Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2012.763050

51 (2013) 5727–5734
August

Taylor & Francis
Taylor & Francis Group

Batch and column study: adsorption of Mo(VI) from aqueous solutions using $FeCl_2$-modified fly ash

Wang Fu-qiang[a], Lian Jian-jun[b,*], Zhang Yi-min[b]

[a]*Department of Water Conservancy Engineering, North China University of Water Conservancy and Electric Power, Zhengzhou 450011, China*
[b]*Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, Nanjing 210042, China*
Tel. +86 025 85287255; email: jjlian@mail.dlut.edu.cn

Received 15 November 2012; Accepted 25 December 2012

ABSTRACT

Removal of Mo(VI) by adsorption on fly ash modified by $FeCl_2$ was investigated in the present study. Various parameters such as pH, agitation time, Mo(VI) concentration, and temperature had been studied in the batch study to evaluate the effectiveness of modified fly ash for Mo(VI) removal from water. Batch study revealed that the uptake of Mo(VI) was effective in the pH range of 4.0–6.0. Kinetic studies showed that the adsorption generally obeyed the pseudo-second-order model. The isotherm data were fitted well in the Langmuir isotherm model, and adsorption capacity was found to be $17.83\,\mathrm{mg\,g^{-1}}$. Subsequently, thermodynamic parameters such as ΔH^0, ΔS^0, and ΔG^0 for the adsorption were also evaluated, which showed that the adsorption of Mo(VI) on treated fly ash were endothermic, entropy increasing, and spontaneous. Continuous column study using a series of fixed bed was also carried out. The bed depth service time model was suitable for predicting breakthrough curve for Mo(VI) adsorption column study. In conclusion, the $FeCl_2$-modified fly ash was proven to be a feasible and cost-efficient treatment technology for Mo(VI) removal.

Keywords: Adsorption; Batch and column tests; Mo(VI) removal; Fly ash

1. Introduction

Molybdenum (Mo) is considered as an essential trace element for both plants and animals. The provisional recommended dietary intake is 75–250 $\mu\mathrm{g\,day^{-1}}$ for adults and older children. However, it would become toxic when the level of Mo concentration in water is over $5\,\mathrm{mg\,L^{-1}}$ [1]. Meanwhile, Mo pollution events have been reported for several years, such as California's San Joaquin Valley [2] and Wujintang reservoir in China [3]. Due to the huge Mo effluents from mining tailings without any pretreatment, Mo pollution has been becoming a major water quality management problem in many regions of the world. However, most of the relevant research was concerned with the removal of cations (e.g. Cu^{2+}, Zn^{2+}, and Hg^{2+}) and anionic complex species (e.g. cyanide, arsenate, and chromate) [1]. Mo is generally found in two oxidation states in nature, Mo(VI) and Mo(VI) [4]. Mo may exist as MoS_2 in reduction environments, although the formation may be kinetically limited [5]. Mo(VI) dominates in oxidization conditions, and it is commonly present as Mo_4^{2-} [4]. Therefore, removal of Mo_4^{2-} from wastewaters is of significant importance from an environmental point of view. From an economic standpoint, its recovery would be more attractive

---

*Corresponding author.

because Mo is a precious metal with many industrial applications.

Adsorption has been showing to be an economical alternative for removing heavy metals from water. The removal of Mo(VI) from aqueous solutions was studied using different adsorbents like iron ore [6], carbon cloth [7], and maghemite nanoparticles [8]. However, the research for environmentally benign, cost effective, and high-efficient materials is being desired.

Industrial waste have been widely used in the removal of various heavy metals such as As [9], Cu(II) [10], Cr(VI) [11], Cd(II), and Zn(II) [12]. However, the study on removal of Mo(VI) by industrial waste is still very rare. Fly ash is an inevitable product of the thermal power plant. In China, there are more than 300 million tonnes of fly ash that are produced per annum. This has triggered a great potential recycle for fly ash as adsorbents to treat the mine tailing effluent issues.

The main objective of this paper was to develop a new modified adsorbent based on fly ash for the removal of Mo(VI) from aqueous solutions. Adsorption dynamics, equilibrium studies, and the effects of pH and temperature were particularly investigated in batch experiments. Subsequently, Column performance for Mo(VI) removal under continuous flow conditions is also studied. The dynamics of the Mo(VI) adsorption through the fixed bed are modeled by the bed depth service time (BDST) model.

