

Dynamic Sorption of Alizarin Red S by Fixed Bed Activated Carbon

Ali Benhmidene¹

¹ The National School of Engineering of Gabes, Tunisia

Received: 15 December 2016 Accepted: 3 January 2017 Published: 15 January 2017

Abstract

Dynamic removal of Alizarin Red S (RAS) by activated carbon Norit GCA830 has been experimentally studied in fixed bed column. We can predicted the value of column parameters as a function of inlet solution dye concentration, flow rate and bed height. A static study has been first conducted, from which maximum adsorption capacity is defined; it's of 385mg/g. Both Freundlich and Langmuir models were found to fit the sorption isotherm data well. For dynamic experimental study; series of column tests using activated carbon were performed to determine the breakthrough curves with varying the bed height, inlet solution dye concentration and flow rate. Adsorption capacity in fixed bed is defined from breakthrough curves is similar of that defined in static study. In addition adsorption capacity of fixed bed is correlated in function of operating conditions cited above. The kinetic model "Bed Depth Service Time?" (BDST) is another method used to defined the adsorption capacity of AC in fixed bed in addition of other kinetic parameters such as constant kinetic, the thickness of mass transfer zone and the velocity of migration of adsorption zone. According to operating conditions the adsorption capacity is mostly depend of residence time.

Index terms— alizarin red S, norit GCA830, fixed bed, adsorption capacity.

1 Introduction

The adsorption studies are generally divided into two parts. The first is the batch adsorption. It has the advantage to provide useful data and parameters on the adsorbent and the adsorbent-adsorbent mass transfer mechanism such as the maximum adsorption capacities and the kinetic constants as well as the type of the isotherm inducing the type of kinetics controlling the adsorption process [14,15]. The second technique is that of continuous adsorption, for which the effluent to be treated flows over a bed of active charcoal or other adsorbent placed in a fixed bed. This process is also necessary for access to practical operational information [16][17][18]. During the adsorption on a fixed bed, the columns can be placed in series or in parallel. In this area, small column studies are started to simulate the potential performances of adsorption, and then the results obtained will be extrapolated in large scale columns or reactors [19,20].

In addition to the kinetic parameters, the adsorption capacity of activated carbon in a fixed bed is of great practical importance because it makes it possible to evaluate the efficiency of the fixed bed with respect to the elimination of the contaminants [21]. This was the subject of several studies. Different methods have been used to access this parameter. We distinguish among others, those who use the curve of breakthrough [22,23]. In addition the BDST model and the Clarks model are frequently used to access in this parameter [14].

In the present work, we have carried out an experimental study for testing the ability of Norit Year 2017 C Ali Benhmidene ? , Khaoula Hidouri ? , Hedi Ben Amor ? & Bechir Chaouachi ? Nowadays, several industrial sectors use dyes in their product such as leather, textiles and food processing industries, there is a primary concern of ue to the rapid urbanization and rapid growth of industrialization, large quantities of waste

containing pigments and dyes are discharged into the receiving aquatic environment. It is expected that the dyeing industry is responsible for the release of 100 tons of dyes per year into the environment, contaminating rivers and springs [1]. Of these dyestuffs, 5-10% is lost in industrial effluents, and consequently, wastewater treatment is one of the biggest problems we face today [2]. In fact, due to ineffective treatment processes, the presence of these dyes will have a negative impact on environmental life in general [3]. Knowing that synthetic dyes are not biodegradable and toxic in nature; their presence in the aquatic ecosystem hinders the growth of biota and affects the food web [4]. In addition, long term human exposure to dye pollutants increases the risk of tumours, cancers, cerebrovascular and lung diseases [5]. D decolorization and treatment of wastewater [6]. In addition to adsorption which has been widely used, there are various methods of physical and chemical treatment for organic dyes. The most important treatment processes are coagulation and flocculation [7], photodegradation, biosorption, oxidizing agents, membrane and ultrafiltration. The advantages, disadvantages and limitations of each technique have been widely studied by many researchers [8][9][10]. However, those technologies are costly, less effective and lack adaptability to a wide range of dyes present in the wastewaters. As a technique obeyed by environmental rules, capable of eliminating a wide range of contaminants even at very low concentrations [11], the adsorption processes presents the most preferable method for the purification of water from synthetic dyes [12,13]. Year 2017 C activated carbon to remove the Alizarin Red S as an example of anionic dye. Our study is realised for static regime in Batch reactor. However series of columns is used in dynamic regime. The adsorption capacity of activated carbon in static and dynamic is calculated by using different methods for different operating conditions.

