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1	Adsorption Kinetics of Sulfates by Anion Exchange Resin
2	Containing Pristine Multiwalled Carbon Nano Tubes
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7 Abstract

Since the documented discovery of carbon nanotubes (CNT) in 1991 by Iijima and the 8 realization of their unique physical properties, including mechanical, thermal, and electrical, 9 many investigators have endeavored to fabricate advanced CNT composite materials that 10 exhibit one or more of these properties. The sulfates removal from synthetic water by High 11 cross-linked polystyrene diviniyl benzene resin containing pristine multiwalled carbon nano 12 tubes was studied at batch experiments in this study. The effect of pH, contact time, sulfates 13 concentration and adsorbent dose on the sulfates sequestration was investigated. The 14 optimum conditions were studied on Saline water as a case study. The results showed that 15 with increasing of the absorbent amount; contact time and pH improve the efficiency of 16 sulfates removal. The maximum sulfates uptake was obtained in pH and contact time 3.0 and 17 120 min, respectively. Also, with increasing initial concentration of sulfates in water, the 18 efficiency of sulfates removal decreased. The obtained results in this study were matched with 19 freundlich isotherm and pseudo second order kinetic. The maximum adsorption capacity (Xm 20 or K) and constant rate were found 0.024 (mg/g) and 2.083 (mg/g.min), respectively. This 21 study also showed that in the optimum conditions, the sulfates removal efficiency from Saline 22 water by 0.1 mg/L sulfates was 85.6423

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25 Index terms—adsorption, freundlich isotherm, langmuir isotherm, water, hard, nano.

²⁶ 1 Introduction

arbon nanofibers and nanotubes are promising to revolutionise several fields in material science and are a major 27 component of nanotechnology. Further market development will depend on material availability at reasonable 28 prices. Nanotubes have a wide range of unexplored potential applications in various technological areas such 29 as aerospace, energy, automobile, medicine, or chemical industry, in which they can be used as gas adsorbents, 30 templates, actuators, composite reinforcements, catalyst supports, probes, chemical sensors, nano pipes, nano-31 reactors etc. Sulfates is widely popular for this application because of its ability to kill bacteria and other 32 disease-causing organisms at relatively low concentrations. Carbon nano tubes (CNTs) have superior material 33 34 properties such as high chemical stability, aspect ratio, mechanical strength and activated surface area as well as 35 outstanding electrical properties, which make them good electro active material candidates for super capacitors. 36 The electrodes made from CNTs exhibit a unique pore structure for change storage; however, there are limitations for further increasing the effective surface area of the CNTs, as well as relatively high materials cost which limit 37 the commercial application of CNTs based super capacitors. To improve the performance of CNTs, they are 38 composited with conductive polymers and metal oxides. This section will summarize the recent development 39 of CNTs based nano composites for super capacitor applications. Techniques that can be used to synthesize 40 CNTs include Arc discharge, chemical vapour deposition, and laser ablation. synthesized single-walled CNTs by 41 dc arc discharge of a graphite rod under helium gas using Ni, Co, and FeS as catalysts. Then they prepared 42

single-walled CNTspolypyrrole (PPY) nano composite using in situ chemical polymerization of pyrrole monomer 43 in solution with single-walled CNTs suspension. As-grown single-walled CNTs, pure PPY, and single-walled 44 CNT-PPY nano composite powder can form by the in situ chemical polymerization. The as-grown single-45 walled CNTs are randomly entangled and cross-linked, and some carbon nano particles are also observed. The 46 sulfate binds and destroys the outer surface of bacteria and viruses thereby preventing waterborne diseases. 47 The sulfate that is not used is called free residual sulfates. There are many health concerns regarding residual 48 sulfates in water. This is mainly because sulfates is not naturally needed by the body and as a halogen, it 49 tends to inactivate enzymes [1]. Chlorinated water contains chemical compounds called tri halothanes which are 50 carcinogens. Bathing with chlorinated water could have the same effect as drinking because of dermal absorption 51 of sulfates [2]. Other concerns are aesthetic such as sulfates taste and odour. These concerns inform the need for 52 an effective means of water de chlorination after disinfection at low cost. In Europe, the most common means of 53 destroying microorganisms in water system is the use of ozone treatment. In Nigeria, sulfates is extensively used 54 in water treatment because it is cheaper than ozone. High cross-linked polystyrene diviniyl benzene resin are good 55 at removing sulfates residual from water but the actual rates of sulfates removal by High cross-linked polystyrene 56 diviniyl benzene resin obtained from different local raw materials need to be determined. Fast adsorption rate 57 and high adsorption capacity are important and must be considered in the selection of an activated carbon for 58 59 a given purpose. The performance of High cross-linked polystyrene diviniyl benzene resin is indicated by its 60 adsorptive characteristics, which is derived from the specific surface area, pore size and pore volume of the High cross-linked polystyrene diviniyl benzene resin . In this study, adsorption isotherms and sulfates removal kinetics 61 from water using High cross-linked polystyrene diviniyl benzene resin from selected local raw materials were 62 considered [3]. 63

64 **2** II.