2. Experimental

2.1. Materials

Fly ash was purchased from Ansteel Company (Liaoning, China). Some important properties of fly ash should be worthwhile to mention, such as, the surface area is $0.38\,\mathrm{m^2/g}$, the chemical composition in terms of oxides is SiO_2 (52.68%), Al_2O_3 (32.02%), Fe_2O_3 (6.48%), CaO (5.02%), and MgO (2.57%), and the water content is 22.41%. Mo(VI) was added to suspensions using $100\,\mathrm{mg\,L^{-1}}$ stock solutions of $Na_2MoO_4{\cdot}2H_2O$. All other chemicals were of standard grade.

2.2. Instruments

A model Optima 2000 DV inductively coupled plasma spectrometer (Perkin Elmer Co., Americal) was used for background correction, and a model 7504 PC UV/visible spectrophotometer with 1 cm glass cells (Shanghai Xinmao Instrument Co., Ltd. Shanghai, China) was used for determination of Mo concentration in the solutions. As for the adsorption experiments, four instruments including a model DHG-9023A serious heating and drying oven (Shanghai Jinghong Laboratory Instrument Co., Ltd. Shanghai, China), a model PHS-3C pH meter (Shanghai Precision & Scientific Instrument Co., Ltd. Shanghai, China), an electronic balance model CP 153 (Ohaus instrument Co., Ltd. Shanghai, China), and an oscillator model KS (Ronghua instrument Co., Ltd. Jiangsu, China) were used collectively. In addition, all glassware were soaked in dilute nitric acid for 12 h and finally rinsed for three times with double-distilled water prior to use.

2.3. Procedures

2.3.1. Preparation of modified fly ash

For removing soluble material of the fly ash surface, a deionization cleaning procedure was applied [13]. The fly ash sample was first placed in a flow-through washing cup and eluted with a total of 5 L of warm (60°C) conductively water in a kind of batch operation over two days. Then, the washed fly ash was rinsed, dried, and kept in a plastic bag for further uses. Fly ash of 10 g and 50 mL of 10% $FeCl_2$ solution were placed in a 150 mL conical flask. The mixture was agitated using a reciprocating shaker for 5 h at 200 rpm. Finally, the supernatant was decanted and the modified fly ash was washed with distilled water several times until neutral pH. The modified fly ash was dried overnight at 105°C and stocked in plastic bags.

2.3.2. Batch Mo(VI) adsorption studies

The fundamental physicochemical data used to evaluate the applicability of adsorption processes as a unit operation were usually described by isotherm models whose parameters express the surface properties and affinity of the sorbent [14]. Four isotherm models were used to fit the experimental data, including Langmuir isotherm [15], Freundlich isotherm [16], Temkin isotherm [17], and Dubinin-Radushkevich isotherm [18]. The four adsorption isotherm models are shown by Eqs. (1)–(4):

$$\frac{C_e}{q_e} = \frac{1}{Q_0}C_e + \frac{1}{Q_0 b} \quad \text{Langmuir equation} \tag{1}$$

$$\ln q_e = \frac{1}{n}\ln C_e + \ln k \quad \text{Freundlich equation} \tag{2}$$

$$q_e = B\ln A + B\ln C_e \quad \text{Temkin equation} \tag{3}$$

$$\ln Q_e = \ln Q_m - \beta\varepsilon^2 \quad \text{Dubinin-Radushkevich equation} \tag{4}$$

where q_e is the amount of metal ions adsorbed per unit mass of adsorbent (mg g^{-1}), Q_0 is the maximum adsorption at monolayer coverage (mg g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}), and b is the adsorption equilibrium constant related to the free energy of adsorption (L mg^{-1}); k and n can be defined as adsorption capacity and intensity of adsorption, respectively. $B = RT/\gamma$, where γ is Temkin constant related to heat of sorption (J mol^{-1}). A is Temkin isotherm constant (L g^{-1}); β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2 kJ^{-2}); ε is the polanyi potential, which is equal to $RT \ln (1 + 1/C_e)$; R is the gas constant 8.314 J mol^{-1} K^{-1}; and T is the temperature (K). Q_e is the equilibrium concentration of Mo(VI) on adsorbents (mg g^{-1}), and Q_m is the theoretical saturation capacity (mg g^{-1}).

The Langmuir isotherm predicts the solid surface saturation with monolayer coverage of adsorbate at high C_e values and a linear adsorption at low C_e values. However, the Freundlich isotherm does not predict any saturation of the adsorbent surface, thus indicating physisorption on the surface. Temkin isotherm model is chosen to evaluate the adsorption potentials of the adsorbent for adsorbates [14]. Dubinin-Radushkevich isotherm model is chosen to estimate the characteristics porosity of the adsorbent and the apparent energy of adsorption.