2 II.

3 Material and Method

4 c) Batch equilibrium studies

The study of the adsorption of RAS by the activated carbon NORIT GCA830 in a static condition was carried out according to the following experimental protocol: 1000 ml of RAS aqueous solution of variable initial concentration are stirred with 50 mg of NORIT GCA830 of particle size between 0.4 and 0.63 mm at ambient temperature. After a given stirring time, samples were taken and then centrifuged at 3000 rpm for 5 minutes. The supernatant is analyzed using a spectrophotometer (HATCH DR / 2000).

5 d) Fixed-bed adsorption experiments

For the experiments under dynamic conditions, we carried out experiments of adsorption in fixed bed by using the prototype given in Figure2: Each column of inner diameter of 1.2cm, contains a given weight of active carbon of particle size of 0.4 to 0.63 mm, corresponding to cumulative height respectively of ??3, 5.3, 7.3, 9.3 and 11.3cm. The inlet solution dye concentration is 25 mg / l to 75 mg / l and its flow rates are 7, 15, 22.5 and 30ml/s.

6 III.

7 Results and Discussion

8 a) Batch equilibrium studies

In order to determine the adsorption parameters of RAS on NORIT GCA830, the sorption isotherms of (3) (4)

a) The Adsorbent In present study we used activated carbon NORIT GCA830; the main characteristics are extracted from Norit Degital Library is shown in Table 1 [24].

9 C

The values of Langmuir parameters such as the maximum adsorption capacity q_m and of the equilibrium constant K_l and their of Freundlich (K_F and n) are presented in Table ??.

We can be seen that the n value is between 2-10 the rung indicates a good favourability of sorption [13]. According of applicability of both Freundlich and Langmuir isotherms, we deduce that both heterogeneous surface and monolayer adsorption conditions exist under the actual studied process of sorption According the results illustrated in above curves, the evolutions of breakthrough and saturation times are function of studied parameters. From Figure 3(b), we can be seen that the breakthrough and saturation times are all the shorter as the height of the bed is short. However they are shorter as the initial concentration and flow rates are high (see Figure 3 In order to understand the evolution of the breakthrough and saturation time as a function of the studied parameters, we have plotted in Figure 4 (a) and (b), those variations respectively versus bed height and the reverse of flow rate. It can be seen, the increase in t_b and t_s is directly proportional to the bed height (Z), but inversely proportional to the flow velocity. However, no relationship could be established to describe the evolution of t_b and t_s the initial concentration.

Langmuir and Freundlich isotherms in their linearized form were determined. We obtain right lines whose regression coefficient ($R^2 > 0.98$).

To obtain these curves, we followed, as a function of the time, the evolution of the concentration of RAS effluents at the columns exit. The curves are represented for different height of the adsorbent bed (Figure 3). An important result can be deduced from these curves is that the time difference ($t_b - t_s$) is independent of the bed height (Figure 4 (a)). Result means that the adsorption zone height (where the concentration varies between 0 and C_0) is independent of the bed height. On the other hand, when the flow rate increases the time difference ($t_b - t_s$) decreases (Figure 4 (b)).

Based on the breakthrough curves, the amount of RAS adsorbed by activated carbon in the fixed bed is calculated by using the following equation [25]: $\int_0^{t_b} C_m F dt = C_0 (V - V_0) = (1)$

The integral in Eq. (1) is equal to the area includes the ordinate axis and the breakthrough curve, where it's calculated by using the Matlab software. Values of adsorption capacity calculated from the breakthrough curves at different experimental conditions are grouped in Table 4.

