Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.811107

52 (2014) 3572–3578
May

Taylor & Francis
Taylor & Francis Group

Removal of Cr(VI) ions from wastewater using nanosized ferric oxyhydroxide loaded anion exchanger on a fixedbed column

Nan Li[a], Jing Ren[a], Lin Zhao[a,*], Zhong-liang Wang[b,*]

[a]*School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, P.R. China*
Tel. +86 22 27891291; email: nli@tju.edu.cn
[b]*Tianjin Normal University, Tianjin Key Lab Water Resources & Environment, Tianjin 300387, P.R. China*
Tel. +86 22 23766557; email: zhongliang_wang@163.com

Received 28 December 2012; Accepted 1 May 2013

ABSTRACT

Continuous fixed-bed studies were carried out in columns packed with nanosized ferric oxyhydroxide loaded anion exchanger (FOAE) to determine the breakthrough curves for different bed heights (5, 10, 15, and 20 cm), contact times (1.6, 0.8, and 0.5 min) and initial concentrations (25, 50, and 75 mg/L) of Cr(VI). Higher bed capacity and longer breakthrough time were obtained by increasing the bed height and contact time. The fixed-bed columns reached breakthrough point at 19, 8, and 4 h for contact times 1.6, 0.8, and 0.5 min, respectively. Correspondingly, the adsorption capacity decreased from 39.84 to 35.16 mg/g due to the shorter contact time. Whereas an increase in initial Cr(VI) concentration resulted in a decrease in breakthrough time and an increase in adsorption capacity. Bed depth service time (BDST) model fitted well with the experimental data, which assumed a linear relationship between bed height and service time.

Keywords: Cr(VI) adsorption; Ferric oxyhydroxide loaded anion exchanger (FOAE); Fixed-bed column; Modeling

1. Introduction

The discharge of heavy metals in industrial effluents caused great concerns because their presence and accumulation have toxic or carcinogenic effect on living species [1]. Chromium is a kind of well-known highly toxic trace metal that introduced into aqueous environment mainly by the wastewater discharge of a variety of industry such as leather tanning, metallurgy, plating, and pigments [2,3]. As given in the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit of total chromium is 0.05 mg/L [4].

Chromium exists in the environment mainly in two oxidation forms, Cr(III) and Cr(VI). Unlike Cr(III) which generally occurs naturally in the environment as an essential nutrient, Cr(VI) is ordinarily produced by industrial processes and considered to be the most toxic form of chromium [5]. Cr(VI) exposure at levels above maximum contaminant can cause skin and stomach ulceration, damage to liver, kidney and nerve tissue, various cancer diseases, and even death in large doses [6,7]. Due to the carcinogenicity, high toxicity and mobility of Cr(VI), the removal of Cr(VI)

---

*Corresponding authors.

contaminants from aqueous environment has attracted serious concerns [2]. Commonly used methods for Cr (VI) removal include reduction and precipitation, ion exchange, reverse osmosis, foam flotation, electrolysis and surface adsorption [8–10].

Adsorption is a widely used method to remove Cr (VI), owing to several significant advantages such as high efficiency, ease of operation, and economically feasibility [11]. It has been proved that a variety of natural and synthetic materials can be applied as Cr (VI) adsorbents, including activated carbons, biological materials, zeolites, chitosan, and biomass wastes [4,12,13].

Ferric oxides have been proved to be effective and environmental benign sorbents for anionic pollutants, such as the removal of arsenite/arsenate [14,15], phosphate [16,17], and chromate [18]. Recently, various new adsorbents were developed by loading ferric oxides onto conventional porous carrier including activated carbon, sand, and alginate beads to overcome the excessive pressure drops and raise the adsorption performance [19–22].

In the last few years, novel hybrid adsorbents by loading ferric oxides on polymers have been proved to be favorable adsorbents to remove ionic pollutants [23,24]. Most of previous adsorption researches that based on batch equilibrium experiments were generally focused on the performance of hybrid adsorbents and surface chemical characteristics. However, to investigate the practical operation of full-scale adsorption processes, continuous flow fixed-bed experiment are often necessary [25].

