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Removal of aluminum from aqueous solutions by adsorption on date-pit and BDH activated carbons

Shaheen A. Al-Muhtaseb¹, Muftah H. El-Naas^{*}, Sami Abdallah

Chemical and Petroleum Engineering Department, U.A.E. University, P.O. Box 17555, Al-Ain, United Arab Emirates

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Abstract

The use of a locally prepared date-pit activated carbon and the commercially available BDH activated carbon for the removal of trivalent aluminum from aqueous solutions was examined at various conditions. In the acidic range of aluminum solubility (up to pH value of 4), both adsorbents exhibited maximum (almost equivalent) capacities for adsorbing aluminum at the pH value of 4. Date-pit activated carbon was more capable of adsorbing traces or low concentrations of aluminum ions in the solution. At low initial concentrations of aluminum and low pH, the uptake of aluminum using date-pit activated carbon was 0.305 mg/g, while that using BDH activated carbon was only 0.021 mg/g. However, the BDH activated carbon was more effective in adsorbing aluminum with high concentrations and low pH. Furthermore, date-pit activated carbon exhibited higher initial adsorption rates as compared to BDH, which showed higher rates at longer periods of time. © 2008 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Activated carbon; Precipitation; Date-pits; Isotherms

1. Introduction

Aluminum and its alloys are commonly used in the construction of siding, aircrafts, motor vehicles and lightweight utensils because of its strength and light weight. Dissolving aluminum compounds with acids produces aluminum salts, which are used widely in water treatment applications to facilitate coagulation of pollutants such as sediments, nutrients, microbes and dissolved organic compounds [1].

Aluminum is known to dissolve in water at acidic and basic conditions [1]. Although water treatment processes by coagulation depend on the precipitation of aluminum (along with impurities) at neutral conditions, residual amounts of dissolved aluminum always remain in the treated water. The American Waste Water Association (AWWA) estimated that drinking water (including treated water) provides about 5% of overall aluminum in human diets [1]. Aluminum is not known to have any positive health effects on humans. On the other hand, adverse effects of aluminum are currently known to be far more chronic (occurring over the long term) than acute (occurring in the short term). Aluminum has been shown to be a neurotoxic compound if it is allowed to enter the bloodstream. Long-term exposure of patients to dialysis water containing aluminum may cause encephalopathy (defect of the brain) and/or bone mineralization disorders [1]. Furthermore, aluminum is a potential cause of Alzheimer's disease, Lou Gehrig's disease and other forms of senile dementia [1]. It is still unclear if aluminum leads to these diseases or if it is that the diseases cause brain tissues to retain aluminum secondarily [1]. The Environmental Protection Agency (EPA) sets the secondary permissible standard for aluminum in drinking water as 0.05–0.20 mg/l [2]. Therefore it is important to remove the aluminum from water before being used as drinking water.

Date-pits are among the most common agricultural byproducts available commercially in the palm-growing countries such as the United Arab Emirates (UAE). Banat et al. prepared date-pit activated carbons by both physical activation (using carbon dioxide activation at 700 °C) [3,4] or by chemical activation (through impregnation with a potassium hydroxide solution prior to its activation with carbon dioxide at 600° C) [5]. They found that chemical activation increased the capacity

^{*} Corresponding author. Tel.: +971 3 713 3637; fax: +971 3 762 4262. E-mail address: muftah@uaeu.ac.ae (M.H. El-Naas).

¹ Current address: Department of Chemical Engineering, Qatar University, P.O. Box 2713, Doha, Qatar.

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Nomenclature

$a_{\rm F}$	Freundlich's adsorption isotherm fitting parame-
	ter

- *a*_{LF} Sips (Langmuir–Freundlich) adsorption isotherm fitting parameter
- *b* adsorption affinity estimated from the Langmuir's adsorption isotherm model (l/mg)
- *b*_F Freundlich's adsorption isotherm fitting parameter
- C_0 initial concentration (mg/l)
- $C_{\rm e}$ equilibrium concentration (mg/l)
- *K*_{LF} Sips (Langmuir–Freundlich) adsorption isotherm fitting parameter
- *m* mass of the adsorbent (g)
- *n*_{LF} Sips (Langmuir–Freundlich) adsorption isotherm fitting parameter
- *q*e equilibrium amount adsorbed (mg adsorbed/g adsorbent)
- $q_{\rm m}$ monolayer (saturation) adsorption capacity estimated from the Langmuir's adsorption isotherm model (mg adsorbed/g adsorbent)
- q_e^0 Henry's law limit of the equilibrium amount adsorbed at infinite dilution (mg adsorbed/g adsorbent)
- *V* volume of the solution (ml)