10 C ii. Assessment of adsorption capacity

Where F is the volumetric flow and m is the weight of activated carbon.

It is found that the adsorbed amount depends of the bed height, the initial concentration and the flow rate. As the bed height increases the liquid residence time in the bed increases, and therefore the molecules of RAS diffuse deeply into the adsorbent grains. This results in an increase in the adsorbed amount which reaches its maximum value of 380 mg / g when the bed height exceeds about 0.08m. Increasing inlet concentration results to increase its gradient in the liquid film. Consequently, an improvement of the solute diffusion from the liquid phase to activated carbon grains. This results in an increasing of adsorbed amount. However, the adsorbed amount decreases, when the flow rate increases (Figure 5). In fact, an increase in flow rate results in a reduction in the thickness of the liquid film around grain, which has the effect of improving external diffusion, hence adsorption. But at the same time there is a reduction in the residence time and the molecules of solute doesn't penetrate enough within the adsorbent grains. In sum, a decrease in the adsorbed amount is observed when the flow rate increases.

It should be noted that at zero flow velocity, the adsorbed amount value is about 385 mg / g (see Figure 5). It is equal to that determined by the Langmuir model. Where: $q_m = 385 \text{ mg/g}$ is the maximum absorption capacity. And S is the column section.

The adsorption capacity of Norit GCA830 in fixed bed for the RAS is given by the following expression: $q = \frac{C_0 V}{C_0 V - C_m V_0} = \frac{C_0 V}{C_0 V - C_m V_0}$

2.96 0.96 2.17, from which we deduce the mean value of w . In addition the thickness of mass transfer zone Z_0 is defined as the length at $t_b = 0$, it given by the following equation: $Z_0 = \frac{C_0 V_0}{C_0 V - C_m V_0}$

BEST model present many advantageous such as it reduce the experiments duration. In fact, it is sufficient to determine the breakthrough time, Where u_0 is the flow velocity (m/s) As it's shown in Figure 8(a), the variation of inlet concentration leads to the variation of the slope m_x , the ordinate at the origin C_x and the thickness of mass transfer zone Z_0 . In addition, increasing the flow rate, results in a decrease in the slope m_x and the ordinate at the origin C_x , Contrary to the thickness of mass transfer zone Z_0 (Figure 8(a)). If m_x , C_x and Z_0 are defined from BDST curves, adsorption capacity q , velocity of migration of adsorption zone v and the kinetic constant k are defined too, their values are shown in Table 5 for the different operating conditions studied. As indicated in Table 5, the absorption capacity increases if we increase the input concentration and if we reduce the flow rate. It reaches its maximum value of 374 mg/g for the lower flow rate studied. For the thickness of mass transfer zone Z_0 , it can be seen that it's proportional of inlet concentration and flow rate. In fact, an increase in the flow rate reduces the residence time of the solution in the bed and consequently the contact time solute-adsorbent. Thus the molecules don't penetrate enough within the adsorbent. This results in a widening of the height of adsorption zone.

11 Global

Concerning the kinetic constant k , it can be seen that k increases as the flow rate increases. That because, the increase in the flow rate results in a reduction in the thickness of the film through which the diffusion becomes faster. With respect to the influence of the initial concentration, k decreases as C_0 increases. This evolution was also observed by Danny et al. [28] during the study of the adsorption of some metals in a fixed bed of activated carbon.

12 IV.

13 Conclusion

In the present work, our aim is to predict the adsorption capacity of fixed bed activated carbon Norit GCA830 to remove Alizarin Red S. From the experiments in Batch reactor the adsorption capacity determine using Langmuir

model is of 385 mg/g. We are found that both model of Langmuir and Freundlich fit well our experimental results, but the Langmuir model is better.

