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Removal of bromate from aqueous solution by corncobs

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ABSTRACT

The native and chemically modified corncobs were utilized as low-cost and efficient adsorbent to remove bromate from aqueous solution in this study. The parameters of the adsorbent i.e. adsorption capacity, selectivity, regenerability were investigated. All the experiments were conducted at the same adsorbent dose (0.2 g/200 ml) and the same temperature of 30°C to investigate the effects of initial concentration of bromate, contact time, ionic strength and solution pH, then the optimal experimental conditions were ascertained. The results showed that the optimum conditions for the removal of bromate were at the aqueous solution with low ion concentration, pH of about 9.0 and equilibrium time of 80 min, respectively. Freundlich model fitted the adsorption data quite reasonably ($R^2 > 0.92$) and the maximum adsorption capacity was 101.01 mg/g. The experimental data followed the pseudo-second-order kinetic model very well. In addition, the removal percentages (%) of bromate by corncob modified by 80% isopropyl alcohol were higher than that by 20% isopropyl alcohol, 20% n-butyl alcohol, citric acid and HCl, similarly, were higher than the native corncob, corncob carbon and corncob ash. The removal percentages (%) of bromate by corncob carbon and corncob ash were higher than that by corncob with the bromate concentration of 40 mg/l.

Keywords: Bromate; Adsorption kinetics; Modified corncob; Remove; Aqueous solution; Adsorbent

1. Introduction

Bromate identified as one kind of ozonation disinfection by-products is formed in bromide-containing waters [1]. Bromide occurs in drinking water due to natural and anthropogenic sources including seawater intrusion, pesticide run-off, industrial waste, and impurities in road de-icing salt. Bromate has been determined to cause the formation of renal cell tumors in rats who have been fed aqueous bromate [2,3]. Therefore, bromate is a known animal carcinogen and genotoxicity on human cell culture system [4]. The United States Environmental Protection Agency (USEPA) and American Water Works Association (AWWA) have set bromate maximum contaminant level in drinking water as 10 μg/l [5]. The European Commission also adopted a value of 10 μg/l based on a balance between the potential risks and the practical application of ozonation as a drinking water treatment process. Thus, an efficient technology is required for bromate removal from drinking water.

Several chemical and physical methods have been employed to remove bromate from drinking water, such as reduction using granular ferric hydroxide (GFH)[6], zero-valent iron (Fe0) [7] and activated carbon [8,9]. The use of agricultural by-products as biosorbent material to depurate heavy metal or dye contaminated water has become increasingly popular over the past decade

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because of their less expensiveness, biodegradability, abundance and efficiency [10]. In addition, modified agricultural by-products can enhance their adsorption capacity through increasing the amount of active polar functional groups of lignin and so are widely used [11,12]. In several years,corncob has been utilized for the adsorption of Cd (II) [13,14], Cu (II) [15], dyes [16], Cr (ε) [17] and Lead [18] .

The main objective of this study was to investigate the native and chemically modified corncobs as an adsorbent for bromate removal from aqueous solution under different experimental conditions, such as solution pH, contact time, the activating temperature and ionic strength. Adsorption isotherms and kinetics parameters were also calculated and discussed.

2. Materials and methods

2.1. Raw corncob

The crude corncob (hereafter, abbreviated as CC) used in this study was collected as solid waste. The collected material, CC, was then washed with deionized water for several times to remove all the dirt particles. The water washed material was dried in a hot air oven at 50°C for 24 h. The dried CC was milled to smaller particle size in the range from 0.15 to 0.20 mm by ball-mill (Tianjin, China). Then the CC granule was removed, weighted and stored in desiccators.

2.2. Preparation of corncob carbon and corncob ash

The corncob granule was activated by carbonization in a muffle furnace (Shenyang, China)for two hours at 600°C in the absence of air by placing the sample in a well-sealed evaporating dish. The corncob carbon prepared by activation is termed CCC. The Corncob granule was chemically burnt in a muffle furnace for several hours at 600°C filled with air by placing the sample in an open evaporating dish. The corncob ash prepared by chemical burning is termed CCA.

2.3. Preparation of modified corncob

2.3.1. Modified with alcohol

Ten grams of CC was treated with 200 ml alcobolic solution, shaked for 24 h at 30°C and 150 rpm in a isothermal rotary. After filtered, the sample was washed with deionized water until the liquid did not turn cloudy. The filter residue were dried in an oven at 50°C for 24 h. In this experiment, 20% isopropyl alcohol, 80% isopropyl alcohol and 20% n-butyl alcohol were used, respectively. The modified samples we obtained, hereafter abbreviated as CCI2, CCI8 and CCN.

