro organisms (bacteria).

#### II. MATERIALS AND METHODS

The castor seeds (or beans) were gotten from the Kawo market at Kaduna, Kaduna state. The operations involved in extraction of castor oil are:

- Pre-treatment of the castor seeds
- Solvent extraction of the castor oil

The pre-treatment of the castor oil and the solvent extraction was carried out in the department of Chemical Engineering, Ahmadu Bello University Zaria.

#### a) Pre-treatment of castor seeds

The pre-treatment involves the preliminary preparations of the seeds in the following:

*Shelling:* This involves the removal of the shells to obtain the seeds. It was done manually.

*Clearing:* This involves the removal of foreign matter introduced during the sun drying and any unshelled seed.

*Drying:* The moisture content of the seed was reduced using the electric oven. The oven was operated at 80°C for about three hours.

*Crushing:* Mortar and pestle were used to reduce the sizes of the dry seeds so as to increase the interfacial area between the solvent and the seeds.

#### b) Extraction of castor oil

100ml of n-hexane was poured into the round bottom flask. 10g of castor beans was placed in the thimble and inserted in the center of the soxhlet extractor as seen in the figure. The extractor was heated at 70°C when the solvent was boiling; the vapor rises through the vertical tube into the condenser at the top. The liquid condensate drips into the filter paper thimble in the center which contains the solid sample to be extracted. The extract sips through the pores of the thimble and fills the siphon tube where it flows back down into the round bottom flask. This was allowed for 30mins after which the sample was removed from the tube, dried in the oven, cooled in the desiccators and weighed to determine the amount of oil extracted.

The experiment was repeated by placing 5g of the sample into the thimble again, and after every 30mins, the samples were withdrawn for drying and weighing. The miscella (extracted oil mixed with solvent) was heated at the end of the extraction to recover the solvent from the oil. The solvent free oil was then refined for further use.

#### c) Refining of castor oil

The refining was needed to remove gum from the extracted oil. Boiling water was added to the oil and the mixture stirred for 2 mins and allowed to stand in the separating funnel. The aqueous layer was then removed. The procedure was repeated to ensure removal of most gums. The de-gummed oil was collected and stored for use.

#### d) Determination of saponification value

2g of the oil was placed in a conical flask to which 25ml of ethanoic potassium hydroxide (0.1M) was added and the mixture allowed to boil gently for about 60 mins with shaking at regular intervals of 5mins.

Few drops of phenophthalin indicator, as specified by International Standards Organization (ISO 3657, 1988) was added to the warm solution and then titrated with 0.5M HCI. The end point was reached when the pink colour of the indicator just disappeared. The same procedure was followed for the blank.

The saponification value (sv) is given by:

$$sv = 56.1 \times N \times \frac{V_o - V_i}{m}$$

where:  $V_o$  = volume of HCl solution used for the blank test,  $V_i$  = volume of HCl solution for the determination, N = actual molarity of HCl used, and m = mass of sample

#### e) Production of detergent

0.1M sodium hydroxide solution was prepared by weighing 40g of NaOH Pellets into a beaker containing 100ml of water and shaking vigorously.

The electric hot plate was switched on; 30ml of castor oil in a stainless steel plate was placed on it and heated at 35°C for about 2 mins. Caustic soda (0.1M) was added and the mixture stirred with a glass rod. 18M sulphuric acid was then added with constant stirring, and the reaction allowed to completion after which hydrogen peroxide (Bleaching agent) was introduced into the reaction mixture. When the foaming had subsided, the heating was continued to allow for more vaporization before putting off the heating system. Finally, perfume was added and the system was allowed to cool. The powdered detergent formed was the subjected to foamability test to ensure the effectiveness of the process.

The same steps were then followed, but this time palm kernel castor oil was used as the base material. The resulting powdered detergent formed was again collected and tested as above. The results are as shown in Tables 1 - 3, while the equations of the chemical reaction of the process are:

$$O - SO_3H$$

 $O - SO_3H$ 

Sulphation  $CH_3(CH_2)_5CHOHCH_2CH = CH(CH_2)_7COOH + H_2SO_4 \rightarrow CH_3(CH_2)_5CHOHCH - CH(CH_2)_7CO_2H$ 

 $O - SO_3H$ 

|

**Neutralization**  $CH_3(CH_2)_5CHOHCH - CH(CH_2)_7CO_2H + NaOH(\partial q) \rightarrow CH_3(CH_2)_5CHOHCH - CH(CH_2)_7CO_2N\partial + HOH$ 

$$O - SO_{3}H O - SO_{3}H$$

$$| \qquad |$$

$$CH_{3}(CH_{2})_{5}CHOHCH - CH(CH_{2})_{7}CO_{2}N\partial + HOH + he\partial t \rightarrow CH_{3}CH_{2})_{5}CHOHCH - CH(CH_{2})_{7}COON\partial$$

#### f) Foamability tests on detergents produced

Vaporization

About 2.0g of the palm kernel based detergent was added to a 500ml measuring cylinder containing 100ml of distilled water. The mixture was shaken vigorously so as to generate foams. After shaken for about 2mins, the cylinder was allowed to stand for about 10mins. The height of the foam in the solution was measured and recorded.

The same steps were followed using the detergent produced with the castor oil so that the foamability of the two could be compared. The results obtained are as recorded in Table 1, 2 and 3.

#### III. Results and Discussion

The results obtained for the percent volume of oil extracted, determination of saponification value and the production as well as the foamability tests of the detergent produced are as seen in Table 1-3.

Weight of raw sample W <sub>1</sub> (g)	Weight of raffinate W <sub>2</sub> (g)	Weight of oil extracted (g)	Percent oil extracted W(g)
25.00	16.45	8.55	34.20
20.00	13.20	6.80	34.00
30.00	22.00	8.00	26.67
35.00	26.80	8.20	23.43
40.00	29.10	10.90	27.25

Table 1: Average percent of oil extracted

Table 2: Comparing the saponification value of refined oil with the standard

Property Refined castor oil		Standard value
Saponification	183.7275mgKOH/g of	176 - 187 mg
value	oil.	KOH/g of oil

Table 3: Height of foam formed by the detergents produced

Detergent base	Height of foam formed in water (cm)	
material	Sample 1 (2.0g)	Sample 2 (2.0g)
Castor oil	2.57	2.60
Palm kernel oil	2.10	2.00

#### IV. DISCUSSIONS

The results obtained for the extraction showed an average percent oil extracted to be 29.11%. This value is low relative to similar works done by Isah, Alhassan and Garba, 2005 using n-hexane as solvnent with an average oil yield of 32.1%. The low yield could be attributed to the nature of the seeds and difference in solvent. The oil quality was very desirable as demonstrated from the saponification value of 183.7275 mg KOH/g of oil, which compares very favorably with that in literature (180.00 mg KOH/g of oil).

Moreover, the sulphation and neutralization reactions gave a powered detergent of high enough efficiently as seen from the result of the foamability tests. Usually, the efficiency of a washing powder is assessed through the amount of foam it is capable of producing. The presence of persistent foam exemplifies a good detergent (Bajar *et al*, 1995). The foam height of 2.6cm persisted for about 10 minutes and is higher than that formed by the palm kernel based detergent. The detergent formed was the result of the esterifications of the castor oil.

When ricinoleic acid (castor oil) is treated with concentrated  $H_2SO_4$ , its gives a complex mixture consisting of hydrogen sulphate (OSO<sub>3</sub>H) of ricinoleic acid in which the hydroxyl group is esterified and a compound in which the  $H_2SO_4$  has added to the double bond. Esterification and addition do not occur together in the same molecule of ricinoleic.

The product which is known as Turkey red oil (sulphated castor oil) has good wetting properties. Neutralization of this with aqueous NaOH gave a detergent plus water. The reaction proceeded at temperatures between 35 - 40%. The water was vaporized by further heating and a solid (powdered) detergent was the result. The bleaching agent (H<sub>2</sub>O<sub>2</sub>) added helped to bleach the color of the castor oil so that milk colored detergent was produced. pH tests showed that the detergent exhibited basic property. The detergent can thus be described as amphoteric. This classification is characteristic of the intrinsic property of

castor oil. This pH range is preferable to that of acidic as it is non - corrosive to the skin and cloths.

From the structure of castor oil (Ricinoleic acid) as shown under literature review, the sulphation reaction occurred at the hydroxyl group while the esterification reaction occurred at the ester linkages and this can be used to produce both soluble and insoluble soaps. Hence the detergent produced was the result of the esterification of the ricinoleic acid.

#### V. Conclusions

The extraction of biodegradable detergent was done using n-hexane as the solvent. The oil was refined by de-gumming to remove most gums. Sulphation and neutralization of the refined oil gave a detergent. Other operations like bleaching, perfuming and drying were done to improve color, scent and texture of the detergent. Although many other additives such as optical brighteners, extenders, re-deposition inhibitors, enzymes, etc. were not added, the active ingredients (surfactants) were used and as such the detergent efficiency was high.

The production of synthetics detergent from castor oil was successively done. The many desirable intrinsic qualities of castor oil makes it very useful in the detergent industry, thus castor oil can serve as a good substitute to petroleum and coal, the conventional detergent bases.

#### References Références Referencias

- Bajah S. T., Teibo B. O., Onwu G., Obikwere A., Senior Secondary Chemistry, Longman Publication, Lagos, Nigeria, pp. 153-156, 1995.
- George T. A., Shreve's Chemical Process Industries, 5<sup>th</sup> ed. McGraw-Hill Book Company, New York, pp. 529, 1984.
- Hong D-Y, Blackmore S. Plants of China: A Companion to the Flora of China. Cambridge University Press; 2015.
- Isah A. G., Mohammed A., Garba M. U., Production, Refining and Evaluation of Castor Oil, Proceedings of 6<sup>th</sup> Annual Engineering Conference, School of Engineering Technology, Federal University of Technology, Minna, Nigeria, 15<sup>th</sup> - 17<sup>th</sup> June 2005, p. 50-56, 2005.
- 5. McKeon T, Hayes D, Hildebrand D, Weselake R. Industrial Oil Crops. Elsevier; 2016.
- Mutlu H, Meier MAR. Castor oil as a renewable resource for the chemical industry. Eur J Lipid Sci Technol. 2010;112(1):10–30.
- Odigure J. O., Safety, Loss and Pollution Prevention in Chemical process Industries, Jodigs Associates Publication, Minna, Nigeria, pp. 89, 1998.
- 8. Ogunniyi DS. Castor oil: a vital industrial raw material. Bioresour Technol. 2006; 97(9):1086–1091.

- 9. OIL WORLD ISTA Mielke GmbH: Forecasting and Information Service for Oilseeds, Oils and Meals.
- Scholz V, da Silva JN. Prospects and risks of the use of castor oil as a fuel. Biomass Bioenergy. 2008; 32(2): 95–100.
- Severino LS, Auld DL, Baldanzi M, et al. A review on the challenges for increased production of castor. Agron J. 2012;104(4): 853.
- Shrirame H, Panwar N, Bamniya B. Bio diesel from castor oil—a green energy option. Low Carbon Econ. 2011; 2:1–6.
- Tewari DD. A historical policy review of success of castor revolution in Gujarat, India. J Hum Ecol New Delhi. 2012; 38(3): 213.
- 14. Thomas A. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA; 2000. Fats and fatty oils.

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## Impact of Ytterbium Ion on Substantial Effects of Biodegradable Equal Mixture of Polymer Blend of PVA and PVP

By Md. Mohsin Uddin Azad & Md. Islamul Haque

University of North Dakota

Abstract- A biodegradable solid polymer blend films of PVA (50)/ PVP (50) filled with Yb(NO3)2 were prepared by solution casting technique. The degree of amorphosity of the polymer blend composites was increased by the incorporation of filler into the polymer blend matrix. The decrease in the optical energy gap values was observed with the addition of filler which is illustrated by UV-Vis studies, indicating the interaction of filler with polymer blend matrix. With the temperature increase, the value of dielectric constant was found to increase depicting the more polar nature of polymer matrix. The tangent loss spectra of the samples showed a broad peak which confirms the presence of relaxing dipoles in the polymer composites.

Keywords: polymer blend, XRD, UV-vis absorption spectroscopy, nano-indentation.

GJRE-C Classification: FOR Code: 290699p



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## Impact of Ytterbium Ion on Substantial Effects of Biodegradable Equal Mixture of Polymer Blend of PVA and PVP

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Abstract- A biodegradable solid polymer blend films of PVA (50)/ PVP (50) filled with Yb(NO3)<sub>2</sub> were prepared by solution casting technique. The degree of amorphosity of the polymer blend composites was increased by the incorporation of filler into the polymer blend matrix. The decrease in the optical energy gap values was observed with the addition of filler which is illustrated by UV-Vis studies, indicating the interaction of filler with polymer blend matrix. With the temperature increase, the value of dielectric constant was found to increase depicting the more polar nature of polymer matrix. The tangent loss spectra of the samples showed a broad peak which confirms the presence of relaxing dipoles in the polymer composites.

*Keywords:* polymer blend, XRD, UV-vis absorption spectroscopy, nano-indentation.

#### I. INTRODUCTION

he polymer blending technology turned out to be a brilliant means for modifying a polymer compound for specific uses/multifunctional device applications, often at much lower fabrication costs than the currently available material. Very often precise properties are achieved by blending crystalline and amorphous polymers. Crystalline polymers have outstanding chemical resistance, better mechanical properties, low viscosity whereas amorphous polymers provide good dimensional stability.<sup>[1]</sup> Solution blending is one of the simple blending techniques which have control over the physical properties of the miscibility compositional regime.