For fixed bed adsorption process, the breakthrough curves have been plotted at various inlet dye concentration, bed height and flow rate. The obtained results show that both breakthrough and © 2017 Global Journals Inc. (US) Dynamic Sorption of Alizarin Red S by Fixed Bed Activated Carbon For the evaluation of the velocity of migration of the adsorption zone, it's clear that an increase in the flow rate or the inlet concentration leads to an increase in the velocity of migration and consequently the exhaustion of the bed and the saturation of the activated carbon, all the faster that u_0 and C_0 are higher. exhaustion times increases with the increase of bed height and the decrease of flow rate and inlet solution dye concentration. According the operating condition, the maximum absorption capacity, calculated from breakthrough curve area, is about 380mg/g. Using breakthrough curve, the absorption capacity of fixed bed is correlated in function of studied operating condition as following: Global Journal of Researches in Engineering () Volume XVII Issue II Version I

14 23

Year 2017

15 C

The adsorption capacity estimated using the BDST model increase with the inlet concentration where it achieved its maximum value of 374mg/g for a lower flow rate studied. In addition from BDST model, allowed to define the thickness of absorption zone it's between 0.02 to 0.05m. The constant kinetic and the velocity of migration of absorption zone estimated by BDST model are mostly influenced by the residence time. ¹

2

Number (CI)	58005
Class	anthraquinone
Molar Wight (g)	342.267
Ionisation	acide
Ebullition temperature (°C)	430
Fusion temperature (°C)	287-289

Figure 1: Table 2 :

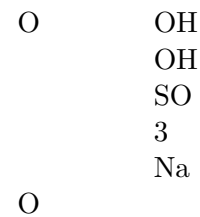
¹© 2017 Global Journals Inc. (US) Dynamic Sorption of Alizarin Red S by Fixed Bed Activated Carbon

1

Specific surface (m ² /g)		1000
Molasses Index		210
		min
Iodine number (mg/g)		920
		min
Moisture conditioning (%)		2 max
Mesh size(%) :		
-	Greaterthan 8mesh (2.36mm)	8 max
-	Lessthan 30 mesh (0.6mm)	4 max
Abrasion number (AWWA)		75 min
Apparent density (mg/l)		0.51
Effective size (mm)		0.86
Density after backwash and drainage (g.cm -3)		0.45

b) The Adsorbate

Our study focused on adsorption of Alizarin Red S dye by NORIT GCA 830 in batch and fixed bed reactor. Alizarin Red S (sodium alizarin sulphonate, CI 58005) is an anthraquinone.



[Note: Figure 1 shows its chemical structure molecule: Fig. 1: Chemical structure molecule of RASThe mains property of RAS is resumed in Table2.]

Figure 2: Table 1 :

4

Bed height (m)	Flow rate (ml/min)	Inlet concentration (mg/l)	Adsorption capacity (mg/g)
0.033			360
0.053 0.073	7.5	75	380 382
0.093			385
0.053		25	222.3
	7.5	50	347.6
		75	380
	7.5		347.6
0.053	15	50	318.7
	22.5		276

Figure 3: Table 4 :

5

C ₀ (mg/l)	u ₀ (m/h)	m ₀ (h/m)	x ₀ (h)	q (mg/g)	Z ₀ (m)	k (l/kg.s)	v (10 ³ m/h)
	2.92	1390	28.57	209.2	0.02	0.854	0.72
25	5.84	680	18.04	204.7	0.026	1.353	1.47
	8.76	415	17.2	187.4	0.041	1.42	2.4
	11.68	270	12.4	162.6	0.045	1.968	3.7
	2.92	1155	25.515	348	0.022	0.478	0.866
50	5.84	545	14.385	328.4	0.026	0.848	1.834
	8.76	332.5	14.973	300.5	0.045	0.815	3
	11.68	167.5	11.093	268.1	0.050	1.1	5.97
25	2.92	1390	28.57	209.2	0.020	0.854	0.72
50		1155	25.515	348	0.022	0.478	0.866
75		830	22.29	374.8	0.027	0.365	1.2

Figure 4: Table 5 :

[Mirzadeh et al.] , S S Mirzadeh , S M Khezri , M A Shahla Rezaei , H Forootanfar , A H Mahvi , M A Faramarzi
, Silica . doi:10.1186%2F2052-336X-12-6. *J. Environ. Health Sci. Eng.*2014 p. 12.