The essential characteristics of the Langmuir isotherm model can be expressed in terms of a dimensionless constant, R_L, defined by Hall et al. [19] as Eq. (5):

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 is the initial Mo(VI) concentration (mg L^{-1}), and R_L is a positive number whose value reveals the feasibility of the sorption process. The process is irreversible if $R_L = 0$, favorable if $R_L < 1$, linear if $R_L = 1$, and unfavorable if $R_L > 1$.

The mean free energy change of adsorption (E) can be calculated using the following expression:

$$E = (2\beta)^{-1/2} \tag{6}$$

where E is the apparent energy of adsorption (kJ mol^{-1}). The adsorption type can be explained by ion-exchange if the magnitude of E is between 8 and 16 kJ mol^{-1} [20]. If the values of E are <8 kJ mol^{-1}, the type of adsorption can be considered as physical adsorption [21]. High values for E of 24.7 ± 3.2 kJ mol^{-1} show that strong chemical bond formation occurs between adsorbate and adsorbent [22].

The adsorption tests were performed by adding 0.1 g of dry material to 50 mL of Mo(VI) solution, at known concentration and pH, in a 150 mL conical flask. The parameters varied in the experiments were the Mo(VI) initial concentration (0–40 mg L^{-1}), the pH (2.0–10.0, adjusted by using dilute HCl and NaOH solutions), and the temperature (5, 15, and 25°C). Thiocyanate photometric method was used for determination of Mo concentrations in aqueous solution, which was performed by using a spectrophotometer (Shanghai Xinmao Instrument Co., Ltd. Shanghai, China). All adsorption experiments were conducted in triplicate. Only the mean values were reported in this paper. The maximum deviation observed was less than 5%.

2.3.3. Column Mo(VI) adsorption studies

Column adsorption tests on Mo(VI) removal were conducted at room temperature and atmospheric pres-

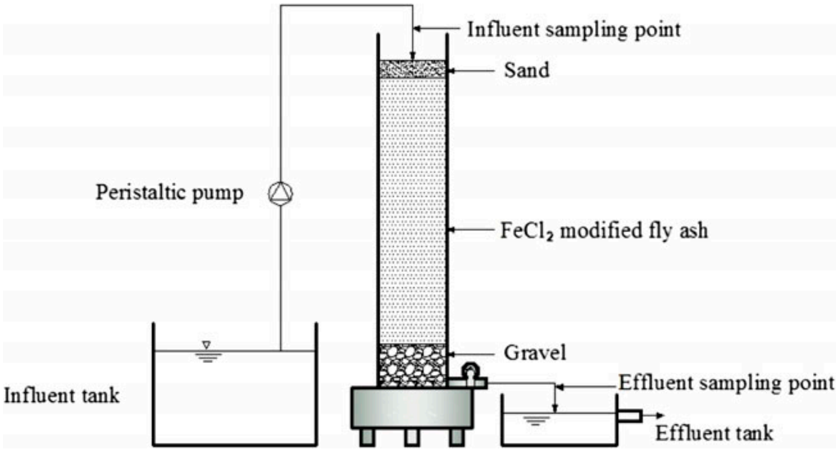

Fig. 1. Schematic diagram of column experimental setup.

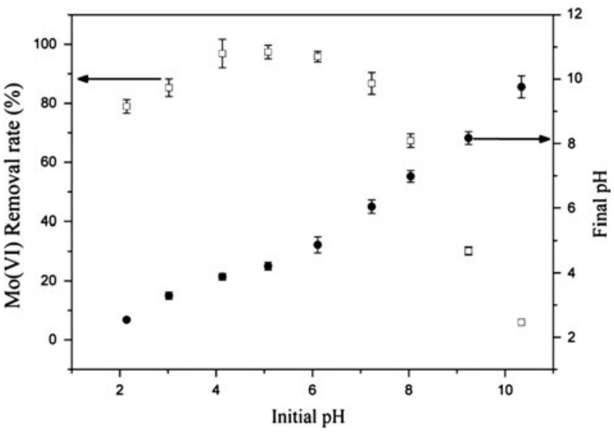

Fig. 2. Effect of equilibrium pH on the adsorption of Mo(VI). Conditions: adsorbent dose, $2\,\mathrm{g\,L^{-1}}$; Mo(VI) concentration, $10\,\mathrm{mg\,L^{-1}}$; temperature, 15℃.

sure. A continuous fixed-bed adsorption study was carried out with a PVC tube (internal diameter 8.0 cm, length 40.0 cm). Three bed depths of 10, 20, and 30 cm were selected for the fixed-bed adsorption of Mo(VI). $FeCl_2$-modified fly ash of 0.05 mm average diameter particles was selected for column sorbent material. The bottom of the columns was filled with a 5-cm layer of gravel to prevent loss of material from the columns. The column was operated in down flow mode at a hydraulic loading rate of $5\,\mathrm{mL\,min^{-1}}$. The operated Mo(VI) solution was $5.0\,\mathrm{mg\,L^{-1}}$, and the influent pH was maintained in range of 6.5–7.5. Samples collected at regular intervals of time from the outlet were used for the measurement of residual Mo(VI). The schematic diagram of the column is shown in Fig. 1.