Poly (vinyl acetate) (PVA) is a semi-crystalline, water soluble, nontoxic synthetic polymer which has the highest application in polymer industry. PVA exhibits interesting physical properties due to the presence of OH groups which are responsible for hydrogen bond formation with other polymers.<sup>[2]</sup> Poly (vinyl pipyridine) (PVP) is a low toxic amorphous vinyl polymer having outstanding physiological compatibility. PVP is soluble in water and most organic solvents.<sup>[3]</sup> The two polymers have polar side groups; PVA contains a hydroxyl proton

and PVP containing pipyridine ring, which has a protonaccepting carbonyl group.<sup>[4]</sup> It is therefore expected that a hydrogen bonding interaction occurs between PVA and PVP.<sup>[5]</sup>

The superiority of polymeric materials is due to the aspects of their tremendous versatility and the amazing degree of tailoring to bring them closer to the novel applications. Polymers in combination with transition metal/ rare earth metal salts give complexes which find applications in high energy electrochemical devices. Dielectric properties of polymers play a dynamic role in device applications such as high performance capacitors, electrical cable insulation, electronic packaging to medical equipment, etc. <sup>[6]</sup>

Rare earth ions filled polymer blend composites are extensively investigated because of their useful applications. The intention of this work is to explain the possibilities of fabrication of new polymer composites containing rare earth ions to make them useful in technological applications. Rare earth metal ion  $Yb^2$ + has shown a significant effect on the crystallinity of the host matrix. Also, Optical, Mechanical and the Dielectric properties of pristine PVA (50)/ PVP (50) polymer blend films are improved with the addition of  $Yb^2$ +metal ions.

#### II. Experimental Work

Poly vinyl acetate (PVA) and (PVP) Poly vinyl pipyridine (PVP) were purchased from Aldrich. Double distilled water was taken as a general solvent for both polymers and filler particles. Initially, PVA (50)/ PVP (50) stock solution was prepared according to the procedure explained by H. M. Ragab. [7] The uniform and homogeneous solution mixture of known quantities of Yb(NO3)2.6H2O (5, 15, and 25%) were added to the polymeric stock solution after ultrasonication at room temperature for 30 minutes. The mixture was stirred continuously for 6-8 hours and then kept for 24 hours to remove the bubbles. The mixture was then transferred into polypropylene plates and dried in the oven for four days at 50oC to make the sample completely free from solvent traces. [8]

Author  $\alpha$ : Senior Lecturer in Chemistry, Northern University Bangladesh. (NUB). e-mail: sacrotica@gmail.com

Author σ: Lecturer in Chemistry, Northern University Bangladesh. (NUB). e-mail: islamulhaqueiuacct@gmail.com

#### III. Results and Discussions

#### a) X-ray diffraction analysis

Fig. 1 represents XRD scans on pristine PVA (50)/ PVP (50) blend and PVA (50)/ PVP (50) blend filled with various concentrations of Yb(NO3)2. In the XRD scan on pristine PVA (50)/ PVP (50) blend the main peak centered at about  $2\theta = 19.430$  reveals the semicrystalline nature of the blend which confirms with earlier reported data. This peak has been shifted slightly in PVA (50)/ PVP (50) matrix filled with 5% and 15% filler to 19.720 and 20.460 respectively. Also, the close observation of the scans suggests that there is a drop in peak intensity values in the case of 5% and 15% filler

mixed blend composites. The absence of sharp peaks confirms the amorphous nature of the polymer blend composites. This may be due to the interaction between the blend and the filler which results in the decrease in intermolecular interaction between the polymers blend chains.[9] This amorphous nature is responsible for ion diffusion in the matrix which can be obtained in the polymers that have flexible backbone.[10] But in the case of 25% filler concentration, the peak reappears at 19.430 and the peak intensity again increases. This shows that lower filler concentration of rare earth metal ions is more effective as a filler in creating an environment which is favorable for ion diffusion in the present chosen blend matrix.



Figure 1: XRD scans on pristine PVA (50)/ PVP (50) and PVA (50)/ PVP (50) filled with filler

#### b) UV-Visible analysis



Figure 2: Absorbance vs Wavelength spectra of pristine PVA (50)/ PVP (50) and PVA (50)/ PVP (50) with filler



Figure 3: Plot of (ahv)1/2 v/s (hv) for pristine PVA (50)/PVP (50)

The band structure of materials is well understood by subjecting the materials to UV-Vis analysis. Pristine blend showed absorption at 220nm. The filler mixed PVA (50)/ PVP (50) blend demonstrated high absorption probability above 220nm and below 250nm which is shown in Fig 2. This shows that there is a shift in the absorption wavelength compared to the pristine blend matrix. In the visible region, the samples were transparent. The absorption coefficient ( $\alpha$ ) is given by the relation,

#### $\alpha h v = -B (h v - Eg)^{r}$

Where, hv-incident photon energy, B –constant. Exponent r is found out from the slope of the linear part of the plot  $(\alpha h \nu)^{1/r} v/s h \nu$ .

Depending on the electronic transition that is taking place in the samples, r can take the value  $\frac{1}{2}$ , 3/2,

2 and 3. From the optical absorption spectra recorded for the samples, best straight line fit is obtained for r =2, which indicates that an indirect transition is allowed near the fundamental band edge [12, 13]. The values of the band gap energies are estimated from the extrapolation of the straight line part of the plot of  $(\alpha h\nu)1/2 \nu/s h\nu$  to the energy axis as the shown in Figure 3. The estimated values of the Eq are given in Table 1. It can be observed from the table that the Eg of the pristine PVA (50) /PVP (50) and Yb(NO3)2 filled PVA (50) /PVP (50) polymer blend decreases with the increase in the concentration of filler. Also, the values recorded in the table justify the change in the behavior of polymer complexes tending towards semiconducting nature. This decrease in the energy band gap may be explained, that during polymer mixing, defects formation may occur, such as voids, which give rise to desirable localized states in the band gap of a material.[11, 12]

Table 1: Band gap energy (Eg) for pristine PVA (50)/PVP (50) and filler incorporated PVA (50)/PVP (50) blend films

Complea	Pristine	PVA(50)/PVP(50)	PVA(50)/PVP(50)	PVA(50)/PVP(50)
Samples	PVA(50)/PVP(50)	+5% filler	+15% filler	+25% filler
Energy band gap (eV)	5.02	4.5	4.46	4.31

#### IV. Conclusions

Yb(NO<sub>3</sub>)<sub>2</sub> incorporated PVA (50)/ PVP (50) polymer blend films have been prepared using solution casting technique. X-ray diffraction scans have shown an increase in the amorphosity of composites which is a favorable condition for ion diffusion. Optical studies have confirmed the decrease in E<sub>9</sub> with the increase of Yb(NO<sub>3</sub>)<sub>2</sub> making the material semiconducting in nature. All these significant results are obtained for 5% and 15%

filler concentration whereas higher concentration 25% is losing its role as effective filler. From the above investigations of physical properties, the results confirm that 15% is the optimized filler concentration showing significant improvement in many areas. Hence based on these results it could be recommended that this Ytterbium filled PVA (50)/ PVP (50) polymer composite films are found to be potential novel multifunctional materials for various optoelectronic and electromechanical devices.

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#### References Références Referencias

- 1. Franck A, Introduction to Polymer blends and Alloys; T A instruments Germany.
- 2. Abdelrazek E M, Elashmawi I S, Labeeb S. Physica B 405 (2010) 2021-2027.
- 3. YuweiJin, Xiaofeng Lu, Ce Wang. Journal of applied Polymer Science, (2006), Volume 102, Issue 6, 6017-6022.
- Rajeswari N, Selvasekarapandian S, Karthikeya C, Sanjeeviraja Y, Iwai, J. Kawamura. Ionics(2013) 19.1105-1113.
- 5. Hatta F F, Yahya M Z A, Ali A M M, Subban R H Y, Harun M K, and Mohamad A A. Ionics 11 (2005).
- Subba ReddyCh , Xia Ha,. Quan-Yao Zhu, Li-Q iang Mai, Wen Chen. Microelectronic Engineering 83(2006) 281- 285.
- 7. Ragab H M, Physica B 406 (2011) 3759.
- El-Houssiny A S, Ward A A M, Mansour S H, Abd-El-Messieh1 S L, Journal of Applied Polymer Science. (2012), Vol. 124, Issue 5, pages, 3879-3891.
- Harish Kumar H G, Mathada R D, Ratiation effects and defects in solids, Volume 166, Issue 3, (2011), 198-207.
- Harish Kumar H G, Mathad R D, Ganesh S, Sarma K S S, HaramghattiC R. Brazilian Journal of Physics 2011, 41 (1).
- Armand M B, Chabangno J M, Duclot In M, Vashistha P, Murthy JN, Shenoy GK (eds.), Fast ion transport in solids. North Holland, Amsterdam (1979).
- 12. M. A. El-Shahawy, Polym.Int.52 (2003) 1919.



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# Characterization of Biodiesel from Gossypium-Barbadense linn. and Helianthus Annuus Seeds Oil

By Nwe Thin Ni, Theingi Win Naing & Aungkyaw Moe

Loikaw University, Loikaw

Abstract- In this research work, the yield percent of the prepared biodiesel from two selected seeds oil: cotton, Gossypiumbarbadense Linn. and sunflower, Helianthus annuuswere observed (82%, 75%) by transesterification method. The biodiesel derived from crude cotton seed oil, sunflower oil and their degummed oil were found to show similar physicochemical properties such as acid value, cloud point, flash point, pour point, solid point, specific gravity, and viscosity, and no moisture was detected. These fuel related properties were observed to be comparable with ASTM standard data, indicating that the biodiesel prepared from cotton and sunflower seed oil have a good fuel quality and it can be used as an alternative in fuel diesel engines..

Keywords: cotton, sunflower, biodiesel, transesterification.

GJRE-C Classification: FOR Code: 290699

CHARACTERIZATION OF BIODIESELFROMGOSSYPIUMBARBADENSELINN. AN DHELIAN THUSAN NUUSSEEDSOIL

Strictly as per the compliance and regulations of:



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## Characterization of Biodiesel from Gossypium-Barbadense linn. and Helianthus Annuus Seeds Oil

Nwe Thin Ni<sup>a</sup>, Theingi Win Naing<sup>e</sup> & Aungkyaw Moe<sup>e</sup>

Abstract- In this research work, the yield percent of the prepared biodiesel from two selected seeds oil: cotton, Gossypiumbarbadense Linn. and sunflower, Helianthus annuuswere observed (82%, 75%) by transesterification method. The biodiesel derived from crude cotton seed oil, sunflower oil and their degummed oil were found to show similar physicochemical properties such as acid value. cloud point, flash point, pour point, solid point, specific gravity, and viscosity, and no moisture was detected. These fuel related properties were observed to be comparable with ASTM standard data, indicating that the biodiesel prepared from cotton and sunflower seed oil have a good fuel quality and it can be used as an alternative in fuel diesel engines.

Keywords: cotton, sunflower, biodiesel, transesterification.

#### I. INTRODUCTION

owadays throughout the world, we are facing with the lack of petroleum, which is the main source of energy in mobile transportation that enhanced the increment of total carbon dioxide in the atmosphere and it can cause the global warming[1]. One of the ways to solve this problem is substitution of petroleum with biodiesel. Biodiesel can be used in diesel engines with little or no modification and can be used as a complete substitute for petroleum-based diesel fuel. It is as biodegradable as sugar, less toxic than salt, and essentially free of sulphur and aromatics [2]. Although the fuels produced from biomass release the carbon dioxide into the atmosphere, because the plants use carbon dioxide from the atmosphere to grow (photosynthesis), the carbon dioxide formed during combustion is balanced by that absorbed [3]. It can also reduce the emission of CO, SO<sub>2</sub>, hydrocarbons and particulate matter in the exhaust gas compared to petrodiesel, resulting in causing less environmental pollution than petrodiesel.

Biodiesel is therefore, a fuel alternative of the conventional, petroleum based diesel engine fuel, and is manufactured from vegetable oil or animal fats by catalytically reacting these with a short-chain aliphatic alcohol (methanol or ethanol), typically using a process called transesterification, or alcoholysis. A catalyst such as sodium or potassium hydroxides or an enzyme, lipase is required. Glycerol is produced as a co-product [2].

In our laboratory, biodiesel as fatty acid methyl ester form has been prepared from different plant oils such as jatropha oil, palm oil, coconut oil, peanut oil, corn oil, sesame oil and the waste oils. Here in, preparation of biodiesel from cotton, *Gossypium barbadense* Linn. and sunflower, *Helianthus annuus* seeds oil by reacting with methanol using NaOH catalyst and their characterization are presented.

#### II. MATERIALSAND METHODS

About 6 kg of cotton and sunflower seeds oil were purchased from Aung-Lan Township, Magway Division, and Demosoe Township LoikawDistrict Myanmar.The collected cotton seeds oil were firstly subjected to degumming and made for the preparation of biodiesel [7].

#### a) Degumming of the GossypiumbarbadenseLinn. andHelianthus annuusseeds oil

The collected seeds oil were degummed by two step process. The first step is water degumming and the second is acid degumming step [5].

100 ml of oil were pre-heated at 70 °C. Simultaneously, 1/3 v/v amount of water were heated at 70 °C and the hot soft water was mixed with the preheated oil by means of an overhead stirred for 1 hr. The temperature was maintained at 70 °C. The hydrated gums were removed from oil by centrifugal method. And then oils were dried by oven drying method to give 95 % and 88 % of water degummed oil from cotton and sunflower seeds oil [3].

The water degummed oil was heated at 85 °C for about 15 min. The hot oil was mixed with 10% (v/v) phosphoric acid with constant stirring for about 1 hr and neutralized with 30% v/v of 0.1 M NaOH solution. Non hydratable phosphatides were separated by centrifugal method. 87% and 80 % of degummed oil from cotton and sunflower seeds oil were obtained [8].

#### b) Preparation of biodiesel

0.34% w/v of sodium methoxide solution was prepared in 99% methanol.

Author α: Department of Chemistry, Loikaw University, Loikaw, Myanmar. e-mail: drntni@gmail.com

Author σ: Department of Chemistry, Bago University, Bago, Myanmar. e-mail: theingiwinnaing85@gmail.com

Author p: Chulalongkorn University, Petroleum & Petrochemical College, Petromat. e-mail: sky.akmoe@gmail.com

100 ml of oil sample were heated in a 250 cm<sup>3</sup> three necked round bottom flask at 100°C, to remove the moisture. After the temperature was allowed to decrease to 55 °C, 25 ml of sodium methoxide (4:1 ratio of oil and sodium methoxide) were added and mixed vigorously with a magnetic stirrer. The temperature was maintained at 55 °C throughout the reaction time for 120 min. This reaction mixture was allowed to stand overnight to provide the better separation of oil and glycerol layers. After removal of the glycerol (lower layer), the upper biodiesel layer was then washed with water to remove alkali and glycerol. The biodiesel was weighed and the yield % was calculated [8].