A previous study has been proved that nanosized ferric oxyhydroxide loaded anion exchanger (FOAE) hybrid adsorbent, which developed in our laboratory, is a benign and efficient material for Cr(VI) adsorption in batch experiment [26]. The most important intention of this work is to investigate the removal performance and adsorption capacity toward Cr(VI) in the FOAE-filled fixed-bed column. The dynamic behavior of a fixed-bed column filled with FOAE is described in terms of breakthrough curve. The effect of important design parameters (contained bed height, contact times, and initial Cr(VI) concentration) were investigated. The breakthrough curves for the adsorption of Cr(VI) were analyzed using bed depth service time (BDST) and Yoon–Nelson model.

2. Materials and methods

2.1. Preparation of FOAE

The hybrid adsorbent referred as FOAE was prepared by loading nanosized ferric oxyhydroxide onto anion exchanger D201 according to the method reported in 2012 [26]. Briefly, the preparation of FOAE hybrid adsorbent was according to the following steps. Firstly, $Fe(NO_3)_3/NaCl/HCl$ mixtures (mol ratio of 1:3:1) were prepared and flew through a column packed with anion exchanger beads and the $FeCl_4^-$ anions in the solution were preloaded on the exchanger. Then, the ferric hydroxide was precipitated onto the inner surface of anion-exchanger beads by soaping the anion-exchanger with a $NH_4Cl/NH_3{\cdot}H_2O$ solution (mol ratio of 1:1). Finally, the resulting anion-exchanger beads were thermally treated on 313 K degree to obtain the FOAE hybrid adsorbents. The particle size of both hybrid adsorbents and exchanger beads used in the experiment was 0.4–0.7 mm.

2.2. Preparation of adsorbate

A stock solution of Cr(VI) (1,000 mg/L) was prepared in double-distilled water with analytical grade potassium dichromate ($K_2Cr_2O_7$). Cr(VI) solutions of different concentrations were obtained by diluting the stock solution with distilled water.

2.3. Adsorption experiments in fixed-bed column

Fixed-bed column experiments were carried out with glass columns (10 mm in diameter and 300 mm in length) equipped with a constant-flow variable-speed peristaltic pump (Longer-BT100) to maintain a constant flow rate. The ratio of column diameter to exchanger bead diameter was approximately 20:1. Liquid samples of the Cr(VI) in the exit of the fixed-bed experiments were collected at predefined time intervals.

2.4. Analysis of column data

The breakthrough time and the shape of the breakthrough curve are very important characteristics to analyze the operation and the dynamic process of fixed-bed column adsorption experiment. The breakthrough curve which illustrates the loading behavior of metal to be removed from solution in a fixed bed is expressed in terms of dimensionless concentration vs. the adsorption time.

2.5. Analyses and calculations

The concentrations of Cr(VI) in the filtered liquid samples were determined by an inductive coupled plasma atomic emission spectrometer (ICP-AES, ICP-optima 2001DV, Perkin-Elmer, USA).

As the high toxicity of Cr(VI), the breakthrough point was intended to be 10% to illustrate the adsorption capacity and breakthrough time for different bed height, contact times, and initial concentration of Cr (VI) ions. Breakthrough time (t_b) is defined as the time required to reach a specific breakthrough concentration C_b (10% of the initial concentration (C_0)).

The adsorption capacity of fixed-bed column experiment was calculated as follows [27]:

$$q(10\%) = \frac{t_b \times Q \times C_0}{M} \tag{1}$$

where $q(10\%)$ is the breakthrough capacity of adsorbent (mg/g) when the concentration of solution reach C_b (10% of C_0), Q is the flow rate (mg/min), and M is adsorption mass packed in the column (g).