3. Results and discussion

3.1. Effect of pH

A solution of $10\,\mathrm{mg\,L^{-1}}$ of Mo(VI) and $2\,\mathrm{g\,L^{-1}}$ of adsorbent were used to examine the pH effect (Fig. 2). The results demonstrate that the maximum amount of Mo(VI) adsorption can be reached when pH value increased from pH 4.0 to 6.0. Adsorption decreased rapidly as the pH values increased from pH 6.0 to 10.0 toward negligible level of removal efficiency in the end. Favorable effect of low pH can be attributed to the neutralization of negative charges on surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion on of Mo(VI) and their subsequent adsorption. Besides, Mo(VI) solution contains a variety of condensed molybdates, and the dominant species is $Mo_xO_y^{2-}$ at acidic pH. This ionic form was found to be preferentially adsorbed on the surface of adsorbents [13].

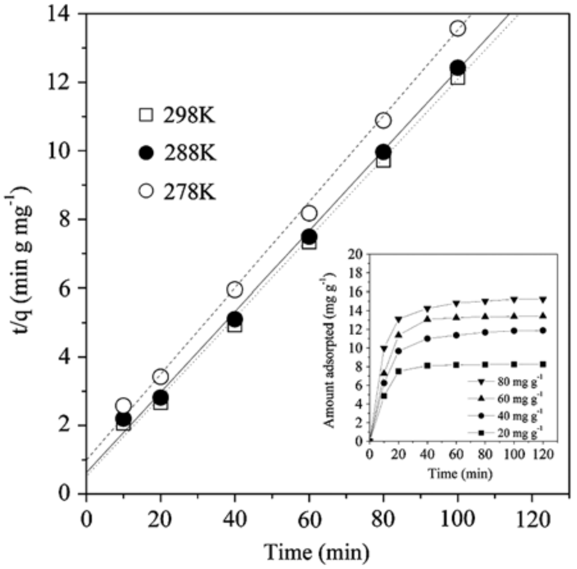

Fig. 3. Pseudo-sencond-order plots for the adsorption of Mo(VI) onto modified fly ash. Conditions: adsorbent dose, $2\,\mathrm{g\,L^{-1}}$; Mo(VI) concentration, $20\,\mathrm{mg\,L^{-1}}$; pH, 6 ± 0.3.

The lower level of adsorption at pH values higher than 6.0 is due to the high negatively charged adsorbent surface sites, which do not favor the adsorption of oxianions for electrostatic repulsion. At pH values lower than 4.0, the lower removal was attributed to the change of $Mo_xO_y^{2-}$ to other spices like: $HMoO_4^-$, H_2MoO_4, and higher groups $Mo_7O_{23}(OH)_5^-$, $Mo_7O_{21}(OH)_3^{3-}$, $Mo_7O_{22}\,(OH)_2^{4-}$ [8].

3.2. Adsorption kinetics

The influence of modified fly ash concentrations on the rate of adsorption of the Mo(VI) was investigated at pH 6 ± 0.3, and 25℃ in the present study (Fig. 3 and inset). All reaction almost reached equilibrium within 40 min. Two kinetic models were tested using $20\,\mathrm{mg\,L^{-1}}$ of Mo(VI) in order to predict the adsorption data of Mo(VI) as function of time using the pseudo-first-order model and the pseudo-second-order model. According to Namasivayam and Kadirvelu [23], the pseudo-first-order model can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where k_1 ($\mathrm{min^{-1}}$) is the pseudo-first-order rate constant, and q_e and q_t ($\mathrm{mg\,g^{-1}}$) are the amounts of matel ion adsorbed at equilibrium and at time t (min), respectively. The values of k_1 and q_e are calculated from the slope and the intercept of the plots of ln (q_e–q_t) versus t, respectively.

The pseudo-second-order model [24] is expressed by Eq. (8):

Table 1
Parameters of the adsorption kinetic models[a]

T (K)	q_e (exp) (mg g^{-1})	First-order			Second-order		
		q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
278	7.85	2.36	0.0280	0.8376	7.97	0.3579	0.9981
288	8.22	2.81	0.0333	0.9437	8.52	0.5525	0.9979
298	8.37	3.22	0.0371	0.8673	8.64	0.6574	0.9982

[a]Conditions: Mo(VI) concentration, 20 mg L^{-1}; adsorbent dose, 2 g L^{-1}; pH 6.0 ± 0.3.

$$\frac{t}{q_1} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}). The values of k_2 and q_e were calculated from the plots of t/q vs. t, see Fig. 3.