The procedure was carried out using oil: NaOMe ratios of 5:1, 6:1 and 7:1 v/v under same conditions.

#### c) Determination of some physicochemical properties of the prepared biodiesel from of Gossypium barbadense Linn. And Helianthus annuusseeds oil

The fuel related properties such as flash point, cloud point, pour point, solid point, specific gravity, and dynamic viscosity, and acid value, moisture content of the biodiesel prepared from the crude cotton seed oil and the degummed oil were determined according to conventional AOCS methods [10].

#### d) Characterization of prepared biodiesel from Gossypium barbadense Linn. and Helianthus annuusseeds oil

The characterization of the prepared biodiesel from the *Gossypiumbarbadense* Linn. and *Helianthus annuus*were also studied by FT-IR spectroscopy and Gas chromatography. The FT-IR spectra were recorded on a Shimadzu FT-IR 8900 Fourier Transform Infrared Spectrophotometer at Department of Chemistry, University of Mandalay. The fatty acid components of the oil samples were analyzed by using Shimadzu Model Autosystem XL Gas Chromatography at the Post-Harvest Technology Application Department, Hlegue Township, Yangon Division.

#### III. Resultsand Discussion

The two crude seeds oil were found in reddish brown colour and if the gum is present in the oil, it can disturb the engine nozzle and can destroy the piston of diesel engine. Therefore it is necessary to remove the gum before transesterification. The degumming process involved two steps: water degumming step to remove hydratable phosphatides and acid degumming step to remove non hydrated phosphatides. After removal of the gum, (87, 80) % of the degummed oil were obtained by acid degumming method.

The biodiesel as a fatty acid methyl ester were prepared using 0.34 % (w/v) sodium methoxide solution in 4:1 volume ratio of oil and methanol at 55 °C for 2 hrs

reaction time to yield (82, 75)% of biodiesel from crude cotton seed oil and sunflower seed oil. While the amounts of NaOMe solution were reduced to 5:1, 6:1 and 7:1 ratios (oil: methoxide volume ratio), the yields of biodiesel were decreased to 70%, 65% and 60%, respectively, and formation of more soaps occurred. In addition, the yield of biodiesel (78,72) % using degummed oil in oil: methoxide volume ratio 4:1 were observed not different from the yield of biodiesel using crude cotton and sunflower seeds oil under same conditions. Consequently, it can be inferred that the biodiesel could be prepared from the crude cotton seed oil without refining via degumming process, on the basis of the yield of biodiesel.

The characterization of prepared biodiesel such as acid value, cloud point, flash point, moisture content, pour point, solid point, specific gravity and viscosity were mentioned. The resulting data are summarized in Table 1 and 2 and their fuel properties were also compared with the ASTM data of biodiesel.

It was found that the physicochemical properties of the prepared biodiesels from crude cotton and sunflower seeds oil and their degummed oil were similar. The prepared biodiesel were found to contain lower acid value (0.1 and 0.35) mg KOH / g than standard data (0.5 mg KOH / g). Since the flash point of prepared biodiesel (80 and 75) °C were significantly lower than ASTM standard (<110 °C), the quality of the prepared biodiesel is good due to high tendency of vaporuization. In addition, cloud point (0 °C), pour point (- 4 and -3)°C and solid point (- 10 and -12) °C of the prepared biodiesel were also observed to be lower than the ASTM standard data indicating the lesser amount of wax present in biodiesel and they could be used even in the cold season. The prepared biodiesel also showed very low viscosity (55.1and 65.3) cP at room temperature compared to ASTM standard data (67 and 73 cP) at 40 °C indicating the good ability of complete burning of biodiesel. It also has the lower specific gravity (0.879, 0.778) than ASTM standard data (0.9186and 0.8891) [4].

The FT-IR spectroscopic study on the prepared biodiesel from two collected seeds sample oil indicated the presence of ester group and aliphatic groups due to the sharp absorption bands appearing at (1747 and 1768) cm<sup>-1</sup> for C=C stretching vibration at (1654,1660)cm<sup>-1</sup> and (2908, 2918) cm<sup>-1</sup> for C-H asymmetric stretching vibrations of CH<sub>3</sub> and CH<sub>2</sub> groups and C=O stretching for ester group occurred at (1739,1747) cm<sup>-1</sup>. In addition, since there occurred no O-H broad absorption band, the biodiesel may not contain the free fatty acid [6].

The types of fatty acid components of prepared biodiesel from cotton seed oil was also studied by GC chromatography. It showed that the prepared biodiesel may be the methyl esters of linoleic acid ( $C_{18}H_{32}O_2$ ),

palmatic acid  $(C_{16}H_{32}O_2)$  and oleic acid  $(C_{18}H_{34}O_2)$ . Consequently, it can be deduced that the biodiesel prepared from cotton seed oil and sunflower oil could be used as alternative diesel fuel, the number of carbons in fatty acids are in the range of that in diesel, between 11 to 25 [9].

Table 1: Physicochemical Properties of the PreparedBiodiesels from Gossypium barbadense Linn. anditsASTM Standard Data

No.	Physicochemical Parameters	Biodiesel	ASTM Standard Data
1	Acid value (mg KOH/g)	0.1	0.5 max
2	Cloud point (°C)	0	2
3	Flash point (°C)	80	< 110
4	Moisture content (%)	0	0
5	Pour point (°C)	- 4	8
6	Solid point (°C)	- 10	- 2
7	Specific gravity at room temperature	0.879	0.9186
9	Viscosity at room temperature (cP)	55.1	67 (at 40 °C)

Table 2: Physicochemical Properties of the Prepared Biodiesels from *Helianthus annuus* and its ASTM Standard Data

No.	Physicochemical Parameters	Biodiesel	ASTM Standard Data
1	Acid value (mg KOH/g)	0.35	0.5
2	Cloud point (°C)	0	-3.0 to 12
З	Flash point (°C)	75	<120
4	Moisture content (%)	0	0
5	Pour point (°C)	- 3	-15 to 16
6	Solid point (°C)	- 12	-10 and 5
7	Specific gravity at room	0.778	0.8891
	temperature		
8	Viscosity at room	65.3	73 at 40°C
	temperature (cP)		



*Figure 1:* FT-IR spectrum of biodiesel from *Gossypiumbarbadense* Linn.seed oil



*Figure 2:* FT-IR spectrum of biodiesel from *Helianthus annuus*seed oil



*Figure 3:* Gas chromatogram of biodiesel from *Gossypium barbadense* Linn. seed oil in n-hexane and methanol solvents

#### IV. Conclusion

From the overall assessment of the research, it can be inferred that the biodiesel prepared from the cotton and sunflower seeds oil without degumming could be used as an alternative fuel diesel since the prepared biodiesel has the good fuel related properties such as acid value, cloud point, flash point, moisture content, pour point, solid point, specific gravity and viscosity.
# References Références Referencias

- 1. J. V., Gerpen, *et al* "Biodiesel Analytical Methods", edited by Renewable Energy Laboratory, Colorado, USA, 2004,
- V., Hofman, "Biodiesel Fuel", Country Commissions, North Dakota State University and Department of Agriculture, U.S.A, 2003,
- 3. M.A., Hanna, "Biodiesel Production", Bioresources Technology, 70, 1-15, 1999,
- 4. A.S.T.M., "American Standard for Testing Methods", D 93, 95, 130, 445, 1120, 1298, and 1500, 1988,
- 5. A., Logan, "Degumming and Centrifuge Selection", Optimization and Maintenance, IUPAC-AOCS Workshop on Fats, Oils and Oil Seeds Analysis and Production, 2002,
- 6. J., Mohan, "Principle and Application of Organic Spectroscopy", Narosa Publishing House, New Delhi, 2000,
- 7. M., Mittelbach, "Diesel Fuel Derived From Vegetable Oil", BioresourceTechnology, 56, 7-11, 1996,
- 8. M., Ozkan, T., Ergenc, and O., Deniz, "Experimental Performing Analysis of Biodiesel, Traditional Diesel and Biodiesel with Glycerine", Turkish Journal of Engineering Environmental Science, 29, 89-94, 2005,
- 9. P. D., Vaal, "Diesel and Its Properties, Department of Chemical Engineering", University of Pretoria, South Africa, 2003,
- 10. AOAC. Official Methods of Analysis, 5<sup>th</sup> Ed., Washington, DC, 1990.



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# Adsorption and Photoelectrodeposition of Heavy Metal Ions from Wastewater using $SnO_{x(1 \le X \le 2)}/CeO_2$ Photocatalysts

By Ryo Shoji, Yusaku Mochizuki, Yasukazu Kobayashi, Noriko Yamauchi & Kazunori Sato

University of Tokyo

Abstract- Novel SnO<sub>x(1<x<2)</sub>/CeO<sub>2</sub> photocatalysts showed high adsorption and UV light-driven photoelectrodeposition activities for removal of heavy metal ions from water. The X-ray diffraction and the X-ray photoelectron spectroscopy analyses revealed that an amorphous SnO<sub>x(1<x<2)</sub> loaded on a high crystallinity CeO<sub>2</sub>. Amounts of Pb<sup>2+</sup> removal of 20 wt% of SnO<sub>x</sub> loading on CeO<sub>2</sub> were significantly higher than those of CeO<sub>2</sub> only and SnO<sub>2</sub> only due to the synergistic interaction between the high photocatalytic activity of the CeO<sub>2</sub> and the high adsorptive ability of the SnO<sub>x</sub>. Results of Pb<sup>2+</sup> removal indicated that the photoelectrodeposition occurred via adsorption of Pb<sup>2+</sup> on the SnO<sub>x</sub> surface with surface hydroxyl groups. Furthermore, it was suggested that not only Pb<sup>2+</sup> but also Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Se<sup>4+</sup>, As<sup>3+</sup> and Cr<sup>6+</sup> can be removed by the SnO<sub>x</sub>/CeO<sub>2</sub> photocatalysts. It is therefore expected that the SnO<sub>x(1<x<2)</sub>/CeO<sub>2</sub> can be used as the photocatalysts for purification of wastewater.

Keywords: amorphous tin oxide, cerium oxide, Leads ion removal, photoelectrodeposition, wastewater treatment.

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# Adsorption and Photoelectrodeposition of Heavy Metal Ions from Wastewater using SnO<sub>x(1<X<2)</sub>/CeO<sub>2</sub> Photocatalysts

Ryo Shoji <sup>a</sup>, Yusaku Mochizuki <sup>a</sup>, Yasukazu Kobayashi <sup>e</sup>, Noriko Yamauchi <sup>a</sup> & Kazunori Sato<sup>‡</sup>

Abstract- Novel SnOx(1<x<2)/CeO2 photocatalysts showed high adsorption and UV light-driven photoelectrodeposition activities for removal of heavy metal ions from water. The X-ray diffraction and the X-ray photoelectron spectroscopy analyses revealed that an amorphous  $SnO_{x(1 < x < 2)}$  loaded on a high crystallinity CeO<sub>2</sub>. Amounts of Pb<sup>2+</sup> removal of 20 wt% of SnO<sub>x</sub> loading on CeO<sub>2</sub> were significantly higher than those of CeO<sub>2</sub> only and SnO<sub>2</sub> only due to the synergistic interaction between the high photocatalytic activity of the CeO<sub>2</sub> and the high adsorptive ability of the SnOx. Results of Pb2+ removal indicated that the photoelectrodeposition occurred via adsorption of Pb<sup>2+</sup> on the SnO<sub>x</sub> surface with surface hydroxyl groups. Furthermore, it was suggested that not only Pb2+ but also Cu2+, Cd2+, Hg2+, Se4+, As3+ and Cr6+ can be removed by the SnO<sub>4</sub>/CeO<sub>2</sub> photocatalysts. It is therefore expected that the SnO<sub>x(1<x<2)</sub>/CeO<sub>2</sub> can be used as the photocatalysts for purification of wastewater.

*Keywords:* amorphous tin oxide, cerium oxide, lead ion removal, photoelectrodeposition, wastewater treatment.

#### I. INTRODUCTION

eavy metal ions, such as lead, copper, cadmium, mercury, etc., existing in water are hazardous to the human health and the environmental ecosystem because of the high toxicity. These heavy metal ions are often found in industrial waste water from plating factories, paint manufactures, refinery plants, etc., and are difficult to be removed especially at low concentrations (Fu et al., 2011; Carolin et al., 2017). According to the drinking water standard of the World Health Organization (WHO) criteria, the concentration of heavy metal ions in discharged water is required to be decreased down to the ppb level, and it is too hard to meet this regulation standard at industrial processes of the developing countries (Chowdhury et al., 2016). The techniques which can remove various heavy metal ions at low concentrations with cost efficiency are therefore still necessary.

Currently, there are several effective techniques for removal of heavy metal ions: chemical precipitation (Fu et al., 2011), ion exchange (Zewail et al., 2015), adsorption (Kumar et al., 2016), membrane filtration (Yurekli et al., 2017), electrodialysis (Nemati et al., 2017), reverse osmosis (Li et al., 2017), etc. Among them, the adsorption seems to be the most attractive technique due to its recovery merit, low cost, easy handling and simple design requirement (Kurniawan et al., 2006). However, it is difficult to remove the total metal ions by the only adsorption because of the physicochemical limitation of adsorptive rate particularly at the low concentration range of target metals. In contrast, a coupling method of the adsorption and the photoelectrodeposition is a more effective technique for the removing heavy metal ions at low concentrations due to utilizing irreversible photocatalytic redox reaction. Commonly, semiconductor photocatalysts have been used as an adsorbent to occur the photoelectrodeposition (Kobayashi et al., 2017; Nozaki et al., 2018).