3. Results and discussion

3.1. Effect of bed height

Adsorption of Cr(VI) in the fixed-bed experiment is largely dependent on the quantity of adsorbent filled in the column which is set by the bed height. To investigate the effect of bed height on the lifespan of the column, the feeding solution containing 50 mg/L Cr(VI) was pumped at 10 mL/min constant flow rate through the column. 3.2, 6.4, 9.6, and 12.8 g of FOAE hybrid adsorbent were added to produce 5, 10, 15, and 20 cm bed height, respectively. The typical breakthrough curves at different bed height for Cr(VI) adsorption on FOAE are illustrated as plots of dimensionless concentration vs. the adsorption time (Fig. 1). It was observed that the breakthrough time have evidently prolonged from 4 to 22 h with increasing of bed height from 5 to 20 cm. The bed capacities of FOAE adsorption column for different bed depth of 5, 10, 15, and 20 cm calculated by Eq. (1) were 37.50, 37.50, 46.88, and 51.56 mg/g, respectively.

Results indicated that both the adsorption capacity and the breakthrough time increased with the increasing of bed height. The increase in binding sites provided by more adsorbent filled in the column conduced to a broadened mass transfer zone available for Cr(VI) adsorption. The contact time was another parameter affecting the removal efficiency of Cr(VI). When the column was packed at a lower bed height, the contact time was too short to make the Cr(VI) ions diffused inside the adsorbent, which led to a reduction of breakthrough time and adsorption capacity.

3.2. Effect of contact time

The effect of contact time on the breakthrough curves of fixed-bed column adsorption was investigated at a fixed bed height of 10 cm and initial metal concentration of 50 mg/L. Plots of breakthrough curves at different contact time were given in Fig. 2. Correspondingly, the flow rates of initial solution were set as 5, 10, and 15 ml/min. The breakthrough times when the Cr(VI) concentration of effluent reached 10% of C_0 for contact time of 1.6, 0.8, and 0.5 min were found as 19, 8, and 4 h, respectively. Accordingly, the breakthrough of the columns occurred at 19, 8, and 4 h for contact time of 1.6, 0.8, and 0.5 min, respectively. In a fixed-bed column with constant bed height, the breakthrough time increased with the increase in contact time, indicating a longer column life with longer contact time. The FOAE column quickly reached its maximum capacity at shorter contact time because of more Cr(VI) ions exchanging with functional group sites in shorter time. The contact time also influences the Cr(VI) adsorption capacity. When the contact time decreased from 1.6 to 0.5 min, the corresponding column capacity decreased from 39.84 to 35.16 mg/g. The probable reason is that the contact time of Cr(VI) with FOAE is too short at

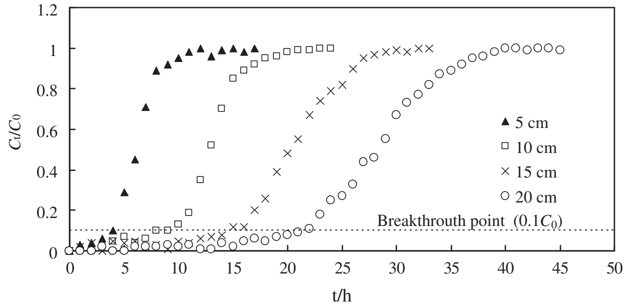


Fig. 1. Effect of bed height on the breakthrough curve of Cr(VI) adsorption on FOAE. (Conditions: initial Cr(VI) concentration 50 mg/L; flow rate 10 ml/min.)

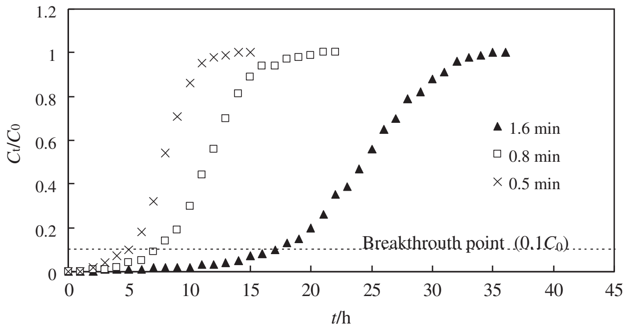


Fig. 2. Effect of contact time on the breakthrough curve of Cr(VI) adsorption on FOAE. (Conditions: initial Cr(VI) concentration 50 mg/L; bed height 10 cm.)

higher flow rate, resulting in a reduction in removal efficiency. However, this decrease was not very significant, suggested that the adsorption of Cr(VI) on the fixed-bed column is a rapid process.