of date-pit activated carbons to adsorb methylene blue by about 53% [5]. They also prepared date-pit activated carbon using a fluidized bed reactor in two steps: carbonization at 700 °C for 2 h in nitrogen atmosphere and activation at 900 °C in carbon dioxide atmosphere [6]. The maximum adsorption capacity of activated date-pits to adsorb phenol was 16 times higher than that of non-activated date-pits [6]. On the other hand, steam-activated carbon date-pits were the most efficient decolorizing adsorbents owing to its higher surface area, total pore volume and the basic nature of the surface [7]. Abdulkarim et al. [8] found that the best carbonization and activation method of date-pits can be achieved with a burn-off ratio of 92%.

Banat et al. also used raw date-pits and date-pit activated carbons for the adsorption of zinc and copper [3] ions from water. Activated date-pit carbons were also used for the adsorption of cadmium ions [4] and other organic compounds [5,6,8] from water. They studied the effect of contact time, pH, temperature, cadmium ion concentration, sorbent dose, salinity, as well as the activation temperature on the removal of cadmium ions by date-pits. They found that the kinetic data for the adsorption process obeyed a second-order rate equation [5,6]. Non-activated date-pits exhibited higher Zn²⁺ and Cu²⁺ ion uptake than activated date-pits [3]. The uptake of both metal ions increased on increasing the pH value of the system from 3.5 to 5.0 as well as on decreasing the temperature from 50 °C to 25 °C [3]. Adsorption capacities for the non-activated date-pits towards Cu²⁺ and Zn^{2+} ions as high as 0.15 mmol/g and 0.09 mmol/g, respectively, were observed [3].

Table 1

Characteristics of date-pit and BDH activated carbons

	Date-pit activated carbon	BDH activated carbon
Particle size (mm)	0.1-0.20	0.85-1.70
BET surface area (m ² /g)	690	1220
BET surface area in the micropore region (m^2/g)	604	1173
Total pore volume (cm ³ /kg)	312	534
Total pore volume in the micropore region (cm ³ /kg)	235	479

The removal of aluminum from water by adsorption was investigated using different adsorbents such as starch [9], activated charcoal [9], wood charcoal [9], clay [9], algae [10] and ion-exchange resins [11]. However, to the best of the authors' knowledge, there is no published literature for the adsorption of aluminum on date-pit or BDH activated carbons. Adsorption processes which utilize natural adsorbents are economical and they have an advantage over other removal methods for removing trace concentrations of pollutants.

In this work, the adsorption of aluminum from aqueous solutions on date-pit and BDH activated carbons is studied. The effect of pH on the adsorption equilibria was examined at both low and high initial concentrations (i.e., at 5 mg/l and 50 mg/l, respectively). The adsorption isotherms were measured at a fixed, optimum, pH value, at which the kinetics of adsorption were studied for both low and high initial concentrations of aluminum solutions.

2. Experimental

2.1. Chemicals and materials

The stock aluminum solution was prepared by dissolving 1 g of aluminum powder in 10 ml of concentrated hydrochloric acid to produce an aqueous solution of aluminum chloride, and diluting the resulting solution with distilled water to a total volume of 11. After that, the solution was filtrated and the concentration of dissolved aluminum in the filtrate is measured with atomic absorption as 937 mg/l. This stock aluminum solution was diluted in different proportions to give samples with the required concentrations for the adsorption experiments.

Aluminum powder was obtained from Riedel-deHaën with an assay of 91%, and hydrochloric acid was obtained from the BDH Company with an assay concentration of 35.4% and a specific gravity of 1.18. All chemicals were used as received.

BDH activated carbon was received from the BDH company in a granular form with a particle size 0.85–1.70 mm (10–18 mesh). Date-pit activated carbon was prepared locally as described in the following section. The date-pit and BDH activated carbons were characterized using a Micromeritics ASAP-2010 apparatus and software. A summary of the characteristics of the date-pit and BDH activated carbon used in this work is shown in Table 1.