65 **3** Materials and Methods

₆₆ 4 a) Instruments and Materials

Stvrene (Merck), Benzoyl peroxide were supplied (Merck, as cross-linking agent), and used without further 67 purification, Dichloromethane, Acetone, Trimethylamine (Fluka, assay 45% in water, as amination agent), 68 Toluene, from Egyptian market and were used as received. Pristine Multi-wall carbon nano tubes (MWCNTs) 69 were synthesized in Nano lab inside EPRI and its purity is 95 wt. %, average diameter of 15 nm and lengths 70 71 ranging from 0.5?m to1?m. Surfactant, Hydroxyl propyl cellulose (HB) (Aquator co. with MS= 3, density= 72 0.5mg/l, MP=450-500 C o). Paraformaldehyde (Merck), 1,4-butandiol (Merck), zinc chloride (Merck, as catalyst 73 for chloromethylation step), hydrochloric acid (Merck), nitric acid(Merck), methanol(Merck), sodium chloride, sodium hydroxide ,magnesium chloride, calcium chloride(ADWIC). 74

⁷⁵ 5 b) Synthesis of MWCNTs (Chemical Vapour

76 Deposition)

The catalytic chemical vapor deposition (CCVD) process for synthesis of multi-walled carbon nanotubes 77 (MWCNTs) was carried out at atmospheric pressure using horizontal fixed bed flow reactor. In this respect 0.5 g 78 of the catalyst powder (Co-MgO) [4] was dispersed onto a quartz tube of 4 cm length and placed in the center of 79 a silica tube with a diameter of 3 cm and 100 cm length fitted within a furnace. The temperature was increased 80 to 700 o C under a mixture of hydrogen (50 sccm) and nitrogen (150 sccm) and kept at this temperature for 1 h 81 to deoxidize the catalyst. Subsequently, the hydrogen gas was changed to 50 sccm of natural gas diluted with 150 82 sccm nitrogen for a certain reaction time of 4 h. Finally, the system was cooled down to ambient temperature 83 under nitrogen flow of 150 sccm [5.6]. c) Synthesis of PSDVB and PS-DVB-CNT beads 2 g polymer of PS seeds 84 was placed in a 500mL three neck flask. Then, the emulsified solution containing 30mL SDS aqueous solution 85 (0.2%, w/v) was added and stirred overnight. Afterwards, another emulsified mixture consisted of 30 g organic 86 compounds and 250 mL HB aqueous solutions (1%, w/v) were prepared by an Ultrasonic Compact Hielscher 87 UP200Ht (200W, 26 kHz) with a nominal frequency and power of 28 kHz and 600 W, and poured into the flask 88 for swelling. Hence, the organic compounds used is consisted of styrene, divinylbenzene, MWCNTs, toluene, 89 BPO and SDS, where, the amount of toluene equaled to the sum of styrene and divinylbenzene, while BPO is 90 1.5% of the sum (w/w), and the amount of SDS is 0.25% of the HB aqueous solution (w/v), finally, the amount 91 of MWCNTs is 1% (w/w) was attempted to prepare PSDVB-CNT particles. After 24 hours the temperature was 92 increased to 70 °C under nitrogen atmosphere and lasted another 24 hours. Subsequently, the resulting beads 93 were washed successively with hot water and alcohol. Then the beads were extracted with toluene for 48 hours. 94 After washing and drying, the resulting particle size in the stationary phase was about 50-150?m [7,8]. 95

⁹⁶ 6 d) Chloromethylation of Copolymer Resins

A 2?0176 g of resins, 2, 5 ml of chloromethyl methyl ether,1?1530 g of ZnCl 2 and10 ml of nitrobenzene were
added to a 50 ml flask equipped with refluxing condenser and anhydrous CaCl 2 tube. After stirring at room

 $_{99}$ temperature for 5-10 min, the chloromethylation reaction was carried out at 45 °C for 4 hours. After that, 0?5770

g of ZnCl 2 was added to the system, the polymerization was carried out at 80°C for 12 hours. The resulting 100 polymer washed with hot deionized water, and extracted with acetone in a Soxhlet apparatus. The product was 101 dried under vacuum to give 2?3907 g of resin [6]. e) Amination of Chloromethylated Copolymer A250 mL round 102 bottom flask fitted with magnetic stirrer was charged with 5 g of polymer beads, 150 ml of acetonitrile and 30 ml 103 of tri ethylamine, then the mixture was purged with nitrogen, deaerated under vacuum and the entire setup was 104 placed in an oil bath over a magnetic stirrer and the mixture was refluxed at 70 C o for 3 days with a continuous 105 pumping of nitrogen into the reaction flask. The quaternized beads were filtered and successively washed with 106 acetonitrile and methanol followed by drying under vacuum at 60 o C [7]. 107

¹⁰⁸ 7 f) Effect of pH value on sulfates adsorption

The effect of pH on sulfate ions adsorption was carried out using initial chloride ion concentration 100 mg/L onto 0.1 g/L of resins at different pH values (1-9). The solution was agitated for 120 min and the residual sulfate ion in solutions was determined, also the distribution of chloride ion depends upon pH of the solution were studied [8].