Besides the shape of breakthrough curve is also affected by the contact time. It is observed in Fig. 2 that the shape of breakthrough curves were steeper at shorter contact time, implying higher intraparticle diffusion effect and a narrow mass transfer zone. The flatter breakthrough curves was observed for longer contact time, which indicate a more prominent effect of film transfer resistance, larger mass transfer zone, and longer service time for the column at longer contact time.

3.3. Effect of initial Cr(VI) concentration

The column performance of FOAE was conducted at various initial Cr(VI) concentrations when other experimental conditions are kept constant. An increase in the initial Cr(VI) concentration influenced the breakthrough curve significantly (Fig. 3). The breakthrough time appears to decrease from 15 to 6 h when the initial Cr(VI) concentration increased from 25 to 75 mg/L. The adsorption capacity of FOAE was 35.16, 37.50, and 42.19 mg/g with initial Cr(VI) concentration of 25, 50, and 75 mg/L. Clearly, a higher column capacity can be achieved at a higher initial Cr(VI) concentration due to the higher driving force. The driving force of adsorption was provided by the concentration gradient between the Cr(VI) on the adsorbent and in the solution. At higher Cr(VI) concentrations, the breakthrough curves were sharper due to a relatively smaller mass transfer zone and a more intraparticle diffusion-controlled process. With the increasing of Cr (VI) initial concentration, the concentration gradient between the Cr(VI) adsorpted on FOAE adsorbent and in the solution could be improved. Also a faster breakthrough at 6 h was obtained with a higher initial Cr(VI) concentrations of 75 mg/L as expected. FOAE reached saturation earlier at higher initial concentration, which leads to the reduction of the breakthrough time and exhaustion time. In contrary, a decreased initial Cr(VI) concentrations delayed breakthrough point and increased the adsorption capacity, since the lower concentration gradient caused slower transport velocity and longer contact time.

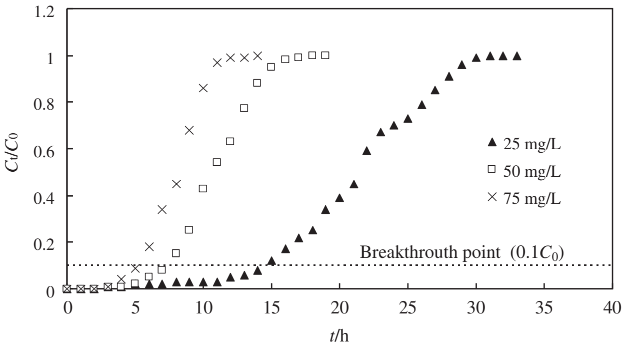


Fig. 3. Effect of initial Cr(VI) concentration on the breakthrough curve of Cr(VI) adsorption on FOAE. (Conditions: flow rate 10 ml/min; bed height 10 cm.)

3.4. Application of the BDST model

The BDST model based on Bohart–Adams equation was used to depict the relationship between bed depth and service time at fixed-bed adsorption. This model assumes that adsorption is a continuous process and the adsorption rate is proportional to both the adsorption capacity (still remains on adsorbent) and the concentration of the solute species [28]. With these assumptions, the BDST model can be applied to most fixed-bed systems and provides useful prediction for variations in process parameters.

The linear BDST equation can be expressed as follows [29]:

$$t = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_t} - 1\right) \tag{2}$$

where C_0 is the initial Cr(VI) concentration (mg/L), C_t is the Cr(VI) concentration at time t (mg/L), N_0 is the adsorption capacity of fixed-bed (mg/L), v is the linear velocity of Cr(VI) solution through the bed calculated by dividing the velocity by the column section area (cm/h), Z is the bed height of column (cm), t is the column service time (h), and K_a is the rate constant (L/mg h). Fig. 4 shows that the plot of service time vs. bed height was linear ($R^2 = 0.9857$), indicating that the BDST model fitted well with the data for Cr (VI) adsorption in this fixed-bed column.