2.2. Procedures

Date-pit activated carbon was prepared through the following procedure. First, date-pits were dried, grinded and screened. The granules collected between the mesh size 200 and the pan were collected to be activated and carbonized. Then, it was carbonated and activated to produce activated carbon. The carbonization is performed in a tube furnace which has been initially purged with a flow of nitrogen for 10 min. After that, the furnace is heated at a rate of 5 °C/min up to 900 °C and then kept at this temperature for 3 h. After cooling the furnace to room temperature, the material contained is considered as carbonized (inactive) carbon. After weighing the inactive carbon sample, it is activated in the same tube furnace and the same temperature program as in the carbonization step, but with a flow of carbon dioxide (instead of nitrogen). The resulting product is activated carbon.

The adsorption equilibria of aluminum were measured by contacting 0.1 g of the studied adsorbent with 50 ml of a solution with a known initial concentration of aluminum. After shaking the sample in a closed container for 24 h, the sample is filtrated, and the final concentration of aluminum in the solution is measured using atomic absorption. The amount adsorbed on the activated carbon is estimated from the difference in the two concentrations using the following equation

$$q_{\rm e} = \frac{C_0 - C_{\rm e}}{m} V \tag{1}$$

where q_e is the equilibrium amount adsorbed (mg adsorbed/g adsorbent), V is the volume of the solution (ml), m is the used mass of the adsorbent, and C_0 and C_e are the initial and equilibrium concentrations (mg/l), respectively. The adsorption kinetics were measured using exactly the same procedures as the adsorption equilibria, but with shaking times ranging from 10 min to 24 h.

When using date-pit activated carbon, it exhibits an alkaline character and raises the pH of the used solution. This alkaline character is believed to be a result of the alkalinity of the carbon, which increases the solution's pH upon stirring. If washed with 50 ml of distilled water, 0.1 g of date-pit activated carbon raises the pH of the water to 9. Therefore, the pH was continuously monitored and fixed at the desired value using counted droplets of 1 M hydrochloric acid solution.

3. Theory

The adsorption equilibria of a species can be correlated using several adsorption isotherms. The most popular adsorption is Langmuir's adsorption model:

$$q_{\rm e} = q_{\rm m} \frac{bC_{\rm e}}{1 + bC_{\rm e}} \tag{2}$$

where $q_{\rm m}$ is the monolayer (saturation) adsorption capacity and b is the adsorption affinity. At very low concentrations of the solute, Langmuir adsorption isotherm approaches to Henry's

law as

$$q_{\rm e}^0 = \left[\lim_{C_{\rm e} \to 0} \frac{q_{\rm e}}{C_{\rm e}}\right] C_{\rm e} = (q_{\rm m}b)C_{\rm e} \tag{3}$$

where $(q_m b)$ is the corresponding Henry's law coefficient. Another popular adsorption isotherm model is Freundlich's adsorption isotherm [12]:

$$q_{\rm e} = a_{\rm F} C_{\rm e}^{b_{\rm F}} \tag{4}$$

where $a_{\rm F}$ and $b_{\rm F}$ are fitting parameters.

Sips proposed a combined adsorption isotherm that combines both Langmuir and Freundlich adsorption isotherm models [13]. This model is known as Sips (or Langmuir–Freundlich) adsorption isotherm, which is expressed as

$$q_{\rm e} = \frac{K_{\rm LF} C_{\rm e}^{n_{\rm LF}}}{1 + (a_{\rm LF} C_{\rm E})^{n_{\rm LF}}}$$
(5)

where K_{LF} , n_{LF} and a_{LF} are fitting parameters. Unlike Langmuir adsorption isotherm model, Freundlich and Sips adsorption isotherm models' fitting parameters do not have significant physical meanings. Furthermore, Freundlich and Sips adsorption isotherm models suffer from thermodynamic inconsistency because they do not exhibit a finite Henry's constant at zero surface coverage. However, Sips adsorption isotherm model describes the adsorption equilibrium data most accurately because of its additional fitting parameter. El-Naas et al. [14] reported that the Sips isotherm model gave the best fit of the equilibrium data for the biosorption of lead on *Chlorella vulgaris*.