The analysis of two kinetic models indicates that the calculated q_e values obtained from the pseudo-second-order kinetic model are closer to the experimental q_e values (Table 1). Moreover, the pseudo-second-order rate equation exhibits higher value of the coefficient of determination when compared to other kinetics equations. Thus, these results indicate that the adsorption process studied generally followed the pseudo-second-order kinetic model. Fig. 3 shows that the rate of adsorption increases with increasing temperatures.

3.3. Adsorption isotherms

The different isotherms were tested for their ability to correlate with the experimental results by comparing theoretical plots of each isotherm with the experimental data. The coefficients of determination and constants for Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich linear isotherms are given in Table 2. It is observed that the coefficient of determination of Langmuir is higher than those obtained from other isotherms, indicating that the Langmuir model has a more appropriate fit for the adsorption of Mo(VI) on these sorption media. Consequently, the amount of Mo(VI) adsorbed increases until its concentration reaches saturation point. The difference in adsorption capacity can be interpreted in terms of the assumptions taken into consideration while deriving these adsorption models [22].

The values of R_L for different initial concentrations at three constant temperatures are found to lie in between 0.05 and 0.40, which signifies that the adsorption module is favorable at all concentrations tested. The magnitude of E can be used to estimate the type of adsorption, so we can infer that the type of adsorption can be generally described as ion-exchange adsorption.

Table 2
Isotherm constants obtained by using linear method

Isotherm model	Parameters	at T: 298 K
Langmuir	Q_0 (mg g^{-1})	17.83
	b (L mg^{-1})	0.305
	R_L	0.076–0.396
	R^2	0.9956
Freundlich	K	3.869
	N	3.308
	R^2	0.9559
Dubinin-Raduskevich	Q_m (mg g^{-1})	15.58
	β (mol^2 kJ^{-2})	0.0018
	E (kJ mol^{-1})	16.67
	R^2	0.9124
Temkin	A (L g^{-1})	3.785
	B	3.563
	R^2	0.9737

Table 3
Langmuir adsorption capacity of adsorbents for Mo(VI)

Adsorbents	Langmuir adsorption capacity Q_0 (mg g^{-1})	Optimum pH	References
Pyrite 0.89 m^2 g^{-1}	1.47	4.5	[6]
Acid treated Fe(III)/Cr(III) hydroxide	7.35	4.0	[25]
$ZnCl_2$ activated coir pitch carbon	11.34	4.0–8.0	[26]
Pyrite 41.7 m^2 g^{-1}	12.47	4.0–7.0	[27]
Carminic acid modified anion exchanger	13.50	2.0	[28]
Maghemite nanoparticles	33.40	4.0–6.0	[8]
$FeCl_2$-modified fly ash	17.83	4.0–6.0	This work

A comparison of the Mo(VI) adsorption capacity of some adsorbents based on the values of Q_0 can be made, see Table 3. The surface area of adsorbents and lower pH is important for Mo(VI) removal, implying that physical adsorption is the major mechanism governing the uptake of Mo(VI). Although the adsorption capacity is not much lower than other adsorbents, this adsorbent and modified process are more economical and expediently.

3.4. Effect of temperature on the adsorption process

The thermodynamic properties: enthalpy change (ΔH^0), free energy change (ΔG^0), and entropy change (ΔS^0) for the adsorption of Mo(VI) by both the adsorbents are calculated from:

$$\Delta G^0 = -RT \ln K_\mathrm{a} \tag{9}$$

$$\ln K_\mathrm{a} = \frac{\Delta S^0}{R_1} - \frac{\Delta H^0}{RT} \tag{10}$$

Where ΔH^0 and ΔS^0 are enthalpy and entropy changes, respectively, R_1 is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The equilibrium constant K_a of the adsorption process, which is equal to the product $q_\mathrm{e}/c_\mathrm{e}$, is calculated first [29]. Then, the Gibbs free energy of adsorption (ΔG^0) is determined from Eq. (9). Plotting ln K_a against $1/T$ gives a straight line with slope and intercept equal to $\Delta H^0/R_1$ and $\Delta S^0/R_1$, respectively, seen Eq. (10).