2.3.2. Modified with acid solution

Ten grams of CC together with 200 ml 0.1 mol/l acid solution (citric acid and HCl) were shaken for 24 h at room temperature (30°C) and 150 rpm in a isothermal rotary. After filtered, the sample was cleaned with deionized water until pH was neutral. The filter residue was dried in an oven at 50°C for 24 h. The modified sample were obtained. Hereafter abbreviated as CCCA (citric acid) and CCH (HCl).

2.4. Preparation of bromate solutions

Bromate used in this study was Potassium bromate purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Potassium bromate has the molecular formula $KBrO_3$ (Mol.wt. 167.00 g/mol). Stock solution was prepared by dissolving accurately weighted potassium bromate in deionized water to the concentration of 200 mg/l. The experimental solutions were obtained by diluting the stock solution accurately to needed concentrations. All chemicals used throughout the study were analytical-grade reagents. Deionized water was used for preparing all the solutions and reagents. All the adsorption experiments were carried out at the same temperature (30°C), shaking speed (250 rpm) and the same adsorbent dose (0.2 g/200 ml).

2.5. Batch adsorption experiments

Biosorption experiments were carried out in beakers containing 200 ml of different initial concentrations (20, 40, 60, 80, 100 and 120 mg/l) of bromate solution without further adjusting pH. The initial pH values of the solutions were previous adjusted with 0.1 mol/l HCl or NaOH by using a pHs-25 model acidity meter (Shanghai, China). Meanwhile, in order to adjust the environmental parameters, 0.1 mol/l NaCl was used for controling the ionic strength. The adsorbent was added to each beaker. The mixture were stirred at 250 rpm and 30°C, After stirring for predetermined time intervals, the adsorbent was separated by alteration with microvoid filter film (0.45 μm), and the bromate residual concentration in the aqueous solution was measured by UV spectrophotometer. The adsorption capacity was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where q_t (mg/g) is the amount of bromate solutions adsorbed, C_0 (mg/l) is the initial bromate solution concentration and C_t (mg/l) is the bromate solution concentration at any time, V (l) is the initial volume of solution, and W (g) is the amount of adsorbent used. The percentage removal of bromate (R%) was calculated using the following equation:

$$R\,(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \qquad (2)$$

The effect of each parameter was studied by fixing the values of other parameters.

2.6. Determination of potassium bromate

The potassium bromate standard solution and the blank solutions were diluted to the scale with deionized water, shaked and placed in the shadow 10 min at room temperature. The absorbencies of the two solutions were determined with UV-9100 double-beam UV-Vis Spectrophotometer in 288 nm, referenced by deionized water, among them, containing potassium bromate is A, the blank for A_0, calculated by $\Delta A = A - A_0$ [19].

3. Results and discussion

3.1. Effect of different contact time and initial BrO_3^- concentrations

The effects of contact time and initial BrO_3^- concentrations (20, 40, 60, 80, 100 and 120 mg/l) on the BrO_3^- adsorption by corncob is shown in Fig. 1. It can be seen that the amount of BrO_3^- adsorbed (mg/g) increases with BrO_3^- concentration increasing and remained constant after equilibrium time. Concentration gradient provides an important driving force to overcome all mass transfer resistance of BrO_3^- between the aqueous and solid phases. Hence a higher initial concentration of BrO_3^- will enhance the adsorption efficiency [20]. The initial BrO_3^- concentrations increases from 20 to 120 mg/l with the adsorption capacity of corncob increasing from 20.99 to 60.83 mg/g and with the removal percentage decreasing from 105.57 to 54.14%. A similar observation was reported of the adsorption of dyes and heavy metals [21,22].

Fig. 1 also indicated that the contact time was less than 60 min which was sufficient time to reach adsorption equilibrium for BrO_3^- solution with initial concentrations of 20–60 mg/l. But for BrO_3^- solution with initial concentrations of 80–120 mg/l, equilibrium time of 80 min was required. Consequently, the experimental data were measured at 90 min to make sure that full equilibriums were attained. The similar trend was also observed for Methylene blue adsorption onto Pineapple stems [20].

3.2. Effect of initial pH

The pH is one of the most important factors controlling the adsorption of BrO_3^- onto the adsorbent. To determine the optimum pH conditions for the adsorption of BrO_3^- over corncob, the effect of pH was observed over the entire pH range (2.0–10.0). As elucidated in Fig. 2, the BrO_3^- removal was minimum at the initial pH 2. The BrO_3^- adsorbed increases as the initial pH increasing from pH 2 to 9, then, the BrO_3^- removal was not significantly altered beyond pH 9. The interpretation of this results by the ion exchange mechanism is that [23]: (1) In the low pH medium, bromate was mainly protonated to molecules form by H^+, which would prevent bromate from being adsorbed onto the surface of