One of the other physically significant equilibrium adsorption models is the Dubinin–Radushkevich (D–R) adsorption isotherm model, which is given as [15]:

$$q_{\rm e} = q_{\rm D} \exp\left(-B_{\rm D} \left[RT \ln\left(1 + \frac{1}{C_{\rm eM}}\right)\right]^2\right) \tag{6}$$

where q_D is the pore filling limit (mg/g), B_D is a fitting parameter related to the adsorption energy and C_{eM} is the molar equilibrium concentration of the solute (mol/l). The D–R equation has the advantage of estimating the mean free energy of sorption from the fitted parameter B_D as [16]:

$$E = \frac{1}{\sqrt{2B_{\rm D}}}\tag{7}$$

The rate of adsorption can be described by applying a pseudosecond-order Lagergren rate equation, which has been modified by Ho and McKay [17] as

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k(q_{\mathrm{c}} - q_{\mathrm{t}})^2 \tag{8}$$

where k is a mass transfer coefficient, q_c is the equilibrium uptake and q_t is the uptake at time t. Eq. (8) can be integrated and rearranged to give

$$q_{t} = q_{c} \left[1 - \frac{1}{1 + ktq_{c}} \right]$$
(9)

Eq. (9) can be used to estimate k and q_c from experimental data of the rate of adsorption.



Fig. 1. Percentage of aluminum precipitated at various pH values at 22 °C.

4. Results and discussion

4.1. Effect of pH on the solubility and adsorption of aluminum

The solubility of aluminum chloride in aqueous solutions was tested in the pH-range of 4–6. Fig. 1 shows that a considerable percentage of aluminum is precipitated at pH values of 5 and 6, especially when using high concentrations of aluminum (such as 50 mg/l). Therefore, to evaluate only the adsorption of aluminum on the selected adsorbents (i.e., without including the amount removed by precipitation), all the adsorption experiments conducted in this work were at pH values of 4 or less. At such pH values, aluminum is virtually completely dissolved in the solution.

The effect of pH (in the range of 2–4) on the equilibrium adsorption of aluminum from aqueous solutions on date-pit (DP) and BDH activated carbons was examined with initial concentrations of 5 mg/l and 50 mg/l of aluminum in the solution. Table 2 and Fig. 2 show that both DP and BDH activated carbons are virtually equivalent in their capacities to adsorb aluminum at pH value of 4, regardless of the initial concentration of aluminum. At lower pH values, DP activated carbon's capacity for adsorbing aluminum surpasses that of BDH activated carbon at low initial concentrations of aluminum (e.g., 5 mg/l) in the solution. However, BDH activated carbon becomes more efficient than DP activated carbon in adsorbing aluminum with high initial concentration of aluminum on its adsorption on DP activated carbon appears to be insignificant at pH values of 3 or less. Conversely, the

Table 2

Effect of pH on the equilibrium uptake of aluminum with initial concentrations of 5 mg/l and 50 mg/l (q_5 and q_{50} , respectively) on date pit and BDH activated carbons at room temperature (22 °C)

рН	Date-pit activ	Date-pit activated carbon		BDH activated carbon	
	q5 (mg/g)	<i>q</i> ₅₀ (mg/g)	$\overline{q_5 \text{ (mg/g)}}$	<i>q</i> ₅₀ (mg/g)	
2	0.305	0.420	0.021	1.066	
3	0.456	0.676	0.024	4.003	
4	1.321	4.426	1.368	4.490	



Fig. 2. Effect of pH value on the equilibrium amount adsorbed of aluminum with initial concentrations of 5 mg/g and 50 mg/g (empty and solid symbols, respectively) on DP (circles) and BDH (squares) activated carbons.

effect of concentration of aluminum on its adsorption on BDH activated carbon was always significant, especially at pH values in the range of 3–4. Nonetheless, both DP and BDH activated carbon exhibited maximum capacities for adsorbing aluminum at the pH value of 4. Therefore, it is adopted in this work as the optimum pH value at which all the following analyses are conducted.

4.2. Equilibrium adsorption isotherms

The equilibrium adsorption isotherms for the adsorption of aluminum on DP and BDH activated carbons were measured at room temperature ($22 \,^{\circ}$ C) and a controlled solution pH of 4. The measured data are given in Table 3 and represented by symbols in Fig. 3. Fig. 3 shows the equilibrium adsorption isotherm data on DP and BDH activated carbon using both linear and logarithmic scales (top and bottom parts, respectively). Clearly, as noted previously in Fig. 2, the two adsorbents are virtually equivalent in their adsorption capacities for adsorbing aluminum from aqueous solutions at pH value of 4. However, DP activated carbon exhibits a slightly higher capacity for adsorbing aluminum with low concentrations (equilibrium concentrations below 40 mg/l). Nonetheless, this behavior is reversed at higher concentrations of aluminum in the solution. This observation gives DP activated carbon an advantage over the commercially available BDH acti-