The slope of the BDST plot is equal to $N_0/C_0\ v$. The C_0 and v may be assumed to be reasonably constant during the column adsorption process. The bed capacity N_0 which changed with time can be calculated from the slope to predict the performance of the bed. The value of K_a calculated from intercept of the plot characterizes the rate of solute transfer from the fluid phase to the solid phase. The computed N_0 and K_a were 466.24 mg/L and 0.015 L/mg min. A significantly high theoretical Cr(VI) adsorption capacity of 466.24 mg/L was obtained in the FOAE fixed-bed column, which proved that the FOAE-filled column was efficient and applicable for Cr(VI) adsorption.

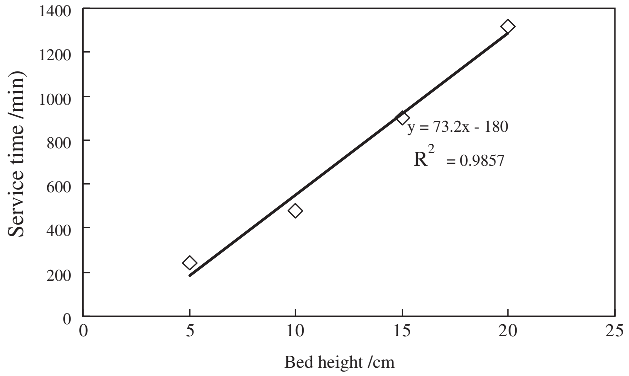


Fig. 4. BDST model for 10% breakthrough time at different bed height.

3.5. Application of the Yoon–Nelson model

Yoon–Nelson model, which was developed by Yoon and Nelson in 1984, is a relatively simple model to investigate the adsorption and breakthrough curves [30].

Yoon–Nelson model is based on the hypothesis that the probability of adsorption decrease rate of each adsorbate molecule is linearly related to the probability of both adsorbate adsorption and adsorbate breakthrough on the adsorbent. This model is less complicated and easier to apply to descript the practical industrial adsorption process [30].

The Yoon–Nelson model is presented as follows [30]:

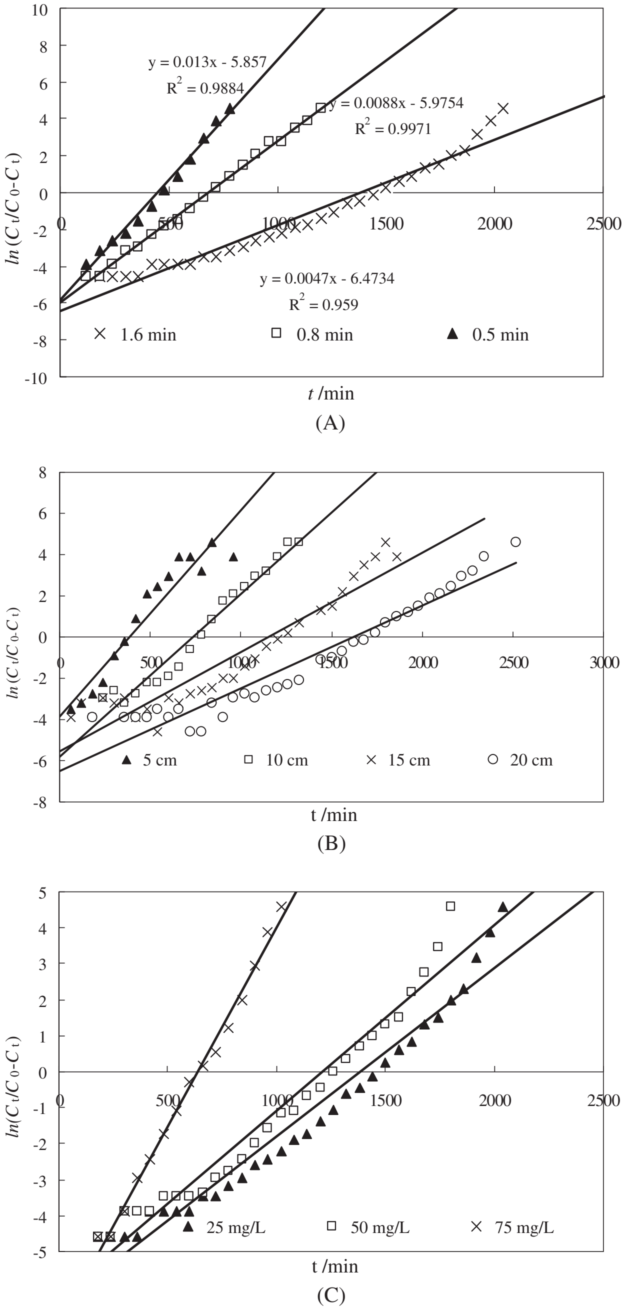
$$\frac{C_t}{C_i} = \frac{\exp(k_{\mathrm{YN}}t - \tau k_{\mathrm{YN}})}{1 + \exp(k_{\mathrm{YN}}t - \tau k_{\mathrm{YN}})} \tag{3}$$