The effect of temperature is investigated from adsorption tests carried out at three constant temperatures: 5, 15, and 25℃. The positive value of enthalpy change (ΔH^0) (8.70 kJ mol^{-1}) indicates the endothermic nature of the adsorption process. The positive values of entropy change (ΔS^0) (42.6 J mol^{-1} K^{-1}) may be related to the increased randomness due to the liberation of water of hydration during the adsorption of molybdate [9]. The values of ΔG^0 at 5, 15, and 25℃ are −3.060, −3.756, and −3.911 kJ mol^{-1}, respectively. The negative values of free energy change (ΔG^0) indicate that the adsorption reaction is spontaneous. The change of the standard free energy decreases with increasing temperatures, which indicates that a better adsorption is obtained at higher temperatures.

3.5. Adsorption mechanism

The surface of fly ash modified with sulfuric acid is generally covered with a large number of hydroxyl groups that vary in forms at different pHs. So, at lower pH, the adsorbent surface is positively charged, and anion adsorption occurs. However, by increasing the pH to 6, uptake of Mo_4^{2-} ions decreases since the adsorption surface sites are negatively charged which increases electrostatic repulsion between Mo_4^{2-} and the adsorbent. In addition, the adsorption of Mo(VI) onto the tested fly ash is well described by the Langmuir model (Table 2). As the theory of Langmuir is actually based on the fixation of a monolayer of adsorbate molecules on the pores surface [30], the accurate fitting means the active sites are certainly homogeneously distributed on the surface of tested adsorbent [31]. Moreover, the mean E is only 16.67 kJ mol^{-1}. Therefore, the adsorption process is mainly controlled by ion-exchange adsorption.

3.6. Removal of Mo(VI) in column experiments

Adsorption isotherm data do not give accurate scale-up data. Therefore, it is necessary to carry out fixed-bed continuous flow tests to obtain design models. The main aim in designing adsorption columns is to predict how much effluent the bed can treat or how long the bed will last before regeneration is necessary. The performance of the packed bed is described through the breakthrough curve. The times for the breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of any solute adsorption column. The breakthrough concentration for the column run is taken to be 0.5 mg L^{-1} (meet Grade IV of groundwater quality standard for

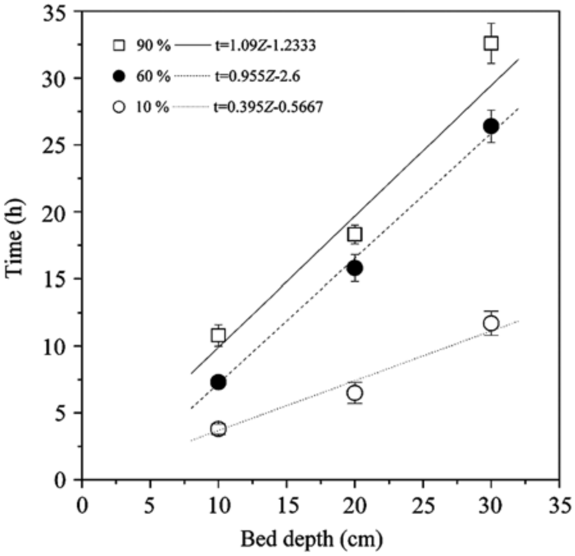

Fig. 4. BDST curves at various percentages of breakthrough (10, 60, and 90%) for the removal of Mo(VI). Conditions: folw rate, 5.0 mL min^{-1}; Mo(VI) concentration, 5.0 mg L^{-1}.

Table 4
BDST model for the adsorption of Mo(VI) on modified fly ash[a]

C_t/C_1	a ($\mathrm{h\,cm^{-1}}$)	b_1 (h)	K_c ($\mathrm{L\,mg^{-1}\,h^{-1}}$)	N_0 ($\mathrm{mg\,L^{-1}}$)	$Z_{\min}$ (cm)	R^2
0.1	0.225	−0.3333	0.146	6.75	13.35	0.9805
0.6	0.91	−0.2667	−0.022	27.3	4.12	0.9735
0.9	1.43	−0.4667	−0.205	42.9	1.50	0.9694

[a]Conditions: bed depth, 30 cm; Mo(VI) concentration, 5.0 mg/L; flow rate, 5.0 mL/min.

Mo(VI) in China, GB/T14848-93). The breakthrough curves obtained by varying the bed depth are presented in the subsequent section.