The wide band gap semiconductors such as TiO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, and CeO<sub>2</sub> have mostly been used as a photocatalyst due to their thermal and chemical stability, low cost and environmental-friendly (Ji et al., 2009; Zhang et al., 2018). Among them, the CeO<sub>2</sub> has received much attention for the unique characteristics. The CeO<sub>2</sub> possesses large oxygen storage and releasing ability derived from the redox cycle between  $Ce^{3+}$  and  $Ce^{4+}$ , and the  $CeO_2$  is often utilized for the catalytic oxidation reaction. The CeO<sub>2</sub> therefore plays an important role as a photocatalyst for photo-oxidation and photo-reduction against adsorbed substances (Ke et al., 2014; Qiang et al., 2015). Furthermore, the CeO<sub>2</sub> shows a strong UV absorption and does not cause the photolysis during the photocatalysis (Magesh et al., 2009), while only CeO<sub>2</sub> nanoparticles show low adsorption capacity of heavy metal ions. In the pioneering reports, improvement on the adsorption capacity was attempted by loading heterogeneous materials possessing semiconductor the high adsorption capacity and the high carrier conductivity for the surface photoelectrodeposition such as Gd<sub>2</sub>O<sub>3</sub> (Ayawanna et al., 2015),  $La_2O_3$  (Ayawanna et al., 2017), ZnO (Nozaki et al., 2018), etc., on the CeO<sub>2</sub> as an auxiliary catalyst. However, these metal oxides easily

Author α σ: Department of Chemical Science and Engineering, National Institute of Technology, Tokyo College, Tokyo 193-0997, Japan.

Author p: Department of Chemical System Engineering, the University of Tokyo, Tokyo 113-8656, Japan.

Author  $\Omega$ : Department of Materials Science and Engineering, Ibaraki University, Ibaraki 316-8511, Japan.

Author ¥: Department of Materials Science and Technology, Nagaoka University of Technology, Niigata 940-2188, Japan.

eluted instead of the adsorption of heavy metal ions as an ion-exchange manner because of their higher ionization tendency (Ayawanna et al., 2015; Ayawanna et al., 2017; Nozaki et al., 2018). Thus, an excellent loading material possessing high adsorption capacity, high carrier conductivity and chemical stability was desired.

Tin-oxide compounds (SnO<sub>x</sub>) are focused in this study. The SnO, has prominent superiorities such as high abundance, non-toxicity, low ionization tendency, high adsorption capacity of heavy metal ions, and fast carrier mobility between band structure and surface (Hamdi et al., 2017; Dey, 2018). Thus, the SnO<sub>x</sub> offers many technological applications such as photocatalysts (Zhao et al., 2018), solid-state gas sensors, and adsorbents for the removal of heavy metal ions (Kumar et al., 2016; Dey, 2018). Motivated by these factors, the  $SnO_x$  was loaded on the CeO<sub>2</sub> surface to prepare a new photocatalyst for the adsorption and the photoelectrodeposition of heavy metal ions.

The primary purpose of this study was to synthesize the  $SnO_x/CeO_2$  photocatalysts and evaluate its removal ability of heavy metal ions especially lead ion (Pb<sup>2+</sup>). In addition, it was also a major purpose to obtain further knowledge of the photoelectrodeposition phenomenon which detailed mechanism has not been elucidated yet.

# II. MATERIALS AND METHODS

### a) Chemicals and reagents

Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O, citric acid, ethylene glycol, SnCl<sub>2</sub> · 2H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O, CdCl<sub>2</sub>, HgCl<sub>2</sub>, Na<sub>2</sub>SeO<sub>3</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, arsenic standard solution (As<sup>3+</sup> 1000 ppm), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O, and L(+)-ascorbic acid were all purchased from Wako Pure Chemical Industries Co., Ltd. 4-(2-pyridylazo)-resorcinol was purchased from Dojindo Molecular Technologies Co., Ltd. 2,3diaminonaphthalene and 1,5-diphenylcarbazide were purchased from Tokyo Chemical Industry Co., Ltd. All other reagents were at least of reagent grade and used without further purification. Milli-Q water was used for the preparation of all aqueous solutions.

### b) Synthesis of $SnO_x/CeO_2$

CeO<sub>2</sub> was prepared by the polymerized complex method. Firstly, 10.0 g of citric acid was dissolved in 11.8 g of ethylene glycol with heating at 50 °C for 30 min under stirring at 600 rpm by a hot magnetic stirrer. Then, 5.0 g of Ce(NO<sub>3</sub>)<sub>3</sub>  $\cdot$  6H<sub>2</sub>O were added to the solution and heated at 200 °C for 1 h under stirring at 600 rpm. Finally, the obtained precursor gel was calcined at 350 °C for 1 h and then at 1000 °C for 5 h with a heating rate of 10°C/min (Kakihana et al., 1992).

 $SnO_{x}/CeO_{2}$  were prepared by the impregnation method. The prepared  $CeO_{2}$  nanoparticles the above-were impregnated in an aqueous solution of  $SnCl_{2}$ .

 $2H_2O$ , and the solution was heated at 150 °C under stirring at 400 rpm. After the evaporation of water, the obtained sample was calcined at 650 °C for 3 h with a heating rate of 10 °C/min (Murayama et al., 2017).

#### c) Characterization

The crystal phase and structure of the obtained photocatalysts were analyzed by the powder X-ray diffraction (XRD, D8 ADVANCE, Bruker AXS) with CuKa radiation. The chemical states and composition of the photocatalyst surface were identified using the X-ray photoelectron spectroscopy (XPS, PHI X-tool, ULVAC-PHI) operated with AIK  $\alpha$  radiation. The Chemical Shifts were calibrated by fixing the C 1s peak of the surface carbonaceous contaminants at 284.8 eV. The Brunauer-Emmett-Teller (BET) specific surface area of the photocatalysts were elucidated using a BET surface area analyzer (Flowsorb III, Shimadzu). The morphology and microstructure of the photocatalysts were elucidated using a field emission scanning electron microscopy (FE-SEM, Quanta 250 FEG, FEI). Determination of the point of zero charge ( $pH_{P7C}$ ) of the photocatalyst surface was employed according to the Park and Regalbuto's procedure (Park et al., 1995).

#### d) Removal of Pb<sup>2+</sup>

An aqueous solution including 20.0 mg/L Pb<sup>2+</sup> was prepared. Then, 0.130 g or 0.200 g of the SnO<sub>x</sub>/CeO<sub>2</sub> photocatalyst particles were added into a 20.0 mL of the prepared aqueous solution in a 30 mL beaker. The suspension was stirred at 500 rpm for 150 min by a magnetic stirrer and was also being irradiated with a UV-LED light (NCSU033B, 7.8 mW/cm<sup>2</sup>, 360-370 nm, NICHIA). Another similar experimental set was carried out on the same suspension under stirring in dark condition. After the experiments, the reaction suspension was sampled and filtered, and the pH of the filtrate was measured using a pH meter (PH-201, SAGA). The residual concentrations of Pb<sup>2+</sup> in the filtrate was measured by the colorimetry with 4-(2-pyridylazo)resorcinol at 520 nm (Kocyła et al., 2015). The effect of different initial pH on Pb2+ removal was examined. The pH was adjusted using either 0.10 M HCl or 0.10 M NaOH solutions.

In the time-course removal experiments of  $Pb^{2+}$ , 1.000 g of the  $SnO_x/CeO_2$  photocatalysts were added into a 100.0 mL of the aqueous solution including 20.0 mg/L  $Pb^{2+}$  in a 100 mL beaker due to sampling 5.0 mL of the reaction suspension at designated times (10, 30, 60, 105 and 150 min). The obtained data were fitted to the pseudo first-order model (Equation (1)) and pseudo second-order model (Equation (2))(Lagergren et al., 1898; Ho et al., 1999):

$$q_t = q_m (1 - exp(-k_1 t))$$
 (1)

$$q_t = \frac{q_m^2 k_2 t}{(1 + q_m k_2 t)} \tag{2}$$

Where  $q_t$  (mg/g) is the adsorption capacity at time t (min),  $q_m$  (mg/g) is the maximum adsorption capacity,  $k_1$  (/min) and  $k_2$  (g/mg/min) are the equilibrium rate constant of pseudo first-order adsorption and pseudo second-order adsorption, respectively.

#### e) Removal of other heavy metal ions

In the removal experiments of heavy metal ions other than Pb<sup>2+</sup>, an aqueous solution including 20.0 mg/L  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ,  $As^{3+}$ ,  $Se^{4+}$ , and  $Cr^{6+}$  was prepared with adjusting pH to about 5~6 by using 0.10 M HCl or 0.10 M NaOH solutions. After each removal experiments, the residual concentrations of  $Cu^{2+}$ ,  $Cd^{2+}$ , and Hg<sup>2+</sup> in the filtrate were measured by the inductivity coupled plasma atomic emission spectroscopy (ICP-AES, PS7800, and HITACHI). The residual concentrations of As<sup>3+</sup>(As<sup>5+</sup>), Se<sup>4+</sup>(Se<sup>6+</sup>), and Cr<sup>6+</sup> in the filtrate were measured by the redox treatment and colorimetry with ammonium molybdate and ascorbic acid at 840 nm (Lenoble et al., 2003), 2,3diaminonaphthalene 489 at nm and 1,5diphenylcarbazide at 540 nm (Pedro et al., 2004; Hesamedini et al., 2018), respectively.

# III. Results and Discussion

# a) Characterization of the obtained photocatalysts

The XRD analysis was implemented to investigate the crystal phase and structure of the obtained photocatalysts. Fig. 1 shows the XRD patterns of CeO<sub>2</sub> and 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub>. In the XRD pattern of CeO<sub>2</sub> only, the diffraction peaks were in good agreement with those of the cubic fluorite-structured CeO<sub>2</sub> crystal phase (ICDD PDF# 00-004-0593), and the sharpness of the peaks demonstrated the obtained CeO<sub>2</sub> particles possessing high crystallinity. In the XRD pattern of the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> composites, no specific peaks were observed except for those of the CeO<sub>2</sub> phase. It was indicated that the loaded SnO<sub>x</sub> existing as amorphous and highly dispersed small nanoparticles on the CeO<sub>2</sub> surface.

The XPS analysis was implemented to investigate the surface chemical states and composition of the obtained photocatalysts. Fig. 2a presents the survey spectrum of the 20 wt% SnO<sub>2</sub>/CeO<sub>2</sub>. The appearance of peaks which are attributed to the Ce 3d, Sn 3d, and O 1 s implied the existence of the Ce. Sn. and O elements on the surface of the obtained photocatalysts, and no specific peaks which are attributed to the other elements were observed except the C 1s peak. To investigate the detailed chemical state of the Ce, Sn, and O elements, the high-resolution XPS spectra of the Ce 3d, Sn  $3d_{5/2}$ , and O 1s were measured (Fig. 2b-d). In the spectrum of the Ce 3d (Fig. 2b), the de-convoluted peaks labeled U and V are corresponding to Ce  $3d_{3/2}$  states and Ce  $3d_{5/2}$  states, respectively. According to the literature, U<sub>0</sub>, U<sub>2</sub>, V<sub>0</sub>, V<sub>2</sub>, and  $V_3$  are all the characteristic peaks of Ce<sup>4+</sup>, and U<sub>1</sub>

and  $V_1$  are attributed to the photoemission from Ce<sup>3+</sup> (Lu et al., 2016). The measured peaks therefore demonstrated the primary existence of a CeO<sub>2</sub> phase with a small  $Ce_2O_3$  phase on the surface of the 20 wt%  $SnO_x/CeO_2$ . In the spectrum of the Sn  $3d_{5/2}$  (Fig. 2c), the de-convoluted Sn 3d<sub>5/2</sub> spectra showed two adjacent peaks located at 486.2 and 486.7 eV, corresponding to the Sn<sup>2+</sup> and Sn<sup>4+</sup>, respectively (Babu et al., 2018). The coexistence of these two peaks indicated the presence of the  $SnO_{x(1 < x < 2)}$  on the photocatalyst surface. According to this coexisting of the two states and the XRD pattern is shown in Fig. 1, it was suggested that the amorphous state  $SnO_{x(1 < x < 2)}$  nanoparticles loading on the CeO<sub>2</sub> with the high dispersion states. In the spectrum of the O 1s (Fig. 2d), three de-convoluted peaks located at 529.3, 530.7, and 531.8 eV were observed. The first two peaks at 529.3 and 530.7 eV are probably associated with the lattice oxygen (O<sup>2-</sup>) in the stronger Ce-O band and Sn-O band, respectively. However, since the peaks of the O 1s of  $Ce_2O_3$ ,  $CeO_2$ , SnO, and SnO<sub>2</sub> are very close, assignment of these peaks was puzzling. The last peak at a higher binding energy of 531.8 eV was attributed to the oxygen in defective sites or surface hydroxyl groups (Nagasawa et al., 1999; Ke et al., 2014). the presence of this peak indicated that much oxygen defects were generated on the SnO<sub>x</sub> surface with the amorphous nature and H<sub>2</sub>O molecules then entered the oxygen defects or coordinated to the Sn<sup>4+</sup> exposed on the surface. Finally, the hydroxyl groups were formed at the surface. According to the literature, the surface hydroxyl groups can be the functional groups for the adsorption of heavy metal ions on the surface of metal oxides (Wu et al., 2018).

### b) Removal of Pb<sup>2+</sup>

To optimize amounts of the SnO<sub>x</sub> loading on the CeO<sub>2</sub>, the relationship between amounts of the  $SnO_x$ loading and amounts of Pb2+ removal was examined as shown in Fig. 4. volumes of Pb<sup>2+</sup> removal by the ADS and ADS + PED linearly increased along the increase of the amounts of the loaded SnO<sub>x1</sub> up to 20 wt%. It was suggested that the SnO<sub>x</sub> loaded on the CeO<sub>2</sub> was efficient for the improvement of a removal ability of Pb<sup>2+</sup> because the available adsorption sites of Pb<sup>2+</sup> are easily formed on the surface of the SnOx. In the case of loading SnO, more than 20 wt%, the amounts of the PED removal decreased than that of 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub>. This result is because the existence ratio of the CeO<sub>2</sub> photocatalyst decreased along with the increase of the SnO<sub>x</sub> latio, and several photocatalytic active sites were physically covered by the excess SnO<sub>x</sub> particles. Thus, the optimum amounts of the loaded SnO<sub>x</sub> were 20 wt%.