Table 3

Equilibrium isotherm data for the adsorption of aluminum on date-pit and BDH activated carbons at pH 4 and room temperature $(22 \,^{\circ}C)$

Date-pit activated carbon		BDH activated carbon	
$\overline{C_{\rm e}~({\rm mg/l})} \qquad q_{\rm e}~({\rm mg/g})$		$\overline{C_{\rm e} ({\rm mg/l})}$	$q_{\rm e} ~({\rm mg/g})$
0.388	1.369	1.122	0.998
2.857	1.647	2.959	1.641
5.714	3.347	7.398	2.544
16.224	4.266	17.245	3.865
40.102	4.648	40.969	4.491
88.140	5.357	87.875	6.063
187.040	5.638	187.550	6.225
380.210	6.283	387.000	6.500



Fig. 3. Measured equilibrium adsorption isotherms of aluminum on DP and BDH activated carbons (circles and squares, respectively) and the Sips correlations (solid and dashed lines, respectively) at pH 4.

vated carbon for treating trace concentrations of aluminum in aqueous solutions, which is the usually expected case for waste water treatment applications.

The fitting parameters for the measured adsorption isotherm data using Langmuir, Freundlich, Sips and D-R adsorption models were obtained by minimizing the sum of squared errors as presented in Table 4, with the Sips isotherm correlation represented by the lines in Fig. 3. The Langmuir adsorption isotherm

Table 4

Adsorption isotherm models' fitting parameters and the corresponding average relative errors (AREs)^a and minimum sum of squared errors $(E^2)^b$ for the adsorption equilibria of aluminum on date-pit and BDH activated carbons at pH 4 and room temperature (22 °C)

Isotherm	Parameter	Date-pit activat	Date-pit activated carbon		BDH activated carbon	
		Value	ARE (%), [<i>E</i> ²]	Value	ARE (%), $[E^2]$	
Langmuir	$q_{\rm m} ({\rm mg/g})$	5.831	16.07, [1.77]	6.562	10.47, [0.75]	
C	<i>b</i> (l/mg)	0.184		0.086		
Freundlich	a_{F}	2.125	16.95, [2.00]	1.689	20.77, [2.84]	
	$b_{ m F}$	0.192		0.245		
Sips	$K_{ m LF}$	2.054	11.59, [0.91]	0.948	4.20, [0.34]	
	$n_{\rm LF}$	0.531		0.738		
	$a_{ m LF}$	0.098		0.064		
D-R	$q_{\rm D} \ ({\rm mg/g})$	5.515	18.81 [2.66]	10.060	12.35, [1.33]	
	$10^8 \times B_{\rm D}$	3.085		0.324		
	E (kJ/mol)	4.026		12.423		

^a ARE = $(100\%/n)\sum_{i=1}^{n} |q_{exp} - q_{calc}|/q_{exp}$; *n* = number of experimental data points in each set. ^b $E^2 = \sum_{i=1}^{n} (q_{exp} - q_{calc})^2$; *n* = number of experimental data points in each set.

model parameters show that the BDH activated carbon has a higher estimated monolayer surface coverage limit (q_m) than the DP activated carbon. This is attributed to the considerably higher total surface area and pore volume of the BDH activated carbon (given in Section 2) in comparison to the DP activated carbon. Nonetheless, the DP activated carbon exhibits a considerably higher affinity coefficient (b) in comparison to that of the BDH activated carbon. This higher affinity leads to the superiority of DP activated carbon in adsorbing aluminum with low initial concentrations in aqueous solutions. Equating the adsorption isotherms of DP and BDH activated carbon gives an equilibrium concentration value of 43.9 mg/l, which is the approximate maximum limit for the superiority of DP activated carbon of adsorbing aluminum from aqueous solutions.