The fundamental equations describing the relationship between normalized concentration (C_t/C_0) and time in a flowing fixed-bed system are established by Adams and Bohart for the case of the adsorption of chlorine on charcoal [32]. The final design equation of the Adams–Bohart model is expressed as Eq. (11).

$$\ln((C_1/C_t) - 1) = K_c N_0 \frac{Z}{u} - K_c C_1 t \tag{11}$$

where C_1 and C_t are the inlet and effluent Mo(VI) concentration at any point in time t, K_c is the kinetic constant, N_0 is the adsorption capacity coefficient, Z is column height, and u is the linear velocity of the fluid. However, Hutchins described a simplified technique of the Adams–Bohart model [33]. This technique is called the BDST model, and he expressed the Adams–Bohart equation as Eq. (12).

$$t = aZ + b1 \tag{12}$$

where a is the slope (N_0/C_0u), and b is the intercept – ($\ln((C_0/C_t) - 1)/K_c\ C_0$). The plot of the bed depth vs. service time for 10, 60, and 90% breakthroughs of the column bed is shown (Fig. 4). From the slope and intercept of the line, the values of N_0 and K_c are calculated from the corresponding equations and are tabulated in Table 4. From R^2 values in Table 4 it is observed that the fitting with the experimental data is good. Thus, the data obtained in this study could be satisfactorily used for the scale up of the fixed-bed adsorption of Mo(VI) on the modified fly ash.

For $t = 0$, the minimum column height ($Z_{\min}$) can be calculated from Eq. (13).

$$Z_{\min} = \frac{u}{K_c N_0} \ln\left(\frac{C_0}{C_t} - 1\right) \tag{13}$$

If C_t is the breakthrough concentration of $0.5\,\mathrm{mg\ L^{-1}}$, the value of $Z_{\min}$ is obtained at 13.35 cm for the inlet Mo(VI) concentration of $5.0\,\mathrm{mg\,L^{-1}}$.

4. Conclusions

This study showed that the fly ash modified by $FeCl_2$ was an effective adsorbent for the removal of Mo (VI) from aqueous solution. The batch adsorption results indicated that Mo(VI) removal rate increased when lowering the pH, and the adsorption process generally followed the pseudo-second-order rate model. The equilibrium data of adsorption were in good agreement with the Langmuir's model, and the Langmuir adsorption capacity (Q_0) is $17.83\,\mathrm{mg\,g^{-1}}$. Thermodynamic studies showed that the adsorption process was endothermic and spontaneous. The adsorption mechanism can be generally described as ion-exchange adsorption. The BDST model showed a good fit to the column adsorption data, and the minimum column height ($Z_{\min}$) is obtained at 13.35 cm for the inlet Mo (VI) concentration of $5.0\,\mathrm{mg\,L^{-1}}$ and the breakthrough concentration of $0.5\,\mathrm{mg\,L^{-1}}$. The method was found to be non-expensive, effective, and simple to use as compared to the present treatment technologies.

Acknowledgments

The authors acknowledge the National Water Pollution Project for Taihu Lake Pollution Control of China (2012ZX07101-007), the National Natural Science Foundation of People's Republic of China (Grant Nos. 51009065 & 51279063), National Key Technology Support Program (Grant No. 2012BAC19B03), and the Key Science and Technology Planning Projects of Henan Province (Grant No. 112102110033).

References

[1] A. Moret, J. Rubio, Sulphate and molybdate ions uptake by chitin-based shrimp shells, Miner. Eng. 16(8) (2003) 715–722.
[2] Y.Q. Zhang, C. Amrhein, W.T. Frankenberger, Effect of arsenate and molybdate on removal of selenate from an aqueous solution by zero-valent iron, Sci. Total Environ. 350(1–3) (2005) 1–11.
[3] C. Yu, S. Xu, M. Gang, G. Chen, L. Zhou, Molybdenum pollution and speciation in Nver River sediments impacted with Mo mining activities in western Liaoning, northeast China, Int. J. Environ. Res. 5(1) (2011) 205–212.
[4] P.M. Fox, H.E. Doner, Trace element retention and release on minerals and soil in a constructed wetland, J. Environ. Qual. 31 (2002) 331–338.

[5] G.R. Helz, C.V. Miller, J.M. Charnock, J.F.W. Mosselmans, R. A.D. Patrick, C.D. Garner, D.J. Vaughan, Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence, Geochim. Cosmochim. Acta 60 (1996) 3631–3642.

[6] N. Xu, C. Christodoulatos, W. Braida, Adsorption of molybdate and tetrathiomolybdate onto pyrite and goethite: Effect of pH and competitive anions, Chemosphere 62(10) (2006) 1726–1735.

[7] A. Afkhami, T. Madrakian, Z. Karimi, A. Amini, Effect of treatment of carbon cloth with sodium hydroxide solution on its adsorption capacity for the adsorption of some cations, Colloids Surf., A 304(1–3) (2007) 36–40.

[8] A. Afkhami, R. Norooz-Asl, Removal, preconcentration and determination of Mo(VI) from water and wastewater samples using maghemite nanoparticles, Colloids Surf., A 346(1–3) (2009) 52–57.

[9] C. Namasivayam, S. Senthilkumar, Removal of Arsenic (V) from aqueous solution using industrial solid waste: Adsorption rates, and equilibrium studies, Ind. Eng. Chem. Res. 37 (12) (1998) 4816–4822.