Although the amorphous  $SnO_x$  has rich defect structures, it probably has the high mobility of the carrier due to the characteristics of the tin oxide compounds

(Dey, 2018). Also, according to the ICP-AES analysis, the ion-exchange elution of Sn ions and Ce ions were not detected in the removal process of  $Pb^{2+}$ . The promising usefulness of the SnO<sub>x</sub> as a loading material was therefore reconfirmed.

Fig. 5 shows the time-course removal of Pb2+ by the 20 wt% SnOx/CeO2. Also, Table 1 shows the analyses of the Pb2+ adsorption kinetics of the 20 wt% SnO<sub>v</sub>/CeO<sub>2</sub> by the pseudo first-order and the pseudo second-order models. As shown in Fig. 5, the adsorption did not reach equilibrium within 150 minutes, and for that, the pseudo second-order model was more suitable than the pseudo first-order model for describing the adsorption process. This result was probably explained by the adsorption of Pb<sup>2+</sup> on the rough surface of the 20 wt% SnO<sub>2</sub>/CeO<sub>2</sub> and the influence of the diffusion-limiting phenomenon. In previous reports, the adsorption of heavy metal ions to the metal oxides was said to be dominated by the process of ligand exchange with surface hydroxyl groups (-OH) on the metal oxides (Kumar et al., 2016), and tin oxide was considered to have more oxygen defects so that the hydroxyl groups are easily formed on the surface (Sun et al., 2018). The adsorption of Pb2+ to the 20 wt% SnO<sub>2</sub>/CeO<sub>2</sub> is therefore very likely to occur through the surface hydroxyl groups. Focusing on the changes of  $Pb^{2+}$  removal by ADS + PED, it could be seen that the difference between the ADS and ADS + PED was definitely appeared after about 10 minutes. It was therefore suggested that the photoelectrodeposition occurred via the adsorption and induced further adsorption by oxidizing the adsorbed Pb<sup>2+</sup> sequentially. Table 2 shows the pH changes of the reaction solution. In the ADS, the pH greatly decreased along with the progress of the adsorption of Pb<sup>2+</sup>. This phenomenon seems to be because H<sup>+</sup> of the surface hydroxyl groups on the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> was replaced with Pb<sup>2+</sup>. In the ADS + PED, the pH once decreased along with the progress of the Pb<sup>2+</sup> adsorption. However, it could be seen that the pH increased along with the progress of the photoelectrodeposition of Pb<sup>2+</sup>. After the experiments of the ADS + PED, the color of the SnO<sub>x</sub>/CeO<sub>2</sub> suspension changed from light yellow to light brown. The adsorbed Pb<sup>2+</sup> was probably oxidized as shown in the following equation previously reported by Kobayashi et al., (2017).

 $Photocatalyst + hv \rightarrow e^- + h^+ \tag{3}$ 

$$Pb^{2+} + 2H_2O + 2h^+ \rightarrow PbO_2 + 4H^+$$
 (4)

According to the above equation, the pH should decrease. It was hence considered that the increase of the pH was due to the elution of the surface hydroxyl groups (-OH) from the 20 wt%  $SnO_x/CeO_2$  surface in the process of PbO<sub>x</sub> deposition on the surface.

Fig. 6a shows the  $Pb^{2+}$  removal in the various initial pH and Fig. 6b shows the point of zero charge (pH<sub>PZC</sub>) of the 20 wt% SnO<sub>4</sub>/CeO<sub>2</sub>. As shown in Fig. 6a, it

could be seen that the removal performance of Pb was drastically decreased at the pH below 3.5. The following three factors were assumed. (1) Since H<sup>+</sup> was released in the formation process of the surface hydroxyl groups, this process hardly proceeded under the acidic conditions. (2) In the adsorption process, Pb<sup>2+</sup> displaced H<sup>+</sup> of the surface hydroxyl groups. Thus, it was unfavorable under the acidic conditions. (3) The estimated pH<sub>PZC</sub> of the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> was 5.3 (Fig. 6b). Thus, under the acidic conditions, the surface hydroxyl groups were positively charged (-OH<sub>2</sub><sup>+</sup>) and electrostatically repelled with Pb<sup>2+</sup> (Ferreira et al., 2015). It was therefore considered that the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> photocatalysts are not suitable for use under the acidic conditions.

#### c) Mechanism of Pb<sup>2+</sup> removal

The mechanism of the adsorption and the photoelectrodeposition of Pb2+ by the 20 wt% SnO<sub>2</sub>/CeO<sub>2</sub> photocatalysts is shown as the schematic diagram in Fig. 7. When the UV light is irradiated on the 20 wt%  $SnO_{x}/CeO_{2}$ , the electrons (e<sup>-</sup>), which are ejected from valence band (VB) of the CeO2, move to the conduction band (CB) by creating the holes (h<sup>+</sup>) in the VB (Equation (5)). While most of the electrons are recombined with the holes and disappeared, some electrons are quickly shifted to the SnO<sub>x</sub> amorphous phase, and some holes are migrated to the CeO<sub>2</sub> surface (Priyadharsan et al., 2017). By the action of the generated carriers, Pb<sup>2+</sup> adsorbed with the surface hydroxyl groups on the SnO<sub>x</sub> is oxidized. The following three hypotheses are conceivable as a route to explain the oxidation reaction. (1) The holes on the  $CeO_2$ surface act on nearby Pb2+ adsorbed on the SnOx, and Pb<sup>2+</sup> is oxidized (Kobayashi et al., 2017). (2) The holes on the CeO<sub>2</sub> surface generate hydroxyl radicals (·OH) from  $OH^{-}$  (Equation (6)), and they oxidize  $Pb^{2+}$  on the  $SnO_x$  surface (Kumar et al., 2017). (3) The electrons on the SnO<sub>x</sub> surface generate superoxide radicals  $(O_2)$ from dissolved oxygens  $(O_2)$  (Equation (7)). The superoxide radicals react with H<sup>+</sup> and produce peroxide radicals (·OOH) (Equation (8)). These peroxide radicals finally interact with the electrons and form additional OH radicals (Equations (9)-(10)) (Wang et al., 2017). As the adsorbed  $Pb^{2+}$  is then deposited as  $PbO_x$  on the photocatalyst surface (Equation (11)), some adsorption sites are regenerated, and the restriction of adsorption equilibrium is resolved. As a result, removal of Pb<sup>2+</sup> further proceeds. The removal of Pb<sup>2+</sup> is finally terminated by occupying all adsorption sites with the deposited PbO<sub>x</sub>. The complete oxidation process can be understood by the following reaction steps (Kobayashi et al., 2017; Kumar et al., 2017; Priyadharsan et al., 2017; Wang et al., 2017):

 $SnO_x/CeO_2 + UV light (hv) \rightarrow e^- (CB) + h^+ (VB)$  (5)

$$OH^- + h^+ (CeO_2VB) \rightarrow OH (radical)$$
 (6)

$$O_2 + e^- (SnO_x CB) \to O_2 \cdot (radical)$$
(7)

$$O_2 \cdot H^+ \to OOH \ (radical)$$
 (8)

$$2 \cdot OOH \rightarrow H_2 O_2 + O_2 \tag{9}$$

$$H_2O_2 + e^- (SnO_xCB) \rightarrow \cdot OH + OH^-$$
(10)

$$Pb^{2+} + h^+ (CeO_2VB); OH + etc. \rightarrow PbO_x + etc.$$
 (11)

#### d) Removal of other heavy metal ions

It was desired to extend the activity of the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> to the removal of other toxic heavy metal ions. The removal of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Se<sup>4+</sup>, As<sup>3+</sup> and Cr<sup>6+</sup> as well as Pb<sup>2+</sup>, were also investigated, and the results were shown in Fig. 8. The heavy metal ions other than Pb<sup>2+</sup> could also be removed by the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> photocatalysts. The removal of Cu<sup>2+</sup> was remarkably proceeded by the photoelectrodeposition. By the XPS analysis, it was revealed that the deposited material was the metallic Cu. The reduction of the Cu<sup>2+</sup> adsorbed on the SnO<sub>x</sub> were efficiently proceeded because of the smooth action of the excited electrons migrated to the SnO<sub>x</sub> surface (Equation (12)) (Canterino et al., 2008).

$$Cu^{2+} + 2e \quad (SnO_xCB) \rightarrow Cu$$
 (12)

SeO<sub>3</sub><sup>2-</sup> and AsO<sub>3</sub><sup>3-</sup> were efficiently adsorbed on the surface of the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub>, because oxygen atoms of the oxide anions easily entered to the oxygen defects or coordinated to the Sn<sup>4+</sup> exposed on the surface of the amorphous  $SnO_{x}$  (Di et al., 2006). According to the XPS analyses, it was revealed that Se<sup>4+</sup> and As<sup>3+</sup> were deposited on the surface as SeO<sub>2</sub> and  $As_2O_3$  after the ADS + PED. In contrast,  $Cr_2O_7^{2-}$  could not be adsorbed at all on the surface of the 20 wt%  $SnO_{x}/CeO_{2}$ . It was therefore suggested that the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> cannot adsorb anything if adsorbate is an oxide anion. However, the reduction of Cr<sup>6+</sup> by the excited electrons was slightly occurred (Ku et al., 2001). Thus, it can be suggested that the 20 wt% SnO<sub>4</sub>/CeO<sub>2</sub> photocatalysts have a potential to remove various toxic heavy metal ions irrespective of cations or anions.

The 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> could remove heavy metal ions at low concentrations by the adsorption and sequential photoelectrodeposition processes under the UV light irradiation. However, for practical applications, further improvement of adsorption capacity is desired (Fu et al., 2011). According to the previous reports, it was indicated that the adsorption performance can be enhanced by making the photocatalyst porous or loading the photocatalyst in a highly dispersed state on the substances having a high specific surface area such as zeolite, (graphene oxide, etc Setthaya et al., 2017; Li et al., 2018; Nozaki et al., 2018).

# IV. Conclusion

The amorphous  $SnO_{x(1 < x < 2)}$  loading on a high crystallinity  $CeO_2$  photocatalysts were synthesized by

the polymerized complex method and the impregnation method for the adsorption and photoelectrodeposition of toxic heavy metal ions. The obtained photocatalysts were characterized by XRD, XPS, SEM, BET, and pH<sub>PZC</sub>. According to the XRD and XPS analyses, the loaded  $SnO_x$  was composed of  $Sn^{2+}$  and  $Sn^{4+}$  and possessed numerous surface hydroxyl groups. In the removal of Pb<sup>2+</sup>, synergistic interaction а between the photocatalytic activity of the CeO<sub>2</sub> and the adsorption ability of the SnOx appeared efficiently when the amounts of SnO<sub>x</sub> was 20 wt%. The photoelectrodeposition of Pb<sup>2+</sup> occurred via adsorption of Pb<sup>2+</sup> to the SnO<sub>x</sub> with surface hydroxyl groups and progressed further removal. It was therefore indicated that the photoelectrodeposition showed a promoting effect of adsorption. In the acidic pH conditions, Pb2+ was almost not removed. Thus, it was suggested that the influence of surface hydroxyl groups of the 20 wt%  $SnO_{2}/CeO_{2}$  was dominant for the adsorption of  $Pb^{2+}$ . A detailed Pb<sup>2+</sup> removal mechanism was devised, suggesting the oxidation of Pb<sup>2+</sup> by the action of holes and hydroxyl radicals. Furthermore, it was revealed that SnO<sub>2</sub>/CeO<sub>2</sub> photocatalysts have a potential to remove various toxic heavy metal ions irrespective of cations or anions. It was therefore shown that SnO<sub>x(1<x<2)</sub>/CeO<sub>2</sub> photocatalysts can purify various wastewater contaminated with heavy metal ions.

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Conflict of Interest

The authors have declared no conflict of interest.

# **References** Références Referencias

- Ayawanna, J., Sato, K. (2017) 'Photoelectrodeposition Effect of Lanthanum oxide-Modified Ceria Particles on The Removal of Lead (II) Ions from Water', Catal. Today, in press.
- Ayawanna, J., Teoh, W., Niratisairak, S., Sato, K. (2015) 'Gadolinia-modified ceria photocatalyst for removal of lead (II) ions from aqueous solutions', Mater. Sci. Semicond. Proc., vol. 40, pp. 136-139.
- Babu, B., Reddy, I.N., Yoo, K., Kim, D., Shim, J. (2018) 'Bandgap tuning and XPS study of SnO<sub>2</sub> quantum dots', Mater. Letters, vol. 221, pp. 211-215.
- Canterino, M., Somma, I.D., Marotta, R., Andreozzi, R. (2008) 'Kinetic investigation of Cu(II) ions photoreduction in presence of titanium dioxide and formic acid',Wat. Res., vol. 42, pp. 4498-4506.
- Carolin, C.F., Kumar, P.S., Saravanan, A., Joshiba, G.J., Naushad, M. (2017) 'Efficient techniques for the removal of toxic heavy metals from aquatic

environment: A review',J. Environ. Chem. Eng., vol. 5, pp. 2782-2799.