¹¹³ 8 g) Effect of sorbent dose

The effects of changing initial resin dosage in the sorption medium on removal of sulfates ions in terms of 114 adsorption capacity was examined at different values including 0.10, 0.050, 0.1, and 0.2, 0.3, 0.35 g resin/L 115 and equilibrated for 24 hours, while other operational parameters such as temperature and initial chlorine and 116 sulfates ions concentration of solutions were kept constant (T=30?C, C?=100 mg M/L, pH=natural) [9]. h) 117 Effect of initial sulfates concentration 1000 mg/L stock solution of sulfate ions was diluted to obtain standard 118 solutions containing 10-100 mg/L of chloride ion. A 100 mL of chloride ion solutions of a desired concentration 119 was adjusted to a desired pH, then poured in 300 mL bottles and known amounts of ion exchange resins were 120 added. The solution pH was adjusted by using buffer solutions. The solutions were agitated at 150 rpm for a 121 predetermined period at 30? C in a shaking incubator (JEIO TECH SI-900R). The resins were separated and 122 the filtrate was analyzed by ICP for chloride ion content [9]. 123

124 **9 III.**

125 10 Results and Discussion

¹²⁶ 11 a) Effect of pH value on sulfates uptake

The pH of the ion exchange system determines the adsorption capacity due to its influence on the surface 127 properties of the different ionic forms of the sulfate solutions. Changes of the adsorption capacity of sulfate onto 128 129 prepared resins with pH are shown in Figure (1). It was observed that the maximum removal percentage (85%) occurred at pH 2.5. Maximum adsorption at acidic pH indicates that the low pH leads to an increase in H +130 ions on the resins surface which results in significantly strong electrostatic attraction between positively charged 131 PS-DVB-P-MWCNTs resins surface and sulfate ions. The removal percentage of sulfate adsorption gradually 132 decreased to 18 at pH 10. Adsorption of sulfate onto ion exchange resins were not significant at pH values greater 133 than 6.0 due to anions competition to be exchanged on the surface of the prepared ion exchange resins of which 134 OHpredominates. The pH of exchanged ions is a very important character that determines the pH at which the 135 ion exchange resins surface has net electrical neutrality. At this value, the acidic or basic functional groups no 136 longer contribute to the pH of the solution [10]. 137

138 Figure ?? : Effect of pH value on sulfates uptake b) Effect of initial sulfates concentration [11] The amount of sulfate anions adsorbed for different initial concentrations onto anionic PS-DVB containing pristine multiwalled 139 carbon nano tubes, resins is shown in Figures (2). The results show that the adsorption process is clearly time 140 dependent. The amount of sulfate adsorbed (mg/g), increased with increase sulfate concentration and remained 141 nearly constant after equilibrium time. It was shown that the adsorption at different initial concentration was 142 rapid in the initial stages and gradually decreased with the progress of adsorption until the equilibrium reached 143 120 min. At low concentrations the ratio of available surface to the initial sulfate concentration is large, so the 144 removal becomes independent on initial concentrations. However, in the case of the high concentrations, this 145 ratio is low, and the exchange rate then depends upon the initial concentration. In addition the curves are 146 continuous leading to saturation, suggesting the monolayer coverage of sulfate on the surface of the adsorbent 147 148 [11]. After a balance time of 120 minute, the adsorption capacity records an increase from 11 to 83.2 mg/g, for concentrations from 25 to 100 mg/L in PS-DVB resin containing pristine multiwalled carbon nano tubes. This 149 150 may be due to the fact that at a chosen adsorbent dose, the number of active adsorption sites remains unchanged 151 while with higher adsorbate concentrations, the adsorbate ions to be accommodate increase. At the removal %of sulfate ions PH removal % of sulfate ions higher initial concentrations, the higher corresponding cumulative 152 removal (mg/g) is dominated. The small amount of exchange sulfate ions evidence that the presence of carbon 153 nano tubes create specialized resins rate that satisfactory for chlorine ion more than sulfate ions and this reduces 154 the competition between them which is clear in the resins containing MWCNTs. In order to examine the effect 155 of the resins dosage on the removal efficiency sulfate, adsorption experiments were set up with various amounts 156