The linearized Yoon–Nelson model is given as [30]:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{\mathrm{YN}}t - \tau k_{\mathrm{YN}} \tag{4}$$

where k_{YN} is the Yoon–Nelson rate constant (min^{-1}) and τ is the breakthrough time required for 50% adsorbate breakthrough (min). The values of k_{YN} and τ can be determined by the linear plot of $\ln\left(\frac{C_t}{C_0-C_t}\right)$ against t.

The statistical parameters of Yoon–Nelson model were calculated and given in Fig. 5 and Table 1 according to Eq. (4) [30]. k_{YN} increased and τ decreased with both increasing of flow rate and initial Cr(VI) concentration. In contrast, when the bed height increased from 5 to 20 cm, the k_{YN} decreased from 0.01 to 0.004 and τ increased from 381.1 to 1622.4 min. From the statistical parameters indicated in Table 1, the theoretical breakthrough curves were very close to the experimental breakthrough curves. Comparing the experimental results and predicted values, it can be found that Yoon–Nelson model fitted well with the experimental data for Cr(VI) adsorption on the FOAE fixed-bed column.



(A)

(B)

(C)

Fig. 5. Yoon–Nelson model of Cr(VI) adsorption on FOAE at (A) different bed height; (B) different contact time; and (C) different initial Cr(VI) concentration [30].

Table 1
Estimated parameters of Yoon-Nelson model for adsorption of Cr(VI) on FOAE granule-packed column

Q (mL/min)	Z (cm)	C_0 (mg/L)	k_{YN} (min^{-1})	τ_{theo} (min)	τ_{exp} (min)	R^2
5	10	50	0.0047	1377.3	1,440	0.959
10	10	50	0.0088	679.9	660	0.9971
15	10	50	0.013	450.5	480	0.9884
10	5	50	0.01	384.1	360	0.9138
10	10	50	0.0079	731.8	780	0.9685
10	15	50	0.0048	1152.9	1,260	0.8942
10	20	50	0.004	1622.4	1,680	0.9296
10	10	25	0.0047	1377.3	1,440	0.959
10	10	50	0.008	741.3	780	0.9288
10	10	75	0.0111	635.8	660	0.9927

4. Conclusions

Fixed-bed adsorption of Cr(VI) from aqueous solutions using a prepared hybrid adsorbent FOAE was experimentally and theoretically studied. The breakthrough time and adsorption capacity of FOAE column could evidently be improved with the increase in the bed height and contact time. Besides shorter breakthrough time and higher adsorption capacity were obtained at higher initial Cr(VI) concentration. Steeper breakthrough curves were observed at shorter contact time and initial Cr(VI) concentration. Based on the results of the column studies, it was showed that FOAE can serve as an effective adsorbent for Cr(VI) removal from aqueous solutions. It has been observed that the BDST model and Yoon–Nelson model fitted well with experimental data, which proved that both models are allowable to estimate the breakthrough curves and characteristic parameters of the column.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (No. 51208352), Natural Science Foundation of Tianjin (No. 13JC QNJC09100), Open Project of State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. QA201209), and Open-end Investment of Tianjin Key Laboratory of Water Resources and Environment, Tianjin Normal University (No. 52XS1203).