- Chowdhury, S.,Mazumder, M.A.J.,Attas, O.A., Husain, T. (2016) 'Heavy metals in drinking water: Occurrences, implications, and future needs in developing countries', Sci. Total Environ., vol. 569-570, pp. 476-488.
- Dey, A. (2018) 'Semiconductor metal oxide gas sensors: A review', Mater. Sci. Eng. B, vol. 229, pp. 206-217.
- Di, Z.C., Ding, J., Peng, X.J., Li, Y.H., Luan, Z.K., Liang, J. (2006) 'Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles', Chemosphere, vol. 62, pp. 861-865.
- Ferreira, R.C., Couto Junior, O.M., Carvalho, K.Q., Arroyo, P.A., Barros, M.A.S.D. (2015) 'Effect of Solution pH on the Removal of Paracetamol by Activated Carbon of Dende Coconut Mesocarp', Chem. Biochem. Eng. Q., vol. 29, pp. 47-53.
- Fu, F., Wang, Q. (2011) 'Removal of heavy metal ions from wastewaters: A review', J. Environ. Manag., vol. 92, pp. 407-418.
- Hamdi, A.M.A., Rinner, U., Sillanpää, M. (2017) 'Tin dioxide as a photocatalyst for water treatment: A review', Proc. Safety Environ. Protect. vol. 107, pp. 190-205.
- Hesamedini, S., Bund, A. (2018) 'Formation of Cr (VI) in cobalt containing Cr (III)-based treatment solution', Surf. Coat. Tech., vol. 334, pp. 444-449.
- Ho, Y., Mckay, G. (1999) 'Pseudo-second order model for sorption processes', Process Biochem., vol. 34, pp. 451-465.
- Ji, P., Zhang, J., Chen, F., Anpo, M. (2009) 'Study of adsorption and degradation of acid orange 7 on the surface of CeO<sub>2</sub> under visible light irradiation', Appl. Catal. B, vol. 85, pp. 148-154.
- Kakihana, M., Yoshimura, M. (1992) 'Polymerized complex synthesis and intergranular coupling of Bi-Pb-Sr-Ca-Cu-O superconductors characterized by complex magnetic susceptibility', J. Appl. Phys., vol. 71, pp. 3904-3910.
- Ke, Y., Lai, S.Y. (2014) 'Comparison of the catalytic benzene oxidation activity of mesoporous ceria prepared via hard-template and soft-template', Microporous Mesoporous Mater., vol. 198, pp. 256-262.
- Kobayashi, Y., Kanasaki, R., Nozaki, T., Shoji, R., Sato, K. (2017) 'Improving Effect of MnO<sub>2</sub> Addition on TiO2-Photocatalytic Removal of Lead Ion from Water', J. Water Environ. Tech., vol. 15, pp. 35-42.
- Kocyła, A., Pomorski, A., Krężel, A. (2015) 'Molar absorption coefficients and stability constants of metal complexes of 4-(2-pyridylazo) resorcinoj (PAR): Revisiting common chelating probe for the study of metallo proteins', J. Inorg. Biochem., vol. 152, pp. 82-92.

- Kumar, K.Y., Raj, T.N.V., Archana, S., Prasad, S.B.B. Olivera, S., Muralidhara, H.B. (2016) 'SnO<sub>2</sub> nanoparticles as effective adsorbents for the removal of cadmium and lead from aqueous solution: Adsorption mechanism and kinetic studies', J. Water Proc. Eng., vol. 13, pp. 44-52.
- Kumar,S., Kumar, A. (2017) 'Enhanced photocatalytic activity of rGO-CeO<sub>2</sub> nanocomposites driven by sunlight', Mater. Sci. Eng. B, vol. 223, pp. 98-108.
- Kurniawan, T.A., Chan, G.Y.S. Lo, W.H., Babel, S. (2006) 'Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals', Sci. Total Environ., vol. 366, pp. 409-426.
- 22. Ku, Y., Jung, I.L. (2001) 'Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide', Wat. Res., vol. 35, pp. 135-142.
- 23. Lagergren, S. (1898) 'Zurtheorie der sogenannten adsorption gelosterstoffe', Kungliga Svenska Veten skapsa kademiens. Handlingar, vol. 24, pp. 1-39.
- 24. Lenoble, V., Deluchat, V., Serpaud, B., Bollinger, J.C. (2003) 'Arsenite oxidation and arsenate determination by the molybdene blue method', Talanta, vol. 61, pp. 267-276.
- 25. Li, X., Shen, R., Ma, S., Chen, X., Xie, J. (2018) 'Graphene-based heterojunction photocatalysts', Appl. Surf. Sci., vol. 430, pp. 53-107.
- Li, Y., Xu, Z., Liu, S., Zhang, J., Yang, X. (2017) 'Molecular simulation of reverse osmosis for heavy metal ions using functionalized nanoporousgraphenes', Comput. Mater. Sci., vol. 139, pp. 65\_74.
- Lu, X., Li, X., Qian, J., Miao, N., Yao, C., Chen, Z. (2016) 'Synthesis and characterization of CeO<sub>2</sub>/TiO<sub>2</sub> nanotube arrays and enhanced photocatalytic oxidative desulfurization perfor-mance', J. Alloys Comp., vol. 661, pp. 363-371.3
- Magesh, G., Viswanathan, B., Viswannath, R.P., Varadarajan, T.K. (2009) 'Photocatalytic behavior of CeO<sub>2</sub>-TiO<sub>2</sub> system for the degradation of Methylene blue', Indian J. Chem., vol. 48, pp. 480-488.
- Murayama, H., Hasegawa, T., Yamamoto, Y., Tone, M., Kimura, M., Ishida, T., Honma, T., Okumura, M., Isogai, M., Fujii, T., Tokunaga, M. (2017) 'Chloridefree and water-soluble Au complex for preparation of supported small nanoparticles by impregnation method', J. Catal., vol. 353, pp. 74-80.
- Nagasawa, Y., Choso, T., Karasuda, T., Shimomura, S., Ouyang, F., Tabata, K., Yamaguchi, Y. (1999) 'Photoemission study of the interaction of a reduced thin film SnO<sub>2</sub> with oxygen', Surf. Sci., vol. 433-435, pp. 226\_229.
- 31. Nemati, M., Hosseini, S.M., Shabanian, M. (2017) 'Novel electrodialysis cation exchange membrane

prepared by 2-acrylamido-2-methylpropane sulfonic acid; heavy metal ions removal',J. Hazard. Mater. vol. 337, pp. 90-104.

- Nozaki, T., Shoji, R., Kobayashi, Y., Sato, K. (2018) 'Feasibility of Macroporous CeO<sub>2</sub> photocatalysts for Removal of Lead Ions from Water', Bullet. Chem. React. Eng. Catal., vol. 13, pp. 256-261.
- Park, J., Regalbuto, J.R. (1995) 'A Simple, Accurate Determination of Oxide PZC and the Strong Buffering Effect of Oxide Surfaces at Incipient Wetness', Colloid Interface Sci., vol. 175, pp. 239-252.
- Pedro, J., Andrade, F., Magni, D., Tudino, M., onivardi, A. (2004) 'On-line sub micellaren hanced fluoro metric determination of Se(IV) with 2, 3diaminonaphthalene', Analyt. Chim. Acta, vol. 516, pp. 229-236.
- Priyadharsan, A., Vasanthakumar, V., Karthikeyan, S., Raj, V., Shanavas, S., Anbarasan, P.M. (2017) 'Multi-functional properties of ternary CeO<sub>2</sub>/ SnO<sub>2</sub>/rGO nanocomposites: Visible light driven photocatalyst and heavy metal removal',J. Photochem. Photobiol. A: Chem., vol. 346, pp. 32-45.
- Qiang, C., Wei, S., Lian, D., Binzhe, S., Xiaoxia, L.,Aihua, X. (2015) 'A comparison between Ce(III) and Ce(IV) ions in photocatalytic degradation of organic pollutants',J. Rare Earths, vol. 33, pp. 249-254.
- Setthaya, N., Chindaprasirt, P., Yin, S., Pimraksa, K. (2017) 'TiO<sub>2</sub>-zeolite photocatalysts made of metakaolin and rice husk ash for removal of

methylene blue dye',Powder Tech., vol. 313, pp. 417-426.

- Sun, Y., Liu, T., Chang, Q., Ma, C. (2018) 'Study on the intrinsic defects in tin oxide with first-principles method', J. Phys. Chem. Solids, vol. 115, pp. 228-232.
- Wang, N., Pan, Y., Lu, T., Li, X., Wu, S., Wu, J. (2017) 'A new ribbon-ignition method for fabricating p-CuO/n-CeO<sub>2</sub> heterojunction with enhanced photocatalytic activity',Appl. Surf. Sci., vol. 403, pp. 699-706.
- Wu, C., Tu, J., Tian, C., Geng, J., Lin, Z., Dang, Z. (2018) 'Defective magnesium ferrite nano-platelets for the adsorption of As(V): The role of surface hydroxyl groups', Environ. Pollut., vol. 235, pp. 11-19.
- 41. Yurekli, Y., Yildirim, M., Aydin, L., Savran, M. (2017) 'Filtration and removal performances of membrane adsorbers', J. Hazard. Mater., vol. 332, pp. 33-41.
- 42. Zewail, T.M., Yousef, N.S. (2015) 'Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed',Alexandria Eng. J., vol. 54, pp. 83-90.
- Zhang, L., Jaroniec, M. (2018) 'Toward designing semiconductor-semiconductor heterojunctions for photocatalytic applications', Appl. Surf. Sci., vol. 430, pp. 2-17.
- Zhao, D., Wu, X. (2018) 'Nanoparticles assembled SnO<sub>2</sub> nanosheet photocatalysts for wastewater purification', Mater. Letters, vol. 210, pp. 354-357.

Table 1:	The analyses of the Pb <sup>2+</sup>	adsorption kinetics of 20 wt% SnO <sub>x</sub> /CeO <sub>2</sub> by the pseudo first-order and pseud	ю
		second-order models	

Pseudo first-order model					
k <sub>1</sub> (/min)	q <sub>m</sub> (mg/g)	R <sup>2</sup>			
0.0152	0.620	0.941			
Pseudo second-order model					
k <sub>2</sub> (g/mg/min)	q <sub>m</sub> (mg/g)	R <sup>2</sup>			
0.00338	0.668	0.966			

Table 2: Time-course changes of solution pH in the removal of  $Pb^{2+}$  using 20 wt% SnO<sub>4</sub>/CeO<sub>2</sub> photocatalysts.

Time (min)	pH (Only ADS)	pH (ADS + PED)
0	5.5	5.5
10	4.3	4.4
30	4.2	4.4
60	4.2	4.5
105	4.1	4.7
150	4.1	4.9



Figure 1: XRD patterns of CeO<sub>2</sub> only and 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> photocatalysts







Figure 2: XPS spectra of 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> photocatalysts: (a) survey spectrum, (b) Ce 3d, (c) Sn 3d<sub>5/2</sub>, (d) O 1s.



Figure 3: FE-SEM images of the synthesized 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> composites at different resolutions (a b).



*Figure 4:* The relationship between amounts of the SnO<sub>x</sub> loading and amounts of Pb<sup>2+</sup> removal by only ADS, PED and ADS + PED, photocatalyst dosage: 0.130 g, solution volume: 20.0 mL, initial concentration of Pb<sup>2+</sup>: 20.0 mg/L, initial pH: 5.5, test time: 150 min. ADS indicates the adsorption of heavy metal ions only by stirring under the dark condition, ADS + PED indicates the adsorption and photoelectrodeposition by stirring under UV light irradiation, and PED indicates the photoelectrodeposition meaning the difference of the Pb<sup>2+</sup> removal amounts between the ADS and ADS + PED, respectively.



*Figure 5:* Time-course changes of amounts of Pb<sup>2+</sup> removed by 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> photocatalyst dosage: 1.000 g, solution volume: 100.0 mL, initial concentration of Pb<sup>2+</sup>: 20.0 mg/L, initial pH: 5.5, test time: 150 min.



*Figure 6:* Effect of pH on the adsorption and photoelectrodeposition of  $Pb^{2+}$  by 20 wt% SnO<sub>x</sub>/CeO photocatalysts, photocatalyst dosage: 0.200 g, solution volume: 20.0 mL, initial concentration of  $Pb^{2+}$ : 20.0 mg/L, initial pH: 2.5~6.5, test time: 150 min (a), and pH<sub>PZC</sub> plots of the 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> (b).







*Figure 8:* Amounts of Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Se<sup>4+</sup>, As<sup>3+</sup>, and Cr<sup>6+</sup> removed by 20 wt% SnO<sub>x</sub>/CeO<sub>2</sub> photocatalysts, photocatalyst dosage: 0.200 g, solution volume: 20.0 mL, initial concentration of each metal ions: 20.0 mg/L, initial pH: 5~6, test time: 150 min.

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The FARSE will be eligible for a free application of standardization of their researches. Standardization of research will be subject to acceptability within stipulated norms as the next step after publishing in a journal. We shall depute a team of specialized research professionals who will render their services for elevating your researches to next higher level, which is worldwide open standardization.

The FARSE member can apply for grading and certification of standards of their educational and Institutional Degrees to Open Association of Research, Society U.S.A. Once you are designated as FARSE, you may send us a scanned copy of all of your credentials. OARS will verify, grade and certify them. This will be based on your academic records, quality of research papers published by you, and some more



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The FARSE member is eligible to join as a paid peer reviewer at Global Journals Incorporation (USA) and can get remuneration of 15% of author fees, taken from the author of a respective paper. After reviewing 5 or more papers you can request to transfer the amount to your bank account.

# MEMBER OF ASSOCIATION OF RESEARCH SOCIETY IN ENGINEERING (MARSE)

The 'MARSE ' title is accorded to a selected professional after the approval of the Editor-in-Chief / Editorial Board Members/Dean.

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MARSE accrediting is an honor. It authenticates your research activities. After becoming MARSE, you can add 'MARSE' title with your name as you use this recognition as additional suffix to your status. This will definitely enhance and add more value and repute to your name. You may use it on your professional Counseling Materials such as CV, Resume, Visiting Card and Name Plate etc.

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As MARSE, you will be given a renowned, secure and free professional email address with 30 GB of space e.g. johnhall@globaljournals.org. This will include Webmail, Spam Assassin, Email Forwarders, Auto-Responders, Email Delivery Route tracing, etc.





We shall provide you intimation regarding launching of e-version of journal of your stream time to time. This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.

The MARSE member can apply for approval, grading and certification of standards of their educational and Institutional Degrees to Open Association of Research, Society U.S.A.





Once you are designated as MARSE, you may send us a scanned copy of all of your credentials. OARS will verify, grade and certify them. This will be based on your academic records, quality of research papers published by you, and some more criteria.

It is mandatory to read all terms and conditions carefully.

# AUXILIARY MEMBERSHIPS

# Institutional Fellow of Open Association of Research Society (USA)-OARS (USA)

Global Journals Incorporation (USA) is accredited by Open Association of Research Society, U.S.A (OARS) and in turn, affiliates research institutions as "Institutional Fellow of Open Association of Research Society" (IFOARS).