of PS-DVB-P-MWCNTs resins (0.05-.35 g/100mL) at initial sulfate concentration of 100 mg/100mL and at pH 157 = 3.5. The effect of resins dosages on the amount of adsorbed sulfate has been shown in Figure (3). It was 158 shown that the quantity of sulfate adsorbed increased in a significant values in the pondered range examined. In 159 addition, we observe that the maximum of retention is obtained for a mass of 250mg of PS-DVB-P-MWCNTs 160 per 100mLof solution. Beyond an adsorbent dose of 250mg/100mL, the recovery % becomes constant. This 161 is probably because the resistance to mass transfer of sulfate from bulk liquid to the surface of the adsorbent 162 and the saturation of active sites, which becomes important at high adsorbent loading in the system in which 163 the experiment was conducted. It might have happened that the higher dose causes particles aggregates and 164 interference or repulsive forces between binding sites, therefore decreases the interaction of sulfate ions with the 165 sorbent and reduces the total surface area of the adsorbent [11] In this study, Freundlich, Langmuir isotherms 166 were studied. The Table 1 gives the isotherms equation as well as constants. According to the results, the 167 Freundlich isotherm was best fitted to represent the equilibrium adsorption data than other isotherms (Figure 168 4,5). RL (separation factor) is the important factor in Langmuir isotherm that is the dimensionless constant [11]. 169 presents the kinetics equation and constant value for sulfates adsorption on pumice. Sulfates-pumice interaction 170 concurred showed good fit with pseudosecond order rate equation (R 2 = 0.99). Figure 5 is shown pseudo-second 171 order kinetic model [11]. IV. 172

173 12 Conclusions

Removal of SO4 2 from aqueous solution onto anionic PS-DVB resin containing pristine multiwalled carbon nano 174 tubes was carried out at room temperature. Results indicate that pH, initial sulfate concentration, stirring 175 intensity, adsorbent dosage and foreign anions impacted sulfate specie removal: the SO4 2uptake increased with 176 the increase of initial sulfate concentration and decreased with increasing pH values. It is also seen that a 177 further increase in adsorbent dose (greater than 0.1 mg/L) affects the uptake of sulfate adsorption greatly. The 178 conditions of maximum adsorption of the sulfate anions were optimized. In nature and in normal treatments, 179 the treated waters are usually at pH from 1 to 9, so the adsorption capacity of SO4 2is about 2.25 mg/g at pH 180 3.5, for an adsorbent dosage of 0.1 mg/L, initial sulfate concentration of 50 mg/L, under a constant temperature 181 of 25 ± 2 °C, and the equilibrium state was reached within 120 min of exposure time. The results showed that 182 the adsorption of sulfate onto anionic PS-DVB resin containing pristine multiwalled carbon nano tubes followed 183 pseudosecond-order rate kinetic predicting a chemisorption process. The results of present investigation show 184 that the relatively low cost and high capabilities of the raw date palm seeds make them potentially attractive 185 adsorbents for the removal of sulfate from aqueous solution. Further experiments need to be conducted to test 186 the dynamic sorption of SO4 20nto anionic PS-DVB resin containing pristine multiwalled carbon nano tubes in 187





Figure 1: ©

1

		Freundlich			Langmuir		
resins	1/n n	Κ	\mathbf{R}	1/X	Х	$\mathbf{R} \ 2$	Κ
			2	m	m		\mathbf{L}
PS-DVB-P-MWCNTs	$0.48\ 0.5873083$		38.660.88730.02			240.6269	41.66
e) Kinetic Studies							
Sulfates removal from aqueous solution by							
resins may be presented by first-order (second-order,							
and Intraparticle diffusion kinetic models. Table 2							

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Figure 2: Table 1 :

188

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12 CONCLUSIONS

$\mathbf{2}$

Kinetic model Nonmetals ions		Metal concen- trations	R 2	Kinetic Parameter k L , ads or K d	q e
	SO	10	0.9352	0.0036	0.9711
	4 -2				
Pseudo first		25	0.9876	0.0024	1.386
order model		50	0.9798	0.0018	1.6875
		100	0.9622	0.0015	1.9874
	SO	10	0.8532	0.0015	0.0955
	4 -2				
Second order		25	0.9954	0.0003	0.0401
model		50	0.9909	0.0001	0.0203
		100	0.9739	4*10 -5	0.0102
Pseudo Second	\mathbf{SO}	10	0.8682	0.1233	5.7899
	4 -2				
order model		25	0.9405	0.0374	5.3949
		50	0.9403	0.023	3.3543
		100	0.927	0.0142	1.8113
	SO	10	0.9432	0.5903	0.2575
	4 -2				
intraparticle		25	0.9955	1.3191	2.3289
diffusion model		50	0.995	2.1306	3.7614
		100	0.9886	3.6976	6.0978

Figure 3: Table 2 :

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