[Gomelya et al.] , N D Gomelya , Shabliyta , A G Trohymenko .
[Global Journal of Researches in Engineering] , *Global Journal of Researches in Engineering*

[Sci et al. ()] , Acad Sci , India , Sect , Phys , Sci . 10.1007/s40010-014-0154-4. 2014. 84 p. .

[Treatment ()] , Treatment . 10.1080/19443994.2015.1027960. 2016. 57 p. .

[Verma et al. ()] ‘A review on chemical coagulation/flocculation technologies for removal of colour from textile
wastewaters’. A K Verma , Dash , Rr , P Bhunia . 10.1016/j.jenvman.2011.09.012. *J. Environ. Manage* 2012.
93 p. .

[Nasiru and Buhari ()] ‘Adsorption of alizarin and fluorescein Dyes onto palm seeds activated carbon: kinetic
and thermodynamic studies’. A S Nasiru , M Buhari . *J. Chem. Soc. Pak* 2016. 38 p. .

[Gautam et al.] ‘Adsorption of Alizarin Red S onto biosorbent of lantana camara: kinetic, equilibrium modeling
and thermodynamic studies’. R K Gautam , P K Gautam , M C Chattopadhyaya , J D Pandey . *Proc. Natl,*
(Natl)

[Hasfalina et al.] *Adsorption of copper (II) from aqueous medium in fixed-bed column by kenaf fibres*, C M
Hasfalina , R Z Maryam , C A Luqman , M Rashid . 10.1016/j.apcbee.2012.06.079.

[Hashem ()] ‘Adsorption of methylene blue from aqueous solutions using Fe₃O₄/bentonite nanocomposite’. F S
Hashem . 10.4172/scientificreports.549. *Hydrol. Current. Res* 2012. p. 143.

[Chinoune et al. ()] ‘Adsorption of reactive dyes from aqueous solution by dirty bentonite’. K Chinoune , K
Bentaleb , Z Boubberka , A Nadim , U Maschke . 10.1016/j.clay.2016.01.006. *Appl. Clay Sci* 2016. 123 p. .

[Postai et al. ()] ‘Adsorption of rhodamine B and methylene blue dyes using waste of seeds of Aleurites
Moluccana, a low cost adsorbent’. D L Postai , C A Demarchi , F Zanatta , Dcc Melo , C A Rodrigues
. 10.1016/j.aej.2016.03.017. *Alexandria Engineering J* 2016. 55 p. .

[Albroomi et al. ()] ‘Batch and fixed-bed adsorption of tartrazine azo-dye onto activated carbon prepared from
apricot stones’. H I Albroomi , M A Elsayed , A Baraka , M A Abdelmaged . 10.1007/s13201-016-0387-2.
Appl. Water Sci 2016.

[Gopel et al. ()] ‘Continuous fixed bed adsorption studies of Rhodamine-B dye using polymer bound adsorbent’.
N Gopel , M Asaithambi , P Sivakumar , V Sivakumar . *Ind. J. Chem. Technol* 2016. p. .

[Biswas and Mishra ()] ‘Continuous fixed-bed column study and adsorption modeling: removal of lead ion from
aqueous solution by charcoal originated from chemical carbonization of rubber wood sawdust’. S Biswas , M
Mishra . 10.1155/2015/907379. *J. of Chemistry* 2015. 9.

[Danny et al. ()] ‘Correlationbased approach to the optimisation of fixed-bed sorption units’. Kokc Danny , J F
Porter , G Mckay . 10.1021/ie9902784. *Ind. Eng. Chem. Res* 1999. 38 p. .

[Danny et al. ()] ‘Determination of solid-phase loading of the removal of meal ion from effluents using fixed-bed
absorbers’. Kokc Danny , J F Porter , G Mckay . *Environ. Sci. Technol* 2001. 35 p. .