The "FARSC" is a dignified title which is accorded to a person's name viz. Dr. John E. Hall, Ph.D., FARSC or William Walldroff, M.S., FARSC.

The IFOARS institution is entitled to form a Board comprised of one Chairperson and three to five board members preferably from different streams. The Board will be recognized as "Institutional Board of Open Association of Research Society"-(IBOARS).

The Institute will be entitled to following benefits:



The IBOARS can initially review research papers of their institute and recommend them to publish with respective journal of Global Journals. It can also review the papers of other institutions after obtaining our consent. The second review will be done by peer reviewer of Global Journals Incorporation (USA) The Board is at liberty to appoint a peer reviewer with the approval of chairperson after consulting us.

The author fees of such paper may be waived off up to 40%.

The Global Journals Incorporation (USA) at its discretion can also refer double blind peer reviewed paper at their end to the board for the verification and to get recommendation for final stage of acceptance of publication.





The IBOARS can organize symposium/seminar/conference in their country on seminar of Global Journals Incorporation (USA)-OARS (USA). The terms and conditions can be discussed separately.

The Board can also play vital role by exploring and giving valuable suggestions regarding the Standards of "Open Association of Research Society, U.S.A (OARS)" so that proper amendment can take place for the benefit of entire research community. We shall provide details of particular standard only on receipt of request from the Board.





The board members can also join us as Individual Fellow with 40% discount on total fees applicable to Individual Fellow. They will be entitled to avail all the benefits as declared. Please visit Individual Fellow-sub menu of GlobalJournals.org to have more relevant details.

Journals Research relevant details.



We shall provide you intimation regarding launching of e-version of journal of your stream time to time. This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.



After nomination of your institution as "Institutional Fellow" and constantly functioning successfully for one year, we can consider giving recognition to your institute to function as Regional/Zonal office on our behalf.

The board can also take up the additional allied activities for betterment after our consultation.

# The following entitlements are applicable to individual Fellows:

Open Association of Research Society, U.S.A (OARS) By-laws states that an individual Fellow may use the designations as applicable, or the corresponding initials. The Credentials of individual Fellow and Associate designations signify that the individual has gained knowledge of the fundamental concepts. One is magnanimous and proficient in an expertise course covering the professional code of conduct, and follows recognized standards of practice.





Open Association of Research Society (US)/ Global Journals Incorporation (USA), as described in Corporate Statements, are educational, research publishing and professional membership organizations. Achieving our individual Fellow or Associate status is based mainly on meeting stated educational research requirements.

Disbursement of 40% Royalty earned through Global Journals : Researcher = 50%, Peer Reviewer = 37.50%, Institution = 12.50% E.g. Out of 40%, the 20% benefit should be passed on to researcher, 15 % benefit towards remuneration should be given to a reviewer and remaining 5% is to be retained by the institution.



We shall provide print version of 12 issues of any three journals [as per your requirement] out of our 38 journals worth \$ 2376 USD.

# Other:

# The individual Fellow and Associate designations accredited by Open Association of Research Society (US) credentials signify guarantees following achievements:

The professional accredited with Fellow honor, is entitled to various benefits viz. name, fame, honor, regular flow of income, secured bright future, social status etc.

- In addition to above, if one is single author, then entitled to 40% discount on publishing research paper and can get 10% discount if one is co-author or main author among group of authors.
- The Fellow can organize symposium/seminar/conference on behalf of Global Journals Incorporation (USA) and he/she can also attend the same organized by other institutes on behalf of Global Journals.
- > The Fellow can become member of Editorial Board Member after completing 3yrs.
- The Fellow can earn 60% of sales proceeds from the sale of reference/review books/literature/publishing of research paper.
- Fellow can also join as paid peer reviewer and earn 15% remuneration of author charges and can also get an opportunity to join as member of the Editorial Board of Global Journals Incorporation (USA)
- This individual has learned the basic methods of applying those concepts and techniques to common challenging situations. This individual has further demonstrated an in-depth understanding of the application of suitable techniques to a particular area of research practice.

# Note :

- In future, if the board feels the necessity to change any board member, the same can be done with the consent of the chairperson along with anyone board member without our approval.
- In case, the chairperson needs to be replaced then consent of 2/3rd board members are required and they are also required to jointly pass the resolution copy of which should be sent to us. In such case, it will be compulsory to obtain our approval before replacement.
- In case of "Difference of Opinion [if any]" among the Board members, our decision will be final and binding to everyone.

# PREFERRED AUTHOR GUIDELINES

#### We accept the manuscript submissions in any standard (generic) format.

We typeset manuscripts using advanced typesetting tools like Adobe In Design, CorelDraw, TeXnicCenter, and TeXStudio. We usually recommend authors submit their research using any standard format they are comfortable with, and let Global Journals do the rest.

Alternatively, you can download our basic template from https://globaljournals.org/Template.zip

Authors should submit their complete paper/article, including text illustrations, graphics, conclusions, artwork, and tables. Authors who are not able to submit manuscript using the form above can email the manuscript department at submit@globaljournals.org or get in touch with chiefeditor@globaljournals.org if they wish to send the abstract before submission.

# Before and during Submission

Authors must ensure the information provided during the submission of a paper is authentic. Please go through the following checklist before submitting:

- 1. Authors must go through the complete author guideline and understand and *agree to Global Journals' ethics and code of conduct,* along with author responsibilities.
- 2. Authors must accept the privacy policy, terms, and conditions of Global Journals.
- 3. Ensure corresponding author's email address and postal address are accurate and reachable.
- 4. Manuscript to be submitted must include keywords, an abstract, a paper title, co-author(s') names and details (email address, name, phone number, and institution), figures and illustrations in vector format including appropriate captions, tables, including titles and footnotes, a conclusion, results, acknowledgments and references.
- 5. Authors should submit paper in a ZIP archive if any supplementary files are required along with the paper.
- 6. Proper permissions must be acquired for the use of any copyrighted material.
- 7. Manuscript submitted *must not have been submitted or published elsewhere* and all authors must be aware of the submission.

#### **Declaration of Conflicts of Interest**

It is required for authors to declare all financial, institutional, and personal relationships with other individuals and organizations that could influence (bias) their research.

# Policy on Plagiarism

Plagiarism is not acceptable in Global Journals submissions at all.

Plagiarized content will not be considered for publication. We reserve the right to inform authors' institutions about plagiarism detected either before or after publication. If plagiarism is identified, we will follow COPE guidelines:

Authors are solely responsible for all the plagiarism that is found. The author must not fabricate, falsify or plagiarize existing research data. The following, if copied, will be considered plagiarism:

- Words (language)
- Ideas
- Findings
- Writings
- Diagrams
- Graphs
- Illustrations
- Lectures

- Printed material
- Graphic representations
- Computer programs
- Electronic material
- Any other original work

# Authorship Policies

Global Journals follows the definition of authorship set up by the Open Association of Research Society, USA. According to its guidelines, authorship criteria must be based on:

- 1. Substantial contributions to the conception and acquisition of data, analysis, and interpretation of findings.
- 2. Drafting the paper and revising it critically regarding important academic content.
- 3. Final approval of the version of the paper to be published.

#### **Changes in Authorship**

The corresponding author should mention the name and complete details of all co-authors during submission and in manuscript. We support addition, rearrangement, manipulation, and deletions in authors list till the early view publication of the journal. We expect that corresponding author will notify all co-authors of submission. We follow COPE guidelines for changes in authorship.

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#### **Appealing Decisions**

Unless specified in the notification, the Editorial Board's decision on publication of the paper is final and cannot be appealed before making the major change in the manuscript.

#### Acknowledgments

Contributors to the research other than authors credited should be mentioned in Acknowledgments. The source of funding for the research can be included. Suppliers of resources may be mentioned along with their addresses.

#### **Declaration of funding sources**

Global Journals is in partnership with various universities, laboratories, and other institutions worldwide in the research domain. Authors are requested to disclose their source of funding during every stage of their research, such as making analysis, performing laboratory operations, computing data, and using institutional resources, from writing an article to its submission. This will also help authors to get reimbursements by requesting an open access publication letter from Global Journals and submitting to the respective funding source.

### Preparing your Manuscript

Authors can submit papers and articles in an acceptable file format: MS Word (doc, docx), LaTeX (.tex, .zip or .rar including all of your files), Adobe PDF (.pdf), rich text format (.rtf), simple text document (.txt), Open Document Text (.odt), and Apple Pages (.pages). Our professional layout editors will format the entire paper according to our official guidelines. This is one of the highlights of publishing with Global Journals—authors should not be concerned about the formatting of their paper. Global Journals accepts articles and manuscripts in every major language, be it Spanish, Chinese, Japanese, Portuguese, Russian, French, German, Dutch, Italian, Greek, or any other national language, but the title, subtitle, and abstract should be in English. This will facilitate indexing and the pre-peer review process.

The following is the official style and template developed for publication of a research paper. Authors are not required to follow this style during the submission of the paper. It is just for reference purposes.



#### Manuscript Style Instruction (Optional)

- Microsoft Word Document Setting Instructions.
- Font type of all text should be Swis721 Lt BT.
- Page size: 8.27" x 11<sup>1</sup>", left margin: 0.65, right margin: 0.65, bottom margin: 0.75.
- Paper title should be in one column of font size 24.
- Author name in font size of 11 in one column.
- Abstract: font size 9 with the word "Abstract" in bold italics.
- Main text: font size 10 with two justified columns.
- Two columns with equal column width of 3.38 and spacing of 0.2.
- First character must be three lines drop-capped.
- The paragraph before spacing of 1 pt and after of 0 pt.
- Line spacing of 1 pt.
- Large images must be in one column.
- The names of first main headings (Heading 1) must be in Roman font, capital letters, and font size of 10.
- The names of second main headings (Heading 2) must not include numbers and must be in italics with a font size of 10.

#### Structure and Format of Manuscript

The recommended size of an original research paper is under 15,000 words and review papers under 7,000 words. Research articles should be less than 10,000 words. Research papers are usually longer than review papers. Review papers are reports of significant research (typically less than 7,000 words, including tables, figures, and references)

A research paper must include:

- a) A title which should be relevant to the theme of the paper.
- b) A summary, known as an abstract (less than 150 words), containing the major results and conclusions.
- c) Up to 10 keywords that precisely identify the paper's subject, purpose, and focus.
- d) An introduction, giving fundamental background objectives.
- e) Resources and techniques with sufficient complete experimental details (wherever possible by reference) to permit repetition, sources of information must be given, and numerical methods must be specified by reference.
- f) Results which should be presented concisely by well-designed tables and figures.
- g) Suitable statistical data should also be given.
- h) All data must have been gathered with attention to numerical detail in the planning stage.

Design has been recognized to be essential to experiments for a considerable time, and the editor has decided that any paper that appears not to have adequate numerical treatments of the data will be returned unrefereed.

- i) Discussion should cover implications and consequences and not just recapitulate the results; conclusions should also be summarized.
- j) There should be brief acknowledgments.
- k) There ought to be references in the conventional format. Global Journals recommends APA format.

Authors should carefully consider the preparation of papers to ensure that they communicate effectively. Papers are much more likely to be accepted if they are carefully designed and laid out, contain few or no errors, are summarizing, and follow instructions. They will also be published with much fewer delays than those that require much technical and editorial correction.

The Editorial Board reserves the right to make literary corrections and suggestions to improve brevity.

# Format Structure

# It is necessary that authors take care in submitting a manuscript that is written in simple language and adheres to published guidelines.

All manuscripts submitted to Global Journals should include:

#### Title

The title page must carry an informative title that reflects the content, a running title (less than 45 characters together with spaces), names of the authors and co-authors, and the place(s) where the work was carried out.

#### Author details

The full postal address of any related author(s) must be specified.

#### Abstract

The abstract is the foundation of the research paper. It should be clear and concise and must contain the objective of the paper and inferences drawn. It is advised to not include big mathematical equations or complicated jargon.

Many researchers searching for information online will use search engines such as Google, Yahoo or others. By optimizing your paper for search engines, you will amplify the chance of someone finding it. In turn, this will make it more likely to be viewed and cited in further works. Global Journals has compiled these guidelines to facilitate you to maximize the web-friendliness of the most public part of your paper.

#### Keywords

A major lynchpin of research work for the writing of research papers is the keyword search, which one will employ to find both library and internet resources. Up to eleven keywords or very brief phrases have to be given to help data retrieval, mining, and indexing.

One must be persistent and creative in using keywords. An effective keyword search requires a strategy: planning of a list of possible keywords and phrases to try.

Choice of the main keywords is the first tool of writing a research paper. Research paper writing is an art. Keyword search should be as strategic as possible.

One should start brainstorming lists of potential keywords before even beginning searching. Think about the most important concepts related to research work. Ask, "What words would a source have to include to be truly valuable in a research paper?" Then consider synonyms for the important words.

It may take the discovery of only one important paper to steer in the right keyword direction because, in most databases, the keywords under which a research paper is abstracted are listed with the paper.

#### **Numerical Methods**

Numerical methods used should be transparent and, where appropriate, supported by references.

#### Abbreviations

Authors must list all the abbreviations used in the paper at the end of the paper or in a separate table before using them.

#### Formulas and equations

Authors are advised to submit any mathematical equation using either MathJax, KaTeX, or LaTeX, or in a very high-quality image.

#### Tables, Figures, and Figure Legends

Tables: Tables should be cautiously designed, uncrowned, and include only essential data. Each must have an Arabic number, e.g., Table 4, a self-explanatory caption, and be on a separate sheet. Authors must submit tables in an editable format and not as images. References to these tables (if any) must be mentioned accurately.

#### Figures

Figures are supposed to be submitted as separate files. Always include a citation in the text for each figure using Arabic numbers, e.g., Fig. 4. Artwork must be submitted online in vector electronic form or by emailing it.