List of symbols

Q_e — amount of solute adsorbed at equilibrium, mg g^{-1}
C_0 — the initial Cr(VI) concentration of solute, mg L^{-1}
C_t — the Cr(VI) concentration at time t, mg L^{-1}
C_b — breakthrough concentration of Cr(VI) (10% of C_0), mg L^{-1}
t_b — the time required to reach C_b, min
q(10%) — the capacity of adsorbent when the concentration of solution reach C_b, mg g^{-1}
Q — the flow rate of solution, mg min^{-1}
t_c — contact time of, min
M — the mass of adsorbent packed in the column, g
Z — the bed height of column, cm
N_0 — adsorption capacity of fixed-bed, mg L^{-1}
v — the linear velocity of Cr(VI) solution through the bed, cm h
t — the column service time, h
K_a — the rate constant, L mg^{-1} h^{-1}
k_{YN} — the Yoon–Nelson rate constant, min^{-1}
τ — the breakthrough time required for 50% adsorbate breakthrough, min
R^2 — the correlation coefficient

List of abbreviations

FOAE — ferric oxyhydroxide loaded anion exchanger
ICP-AES — inductively coupled plasma atomic emission spectroscopy
BDST — bed depth service time

References

[1] P.C. Nagajyoti, K.D. Lee, T.V.M. Sreekanth, Heavy metals, occurrence and toxicity for plants: A review, Environ. Chem. Lett. 8 (2010) 199–216.

[2] N.R. Bishnoi, M. Bajaj, N. Sharma, A. Gupta, Adsorption of Cr(VI) on activated rice husk carbon and activated alumina, Biosour. Technol. 91 (2004) 305–307.

[3] M. Bansal, D. Singh, V.K. Garg, Chromium (VI) uptake from aqueous solution by adsorption onto timber industry waste, Desalin. Water Treat. 12 (2009) 238–246.

[4] M. Owlad, M.K. Aroua, W.A.W. Daud, S. Baroutian, Removal of hexavalent chromium-contaminated water and wastewater: A review, Water Air Soil Pollut. 200 (2009) 59–77.

[5] Y.X. Liu, L. Deng, Y. Chen, F. Wu, N.S. Deng, Simultaneous photocatalytic reduction of Cr(VI) and oxidation of bisphenol A induced by Fe(III)–OH complexes in water, J. Hazard. Mater. 139 (2007) 399–402.

[6] J. Kotas, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environ. Pollut. 107 (2000) 263–283.

[7] R.A. Gil, S. Cerutti, J.A. G'asquez, R.A. Olsina, L.D. Martinez, Preconcentration and speciation of chromium in drinking water samples by coupling of online sorption on activated carbon to ETAAS determination, Talanta 68 (2008) 1065–1070.

[8] J. Wu, H. Zhang, P.J. He, Q. Yao, L.M. Shao, Cr(VI) removal from aqueous solution by dried activated sludge biomass, J. Hazard. Mater. 176 (2010) 697–703.

[9] J. Sun, J.D. Mao, H. Gong, Y. Lan, Fe(III) photocatalytic reduction of Cr(VI) by low-molecular-weight organic acids with α-OH, J. Hazard. Mater. 168 (2009) 1569–1574.

[10] W. Kuang, Y.B. Tan, L.H. Fu, Adsorption kinetics and adsorption isotherm studies of chromium from aqueous solutions by HPAM-chitosan gel beads, Desalin. Water Treat. 45 (2012) 222–228.

[11] A. Hashem, R.A. Akasha, A. Ghith, D.A. Hussein, Adsorbent based on agricultural wastes for heavy metal and dye removal. A review, Energy Edu. Sci. Technol. 19 (2007) 69–86.