[10] S.I. Hanan, N.S. Ammar, H.H.A. Ghafar, M. Farahat, Adsorption of Cd(II), Cu(II) and Pb(II) using recycled waste glass: Equilibrium and kinetic studies, Desalin. Water Treat. 48 (2012) 320–328.

[11] G. Suresh, B.V. Babu, Experimental, kinetic, equilibrium and regeneration studies for adsorption of Cr(VI) from aqueous solutions using low cost adsorbent (activated flyash), Desalin. Water Treat. 20 (2010) 168–178.

[12] H.U. Kim, K.H. Kim, Y.Y. Chang, S.M. Lee, J.K. Yang, Heavy metal removal from aqueous solution by tannins immobilized on collagen, Desalin. Water Treat. 48(1–3) (2012) 1–8.

[13] A. Afkhami, B.E. Conway, Investigation of removal of Cr(VI), Mo(VI), W(VI), V(VI), and V(V) oxy-ions from industrial wastewaters by adsorption and electrosorption at high-area carbon cloth, J. Colloid Interface Sci. 251(2) (2002) 248–255.

[14] S.H. Kalal, A.H. Panahi, N. Faramarzi, E. Moniri, A. Naeemy, H. Hoveidi, A. Abhari, New chelating resin for preconcentration and determination of molybdenum by inductive couple plasma atomic emission spectroscopy, Int. J. Environ. Sci. Technol. 8(3) (2011) 501–512.

[15] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40(9) (1918) 1361–1403.

[16] H.M.F. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem. 57A (1906) 385–470.

[17] M.J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, Acta Physiochim. U.S.S.R. 12 (1940) 217–222.

[18] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Sorption and structure of active carbons. I. Adsorption of organic vapors, Zh. Fiz. Khim. 21 (1947) 1351–1362.

[19] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion Kinetics in fixed bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5(2) (1966) 212–223.

[20] M. Mahramanlioglu, I. Kızılcıklı, I.O. Bicer, Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, J. Flourine Chem. 115(1) (2002) 41–47.

[21] Y. Seki, K. Yurdakoc, Paraquat adsorption onto clays and organoclays from aqueous solution, J. Colloid Interface Sci. 287(1) (2005) 1–5.

[22] S.M. Hasany, M.M. Saeed, M. Ahmed, Sorption of traces of silver ions onto polyurethane foam from acidic solution, Talanta 54 (2001) 89–98.

[23] C. Namasivayam, K. Kadirvelu, Uptake of mercury (II) from wastewater by activated carbon from an unwanted agricultural solid byproduct: coirpith, Carbon 37(1) (1999) 79–84.

[24] C. Namasivayam, M.V. Sureshkumar, Removal and recovery of molybdenum from aqueous solutions by adsorption onto surfactant modified coir pith, a lignocellulosic polymer, Clean-Soil Air Water 37(1) (2009) 60–66.

[25] C. Namasivayam, K. Prathap, Uptake of molybdate by adsorption onto industrial solid waste Fe(III)/Cr(III) hydroxide: Kinetic and equilibrium studies, Environ. Technol. 27(8) (2006) 923–932.

[26] C. Namasivayam, D. Sangeetha, Removal of molybdate from water by adsorption onto $ZnCl_2$ activated coir pith carbon, Bioresour. Technol. 97(10) (2006) 1194–1200.

[27] B.C. Bostick, S. Fendorf, G.R. Helz, Differential adsorption of molybdate and tetrathiomolybdate on pyrite, Environ. Sci. Technol. 37(2) (2003) 285–291.

[28] M.M.E. Moselhy, A.K. Sengupta, R. Smith, Carminic acid modified anion exchanger for the removal and preconcentration of Mo(VI) from wastewater, J. Hazard. Mater. 185(1) (2011) 442–446.

[29] J.R. Aravindhan, B.U. Rao, Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*, J. Hazard. Mater. 142(1–2) (2007) 68–76.

[30] K.K. Pandey, G. Prasad, V.N. Singh, Removal of Cr(VI) from aqueous solution by adsorption of flyash-Wollastonite, J. Chem. Technol. Biotehnol. 34 (1984) 367–374.

[31] L. Khezami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: Kinetic and equilibrium studies, J. Hazard. Mater. 123 (2005) 223–231.

[32] G.S. Bohart, E.Q. Adams, Some aspects of the behavior of charcoal with respect to chlorine, J. Am. Chem. Soc. 42(3) (1920) 523–544.

[33] R.A. Hutchins, New simplified design of activated carbon system, Am. J. Chem. Eng. 80 (1973) 133–138.