# Preparation of Eletronic Figures for Publication

Although low-quality images are sufficient for review purposes, print publication requires high-quality images to prevent the final product being blurred or fuzzy. Submit (possibly by e-mail) EPS (line art) or TIFF (halftone/ photographs) files only. MS PowerPoint and Word Graphics are unsuitable for printed pictures. Avoid using pixel-oriented software. Scans (TIFF only) should have a resolution of at least 350 dpi (halftone) or 700 to 1100 dpi (line drawings). Please give the data for figures in black and white or submit a Color Work Agreement form. EPS files must be saved with fonts embedded (and with a TIFF preview, if possible).

For scanned images, the scanning resolution at final image size ought to be as follows to ensure good reproduction: line art: >650 dpi; halftones (including gel photographs): >350 dpi; figures containing both halftone and line images: >650 dpi.

Color charges: Authors are advised to pay the full cost for the reproduction of their color artwork. Hence, please note that if there is color artwork in your manuscript when it is accepted for publication, we would require you to complete and return a Color Work Agreement form before your paper can be published. Also, you can email your editor to remove the color fee after acceptance of the paper.

# Tips for Writing A Good Quality Engineering Research Paper

Techniques for writing a good quality engineering research paper:

**1.** *Choosing the topic:* In most cases, the topic is selected by the interests of the author, but it can also be suggested by the guides. You can have several topics, and then judge which you are most comfortable with. This may be done by asking several questions of yourself, like "Will I be able to carry out a search in this area? Will I find all necessary resources to accomplish the search? Will I be able to find all information in this field area?" If the answer to this type of question is "yes," then you ought to choose that topic. In most cases, you may have to conduct surveys and visit several places. Also, you might have to do a lot of work to find all the rises and falls of the various data on that subject. Sometimes, detailed information plays a vital role, instead of short information. Evaluators are human: The first thing to remember is that evaluators are also human beings. They are not only meant for rejecting a paper. They are here to evaluate your paper. So present your best aspect.

**2.** *Think like evaluators:* If you are in confusion or getting demotivated because your paper may not be accepted by the evaluators, then think, and try to evaluate your paper like an evaluator. Try to understand what an evaluator wants in your research paper, and you will automatically have your answer. Make blueprints of paper: The outline is the plan or framework that will help you to arrange your thoughts. It will make your paper logical. But remember that all points of your outline must be related to the topic you have chosen.

**3.** Ask your guides: If you are having any difficulty with your research, then do not hesitate to share your difficulty with your guide (if you have one). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work, then ask your supervisor to help you with an alternative. He or she might also provide you with a list of essential readings.

**4.** Use of computer is recommended: As you are doing research in the field of research engineering then this point is quite obvious. Use right software: Always use good quality software packages. If you are not capable of judging good software, then you can lose the quality of your paper unknowingly. There are various programs available to help you which you can get through the internet.

**5.** Use the internet for help: An excellent start for your paper is using Google. It is a wondrous search engine, where you can have your doubts resolved. You may also read some answers for the frequent question of how to write your research paper or find a model research paper. You can download books from the internet. If you have all the required books, place importance on reading, selecting, and analyzing the specified information. Then sketch out your research paper. Use big pictures: You may use encyclopedias like Wikipedia to get pictures with the best resolution. At Global Journals, you should strictly follow here.



**6.** Bookmarks are useful: When you read any book or magazine, you generally use bookmarks, right? It is a good habit which helps to not lose your continuity. You should always use bookmarks while searching on the internet also, which will make your search easier.

7. Revise what you wrote: When you write anything, always read it, summarize it, and then finalize it.

**8.** *Make every effort:* Make every effort to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in the introduction—what is the need for a particular research paper. Polish your work with good writing skills and always give an evaluator what he wants. Make backups: When you are going to do any important thing like making a research paper, you should always have backup copies of it either on your computer or on paper. This protects you from losing any portion of your important data.

**9.** Produce good diagrams of your own: Always try to include good charts or diagrams in your paper to improve quality. Using several unnecessary diagrams will degrade the quality of your paper by creating a hodgepodge. So always try to include diagrams which were made by you to improve the readability of your paper. Use of direct quotes: When you do research relevant to literature, history, or current affairs, then use of quotes becomes essential, but if the study is relevant to science, use of quotes is not preferable.

**10.** Use proper verb tense: Use proper verb tenses in your paper. Use past tense to present those events that have happened. Use present tense to indicate events that are going on. Use future tense to indicate events that will happen in the future. Use of wrong tenses will confuse the evaluator. Avoid sentences that are incomplete.

11. Pick a good study spot: Always try to pick a spot for your research which is quiet. Not every spot is good for studying.

**12.** *Know what you know:* Always try to know what you know by making objectives, otherwise you will be confused and unable to achieve your target.

**13.** Use good grammar: Always use good grammar and words that will have a positive impact on the evaluator; use of good vocabulary does not mean using tough words which the evaluator has to find in a dictionary. Do not fragment sentences. Eliminate one-word sentences. Do not ever use a big word when a smaller one would suffice.

Verbs have to be in agreement with their subjects. In a research paper, do not start sentences with conjunctions or finish them with prepositions. When writing formally, it is advisable to never split an infinitive because someone will (wrongly) complain. Avoid clichés like a disease. Always shun irritating alliteration. Use language which is simple and straightforward. Put together a neat summary.

**14.** Arrangement of information: Each section of the main body should start with an opening sentence, and there should be a changeover at the end of the section. Give only valid and powerful arguments for your topic. You may also maintain your arguments with records.

**15.** Never start at the last minute: Always allow enough time for research work. Leaving everything to the last minute will degrade your paper and spoil your work.

**16.** *Multitasking in research is not good:* Doing several things at the same time is a bad habit in the case of research activity. Research is an area where everything has a particular time slot. Divide your research work into parts, and do a particular part in a particular time slot.

**17.** *Never copy others' work:* Never copy others' work and give it your name because if the evaluator has seen it anywhere, you will be in trouble. Take proper rest and food: No matter how many hours you spend on your research activity, if you are not taking care of your health, then all your efforts will have been in vain. For quality research, take proper rest and food.

18. Go to seminars: Attend seminars if the topic is relevant to your research area. Utilize all your resources.

**19.** Refresh your mind after intervals: Try to give your mind a rest by listening to soft music or sleeping in intervals. This will also improve your memory. Acquire colleagues: Always try to acquire colleagues. No matter how sharp you are, if you acquire colleagues, they can give you ideas which will be helpful to your research.

**20.** Think technically: Always think technically. If anything happens, search for its reasons, benefits, and demerits. Think and then print: When you go to print your paper, check that tables are not split, headings are not detached from their descriptions, and page sequence is maintained.

**21.** Adding unnecessary information: Do not add unnecessary information like "I have used MS Excel to draw graphs." Irrelevant and inappropriate material is superfluous. Foreign terminology and phrases are not apropos. One should never take a broad view. Analogy is like feathers on a snake. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Never oversimplify: When adding material to your research paper, never go for oversimplification; this will definitely irritate the evaluator. Be specific. Never use rhythmic redundancies. Contractions shouldn't be used in a research paper. Comparisons are as terrible as clichés. Give up ampersands, abbreviations, and so on. Remove commas that are not necessary. Parenthetical words should be between brackets or commas. Understatement is always the best way to put forward earth-shaking thoughts. Give a detailed literary review.

**22. Report concluded results:** Use concluded results. From raw data, filter the results, and then conclude your studies based on measurements and observations taken. An appropriate number of decimal places should be used. Parenthetical remarks are prohibited here. Proofread carefully at the final stage. At the end, give an outline to your arguments. Spot perspectives of further study of the subject. Justify your conclusion at the bottom sufficiently, which will probably include examples.

**23.** Upon conclusion: Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium though which your research is going to be in print for the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects of your research.

### Informal Guidelines of Research Paper Writing

#### Key points to remember:

- Submit all work in its final form.
- Write your paper in the form which is presented in the guidelines using the template.
- Please note the criteria peer reviewers will use for grading the final paper.

#### **Final points:**

One purpose of organizing a research paper is to let people interpret your efforts selectively. The journal requires the following sections, submitted in the order listed, with each section starting on a new page:

*The introduction:* This will be compiled from reference matter and reflect the design processes or outline of basis that directed you to make a study. As you carry out the process of study, the method and process section will be constructed like that. The results segment will show related statistics in nearly sequential order and direct reviewers to similar intellectual paths throughout the data that you gathered to carry out your study.

#### The discussion section:

This will provide understanding of the data and projections as to the implications of the results. The use of good quality references throughout the paper will give the effort trustworthiness by representing an alertness to prior workings.

Writing a research paper is not an easy job, no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record-keeping are the only means to make straightforward progression.

#### General style:

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear: Adhere to recommended page limits.

#### Mistakes to avoid:

- Insertion of a title at the foot of a page with subsequent text on the next page.
- Separating a table, chart, or figure—confine each to a single page.
- Submitting a manuscript with pages out of sequence.
- In every section of your document, use standard writing style, including articles ("a" and "the").
- Keep paying attention to the topic of the paper.

- Use paragraphs to split each significant point (excluding the abstract).
- Align the primary line of each section.
- Present your points in sound order.
- Use present tense to report well-accepted matters.
- Use past tense to describe specific results.
- Do not use familiar wording; don't address the reviewer directly. Don't use slang or superlatives.
- Avoid use of extra pictures—include only those figures essential to presenting results.

#### Title page:

Choose a revealing title. It should be short and include the name(s) and address(es) of all authors. It should not have acronyms or abbreviations or exceed two printed lines.

**Abstract:** This summary should be two hundred words or less. It should clearly and briefly explain the key findings reported in the manuscript and must have precise statistics. It should not have acronyms or abbreviations. It should be logical in itself. Do not cite references at this point.

An abstract is a brief, distinct paragraph summary of finished work or work in development. In a minute or less, a reviewer can be taught the foundation behind the study, common approaches to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Use comprehensive sentences, and do not sacrifice readability for brevity; you can maintain it succinctly by phrasing sentences so that they provide more than a lone rationale. The author can at this moment go straight to shortening the outcome. Sum up the study with the subsequent elements in any summary. Try to limit the initial two items to no more than one line each.

Reason for writing the article—theory, overall issue, purpose.

- Fundamental goal.
- To-the-point depiction of the research.
- Consequences, including definite statistics—if the consequences are quantitative in nature, account for this; results of any numerical analysis should be reported. Significant conclusions or questions that emerge from the research.

#### Approach:

- Single section and succinct.
- An outline of the job done is always written in past tense.
- Concentrate on shortening results—limit background information to a verdict or two.
- Exact spelling, clarity of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else.

#### Introduction:

The introduction should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable of comprehending and calculating the purpose of your study without having to refer to other works. The basis for the study should be offered. Give the most important references, but avoid making a comprehensive appraisal of the topic. Describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will give no attention to your results. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here.

#### The following approach can create a valuable beginning:

- Explain the value (significance) of the study.
- Defend the model—why did you employ this particular system or method? What is its compensation? Remark upon its appropriateness from an abstract point of view as well as pointing out sensible reasons for using it.
- Present a justification. State your particular theory(-ies) or aim(s), and describe the logic that led you to choose them.
- o Briefly explain the study's tentative purpose and how it meets the declared objectives.

#### Approach:

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#### Procedures (methods and materials):

This part is supposed to be the easiest to carve if you have good skills. A soundly written procedures segment allows a capable scientist to replicate your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order, but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt to give the least amount of information that would permit another capable scientist to replicate your outcome, but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section.

When a technique is used that has been well-described in another section, mention the specific item describing the way, but draw the basic principle while stating the situation. The purpose is to show all particular resources and broad procedures so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step-by-step report of the whole thing you did, nor is a methods section a set of orders.

#### Materials:

Materials may be reported in part of a section or else they may be recognized along with your measures.

#### Methods:

- o Report the method and not the particulars of each process that engaged the same methodology.
- Describe the method entirely.
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures.
- o Simplify-detail how procedures were completed, not how they were performed on a particular day.
- o If well-known procedures were used, account for the procedure by name, possibly with a reference, and that's all.

#### Approach:

It is embarrassing to use vigorous voice when documenting methods without using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result, when writing up the methods, most authors use third person passive voice.

Use standard style in this and every other part of the paper—avoid familiar lists, and use full sentences.

#### What to keep away from:

- Resources and methods are not a set of information.
- o Skip all descriptive information and surroundings—save it for the argument.
- $\circ$   $\$  Leave out information that is immaterial to a third party.

#### **Results:**

The principle of a results segment is to present and demonstrate your conclusion. Create this part as entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Use statistics and tables, if suitable, to present consequences most efficiently.

You must clearly differentiate material which would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matters should not be submitted at all except if requested by the instructor.



#### Content:

- o Sum up your conclusions in text and demonstrate them, if suitable, with figures and tables.
- o In the manuscript, explain each of your consequences, and point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation of an exacting study.
- Explain results of control experiments and give remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or manuscript.

#### What to stay away from:

- o Do not discuss or infer your outcome, report surrounding information, or try to explain anything.
- o Do not include raw data or intermediate calculations in a research manuscript.
- Do not present similar data more than once.
- o A manuscript should complement any figures or tables, not duplicate information.
- o Never confuse figures with tables—there is a difference.

#### Approach:

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Put figures and tables, appropriately numbered, in order at the end of the report.

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#### Figures and tables:

If you put figures and tables at the end of some details, make certain that they are visibly distinguished from any attached appendix materials, such as raw facts. Whatever the position, each table must be titled, numbered one after the other, and include a heading. All figures and tables must be divided from the text.

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Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact, you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved the prospect, and let it drop at that. Make a decision as to whether each premise is supported or discarded or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."

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- Give details of all of your remarks as much as possible, focusing on mechanisms.
- Make a decision as to whether the tentative design sufficiently addressed the theory and whether or not it was correctly restricted. Try to present substitute explanations if they are sensible alternatives.
- One piece of research will not counter an overall question, so maintain the large picture in mind. Where do you go next? The best studies unlock new avenues of study. What questions remain?
- o Recommendations for detailed papers will offer supplementary suggestions.



#### Approach:

When you refer to information, differentiate data generated by your own studies from other available information. Present work done by specific persons (including you) in past tense.

Describe generally acknowledged facts and main beliefs in present tense.

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Result	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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