[12] J.K. Yang, S.M. Lee, M. Farrokhi, O. Giahi, M. Shirzad, Photocatalytic removal of Cr(VI) with illuminated TiO_2, Desalin. Water Treat. 46 (2012) 375–380.

[13] A. Choudhury, S. Sengupta, C. Bhattacharjee, S. Datta, Effects of co-solutes on Cr(VI) removal by micellar enhanced ultrafiltration (MEUF) process, Desalin. Water Treat. 44 (2012) 67–74.

[14] M. Jang, W.F. Chen, F.S. Cannon, Preloading hydrous ferric oxide into granular activated carbon for arsenic removal, Environ. Sci. Technol. 42 (2008) 3369–3374.

[15] G. Liu, N. Liu, H. Zhang, L. Zhang, The adsorption of arsenic on magnetic iron oxide in aqueous solutions, Desalin. Water Treat. 21 (2010) 96–101.

[16] N. Khare, D. Hesterberg, J.D. Martin, XANES investigation of phosphate sorption in single and binary systems of iron and aluminum oxide minerals, Environ. Sci. Technol. 39 (2005) 2152–2160.

[17] B.C. Pan, B.J. Pan, J. Wu, L. Lv, W.M. Zhang, L.L. Xiao, X.S. Wang, X.C. Tao, S.R. Zheng, Development of polymer-based nanosized hydrated ferric oxides (HFOs) for enhanced phosphate removal from waste effluents, Water Res. 43 (2009) 4421–4429.

[18] J. Hu, I.M.C. Lo, G. Chen, Performance and mechanism of chromate (VI) adsorption by δ-FeOOH-coated maghemite (γ-Fe_2O_3) nanoparticles, Sep. Purif. Technol. 58 (2007) 76–82.

[19] A. Gu, F. Fang, B. Deng, Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal, Environ. Sci. Technol. 39 (2005) 3833–3843.

[20] X. Guo, F. Chen, Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater, Environ. Sci. Technol. 39 (2005) 6808–6818.

[21] L. Cumbal, A.K. Sengupta, Arsenic removal using polymersupported hydrated iron(III) oxide nanoparticles: Role of Donnan membrane effect, Environ. Sci. Technol. 39 (2005) 6508–6515.

[22] M.J. DeMarco, A.K. SenGupta, J.E. Greenleaf, Arsenic removal using a polymeric/inorganic hybrid sorbent, Water Res. 37 (2003) 164–176.

[23] Q.J. Zhang, B.C. Pan, X.Q. Chen, W.M. Zhang, B.J. Pan, Q.X. Zhang, L. Lv, X.S. Zhao, Preparation of polymer-supported hydrated ferric oxide based on Donnan membrane effect and its application for arsenic removal, Sci. China Series B 51 (2008) 379–385.

[24] L.M. Blaney, S. Cinar, A.K. SenGupta, Hybrid anion exchanger for trace phosphate removal from water and wastewater, Water Res. 41 (2007) 1603–1613.

[25] K.H. Chu, Improved fixed-bed models for metal biosorption, Chem. Eng. J. 97 (2004) 233–239.

[26] J. Ren, N. Li, L. Zhao, Adsorptive removal of Cr(VI) from water by anion exchanger based nanosized ferric oxyhydroxide hybrid adsorbent, Chem. Biochem. Eng. Q. 26 (2012) 111–118.

[27] R. Treybal, Mass Transfer Operations, 3rd ed., McGraw-Hill, New York, 1980.

[28] G.S. Bohart, E.Q. Adams, Some aspects of the behavior of charcoal with respect to chlorine, J. Chem. Soc. 42 (1920) 523–529.

[29] G. McKay, M.J. Bino, Fixed bed adsorption for the removal of pollutants from water, Environ. Pollut. 66 (1990) 33–53.

[30] Y.H. Yoon, J.H. Nelson, Application of gas adsorption kinetics. I. A theoretical model for respirator cartridge service time, Am. Ind. Hyg. Assoc. J. 45 (1984) 509–516.