The Freundlich isotherm model was less capable of describing the adsorption equilibrium data than the Langmuir adsorption isotherm model. This is demonstrated clearly by the higher ARE and E^2 values (calculated using the expressions presented in the footnote of Table 4) for the Freundlich adsorption isotherm model in comparison to those of the Langmuir adsorption isotherm model as shown in Table 4. Therefore, in addition to its thermal inconsistency, this makes the use of the Freundlich adsorption isotherm model less favorable than the Langmuir adsorption isotherm model. Nonetheless, the Langmuir-Freundlich (or Sips) adsorption isotherm model is much more capable of correlating the adsorption equilibrium data than both the Langmuir and Freundlich adsorption isotherm models. This is attributed to the additional fitting parameter that the Sips isotherm model contains, and to the form of the Langmuir-Freundlich isotherm which combines both the Langmuir and Freundlich models' behaviors. Therefore, it is more desired to use the Sips adsorption isotherm model than both the Langmuir and Freundlich adsorption isotherm models except at very low concentrations where its thermal inconsistency can be an important issue. In that situation, the Langmuir adsorption isotherm is more preferred for approaching a finite Henry's law limit.

Table 5 Kinetic adsorption uptakes of aluminum with initial concentrations of 5 mg/l and 50 mg/l (q_5 and q_{50} , respectively) on date-pit and BDH activated carbons at pH 4 and room temperature (22 °C)

t (min)	Date-pit activated carbon		BDH activated carbon	
	$\overline{q_5 \text{ (mg/g)}}$	<i>q</i> ₅₀ (mg/g)	q5 (mg/g)	<i>q</i> ₅₀ (mg/g)
10	0.564	1.834	0.747	1.484
20	0.676	2.880	0.670	1.760
30	0.823	3.171	0.820	1.990
45	0.924	3.545	0.922	2.257
60	1.052	3.835	1.073	2.449
120	1.099	4.094	1.181	3.469
180	1.124	4.387	1.232	4.133
1440 (24 h)	1.320	4.430	1.370	4.495

The D–R adsorption isotherm model's parameter q_D , which indicates the pore filling limit, was consistent with the Langmuir adsorption isotherm model parameter q_m , which indicates the monolayer surface coverage limit. Both q_D and q_m for BDH activated carbon were significantly higher than those for DP activated carbon as shown in Table 4.

In general, adsorption of heavy metals is a complex process, and its mechanism is difficult to predict because it depends on the characteristics of both the adsorbent and sorbate. Adsorption of metal ions on solid surfaces can take place through physical adsorption, chemical adsorption or ion-exchange [14]. The typical range of bonding energy for ion-exchange mechanisms of divalent metal ions is 8–16 kJ/mol [18,19]. For the adsorption of aluminum on DP and BDH activated carbons, the adsorption energies were 4.0 kJ/mol and 12.4 kJ/mol, respectively, as shown in Table 4. Assuming that the same energy limits for the divalent ion-exchange are applicable, this indicates that the adsorption of aluminum on BDH activated carbon is controlled by an ion-exchange mechanism, whereas its adsorption on DP activated carbon is controlled by physical or chemical adsorption mechanisms.

4.3. Rate of aluminum adsorption

The rates of adsorption of aluminum on DP and BDH activated carbons were also measured at a pH value of 4 and room temperature $(22 \,^{\circ}C)$ for the two initial concentrations of 5 mg/l and 50 mg/l of aluminum in the aqueous solutions. The measured data are presented in Table 5. The pseudo second-order Lagergren rate equation (Eq. (8)) was fitted to each set of the measured rate data in the range of 10 through 180 min by minimizing the sum of squared errors of q_t as expressed in Eq. (9). The resulting fitting parameters, minimum sum of squared errors (E^2) and average relative errors (AREs) are shown in Table 6. The measured and correlated rate of adsorption data are also shown in Fig. 4. It is noteworthy that the fitted q_c values are in agreement with the measured q_t values at 24 h (which were not included in the fitted data). This adds credence to the measured values in the whole time range of 10 min through 24 h. Furthermore, the mass transfer coefficient (k) values for the adsorption of dilute solutions of aluminum (i.e., with an initial concentration of 5 mg/l) on both adsorbents were much higher than those



Fig. 4. Measured (symbols) and correlated (lines) adsorption kinetics of aluminum on DP and BDH activated carbons (circles and squares, respectively) at pH 4.