[Hamdouni ()] ‘Dynamic sorption of methylene blue by cedar sawdust and crushed brick in fixed bed columns’.
O Hamdouni . 10.1016/j.jhazmat.2006.04.061. *J. Hazardous mater* 2006. 38 p. .

[Ebrahimi et al. ()] *Fish Bone as a low-cost adsorbent for dye removal from wastewater: response surface
methodology and classical method*, Environ. Model. Assess, A Ebrahimi , M Arami , H Bahrami , E Pajootan
. 10.1007/s10666-013-9369-z. 2013. 18 p. .

[Auta ()] ‘fixed bed adsorption studies of Rhodamine-B dye using oil palm empty fruits bunch activated carbon’.
M Auta . *J. Eng. Res. Stud* 2012. 3 p. .

[Vieira et al. ()] ‘Glass beads coated with chitosan for the food azo dyes adsorption in a fixed bed column’. Mlg
Vieira , V M Esquerdo , Nobre , Lr , Dotto , Gl , Laa Pinto . 10.1016/j.jiec.2013.12.024. *J. Ind. Eng. Chem*
2014. 20 p. .

[Ramaraju et al.] ‘Low cost absorbent from agricultural waste for removal of dyes’. B Ramaraju , Pmk Reddy ,
C Subrahmanyam . 10.1002/ep.11742. *Environ. Prog. Sustain. Energy.*2014 33 p. .

[Shuryberko ()] ‘New inhibitors of corrosion and depositions of sediments for water circulation systems’. M
Shuryberko . 10.3103/S1063455X17020060. *J. water Chem. Technol* 2017. 39 p. .

[Hutchins ()] ‘New method simplified design of activated carbon systems’. R A Hutchins . *Chem. Eng* 1973. 20
p. .

[Bergamasco et al.] ‘Performance of a coagulation-ultrafiltration hybrid process for water supply treatment’. R
Bergamasco , L C Konradt-Moraes , M F Vieira , M R Fagundes-Klen , A Vieira . 10.1016/j.cej.2010.10.076.
2011.166.483-489.doi.org/10.1016/j.cej.2010.10.076 *Chem. Eng. J*

- 227 [Reynel-Avila et al. ()] 'Relevance of anionic dye properties on water decolorization performance using bone
228 char: Adsorption kinetics, isotherms and breakthrough curves'. H E Reynel-Avila , D I Mendoza-Castillo , A
229 Bonilla-Petriciolet . 10.1016/j.molliq.2016.03.051. *J. Molecular Liquids* 2016. 2016. 219 p. .
- 230 [Robinson et al. ()] 'Remediation of dyes in textile effluent: A critical review on current treatment technologies
231 with a proposed alternative'. T Robinson , G Mccmullan , R Marchant , P Nigam . 10.1016/S0960-
232 8524(00)00080-8. *Bioresource Technol* 2001. 77 p. .
- 233 [Yaghmaeian et al. ()] 'Removal of amoxicillin from contaminated water using NH₄ Clactivated carbon:
234 Continuous flow fixed-bed adsorption and catalytic ozonation regeneration'. K Yaghmaeian , G Moussavi
235 , A Alahabadi . 10.1016/j.cej.2013.08.118. *Chem. Eng. J* 2014. p. .
- 236 [Muliwa et al. ()] 'Removal of multi-active-blue dye from aqueous phase using magnetic poly-pyrrole nanocom-
237 posites: fixed-bed adsorption studies'. A M Muliwa , A C Mecha , A Grobler , M S Onyango .
238 10.19026/rjaset.13.3017. *Research J. App. Sc., Eng. Technol* 2016. 13 p. .
- 239 [Kant ()] *Textile dyeing industry an environmental hazard, Natural Science*, R Kant . 10.4236/ns.2012.41004.
240 2012. 4 p. .
- 241 [Bazrafshan et al.] 'Textile wastewater treatment by application of combined chemical coagulation, electrocoag-
242 ulation, and adsorption processes'. E Bazrafshan , M R Alipour , A H Mahvi . *J. Desalination and Water*