for relatively high initial concentrations of aluminum (i.e., at 50 mg/l). This phenomenon is attributed to the relatively higher competition in the latter case, which reduces the corresponding mass transfer coefficient. The k values for the adsorption of aluminum at low initial concentrations (5 mg/l) on both DP and BDH activated carbons were comparable to each other. On the other hand, the k value for the adsorption of aluminum with high initial concentration (50 mg/l) on DP activated carbon was much higher than that on BDH activated carbon. This indicates that the adsorption of aluminum with high initial concentrations on DP activated carbon is much faster than on BDH activated carbon. This can be linked to the considerably high ratio of micropore surface areas and pore volumes for the BDH activated carbons (96.1 and 89.7%, respectively) compared to those of DP activated carbons (87.5 and 75.3%, respectively) as indicated in the characteristics given in Section 2 for these two adsorbents. Therefore, aluminum takes a longer time to diffuse through the micropores of BDH activated carbon than those of the DP activated carbon. On the other hand, Table 1 shows that the particles of DP activated carbon were much smaller than the BDH activated carbon. This observation can constitute a mass transfer limitation for the adsorption of aluminum on BDH activated carbon, which may contribute to its slower rate of adsorption. The same conclusions can be obtained from Fig. 4 where the kinetic adsorption of aluminum with low initial concentrations on the two adsorbents was almost equal throughout the time range, and the kinetic adsorption of aluminum with

Table 6

Fitting parameters for the pseudo second-order Lagergren rate equation (Eq. (9)) with initial concentrations of 5 mg/l and 50 mg/l (q_{t5} and q_{t50} , respectively) on date-pit and BDH activated carbons at pH 4 and room temperature (22 °C)

	Date-pit activated carbon		BDH activated carbon	
	q_{t5}	<i>qt</i> 50	q_{t5}	q_{t50}
$ \frac{q_{c} (mg/g)}{k (g/mg min)} $ $ \frac{E^{2} (mg^{2}/g^{2})^{a}}{ARE (\%)^{a}} $	1.222 0.0601 0.00866 3.74	4.682 0.0152 0.0435 2.30	1.263 0.0643 0.0601 9.57	4.660 0.00552 0.670 11.83

^a E^2 and ARE are defined as in Table 4.



Fig. 5. Estimated rates of adsorption of aluminum on DP and BDH activated carbons (solid and dashed lines, respectively) at pH 4.

a high initial concentration on DP activated carbon was faster than that on the BDH activated carbon. Fig. 5 also shows that the rate of adsorption of aluminum with low initial concentrations was the same on the two adsorbents. Fig. 5 also shows that the initial rate of adsorption of aluminum with high concentration on DP activated carbon is higher than that on BDH activated carbon. However, Fig. 5 shows that this last observation is reversed later at times beyond ~20 min. Nonetheless, at such times the rates of adsorption of aluminum with a high initial concentration on both adsorbents remain approximately comparable.

5. Conclusions

The equilibrium and kinetic adsorption of aluminum from aqueous solutions was examined on two adsorbents: the datepit (DP) and BDH activated carbons. In the acidic region, the aluminum chloride salt was found to be completely soluble for pH values of 4 or less. In this range, the optimum adsorption capacities for the two adsorbents were obtained at a pH value of 4. The equilibrium data indicated that DP activated carbon was more capable of adsorbing aluminum than BDH activated carbon in the low concentration region, which favors using the DP activated carbon over the commercially available activated carbon for the removal of trace concentrations of aluminum in aqueous solutions. At low initial concentrations of aluminum and low pH, the uptake of aluminum using date-pit activated carbon was only 0.021 mg/g. The adsorption equilibria were fitted most satisfactorily with Sips isotherm. Both Langmuir and Dubinin–Radushkevich (D–R) adsorption isotherm models agreed qualitatively in predicting the monolayer saturation limits and the micropore filling limits, respectively, by indicating a higher saturation capacity for BDH activated carbon in comparison to DP activated carbon. Furthermore, the energies of adsorption of aluminum on both adsorbents were estimated using the D–R equation. These energies hint that the adsorption of aluminum on BDH activated carbon is controlled by an ion-exchange mechanism, whereas its adsorption on DP activated carbon is controlled by physical or chemical adsorption mechanisms.

The rates of adsorption of aluminum on DP and BDH activated carbons were found to be virtually equivalent on both adsorbents. Nonetheless, at high initial concentrations of aluminum, DP activated carbon exhibits faster adsorption of aluminum at initial time ranges, and then BDH activated carbon becomes faster at longer time ranges. This makes DP activated carbon more favorable for the adsorption of aluminum from aqueous solutions in continuous processes with short residence time.

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