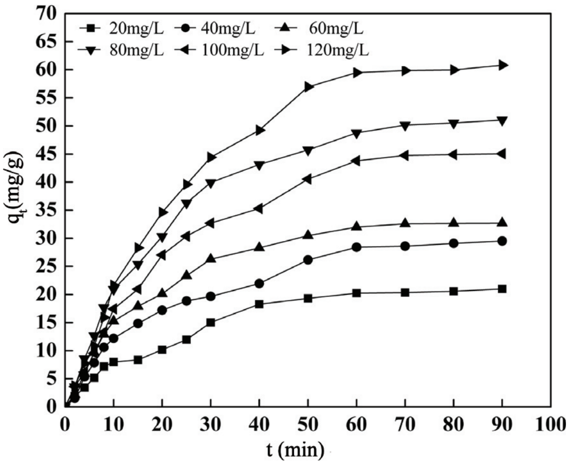

Fig. 1. Effect of initial concentrations on removal of BrO_3^- by corncob (adsorbent dose: 0.2 g/200 ml; temperature: 30°C; pH: 8.25; shaking speed: 250 r/min; contact time: 90 min).

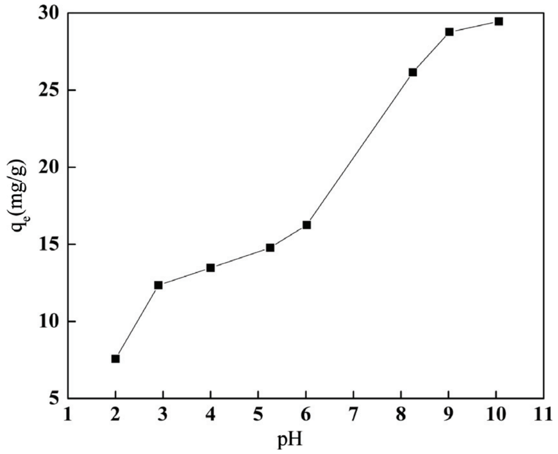

Fig. 2. Effect of pH on removal of BrO_3^- by corncob (BrO_3^- concentration: 40 mg/l; adsorbent dose: 0.20 g/200 ml; temperature: 30°C; shaking speed: 250 r/min; contact time: 60 min).

CC by means of ion exchange. (2) The level of bromate protonation decreased with the increaseing solution pH value, which would be helpful to the adsorption. (3) In the higher pH medium(pH > 9), the OH^- has a high concentration, which has two effects: the fisrt is that OH^- compete with bromate for the adsorption active site on the surface CC, which leads to inhibit bromate adsorption slightly; the first is that OH^- also decrease the level of bromate protonation, which would be helpful to the adsorption. With the increasing of OH^- concentration, the inhibition is increasing and adsorption reaches equilibrium. The increasing pH value (pH > 9) does not get a satisfactory effect on the adsorption and the initial pH 8 was selected for future experiments in terms of cost.

3.3. Effect of ionic strength

The effect of ionic strength on the adsorption of BrO_3^- was examined and the result was shown in Fig. 3. It can be seen that the presence of NaCl could inhibit adsorption of BrO_3^- due to its competition between BrO_3^- cation and Cl^- ion for the adsorption sites [24].

3.4. Effect of different adsorbents

The effect of modified corncob adsorption capacity was studied by CCN, CCH, CCI2, CCI8, CCCA, CCC and CCA. The adsorption isotherms of bromate on the natural and modified corncobs are shown in Fig. 4. CCI8 and CCCA exhibited a higher capacity than the CCI2, CCN and the nature corncob (CC). However, the adsorption capacity of CCC, CCA for bromate were equivalent to that of CCCA. The removal percentages (%) of bromate by CC were lower than by CCC and CCA, and were higher than by CCN, CCH, CCI2. Results indicate that the 80%-isopropyl alcohol modified corncob cellulose has greater number of surface charge and functional groups than additional modified corncobs and this appears to be due to the greater efficiency of reaction, thus increasing the number of binding sites of bromate in corncobs[18,25].

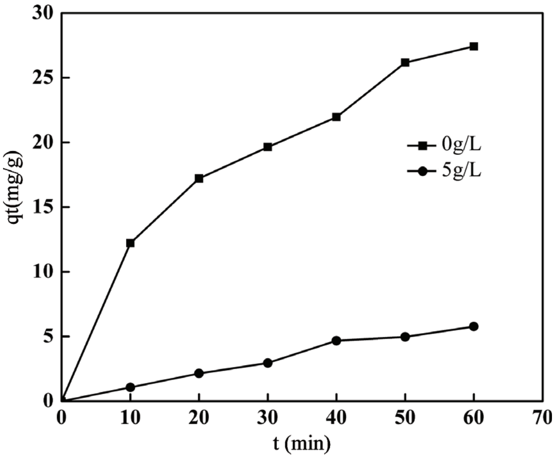

Fig. 3. Effect of ionic strength on removal of BrO_3^- by corncob (BrO_3^- concentration: 40 mg/l; adsorbent dose: 0.20 g/200 ml; temperature: 30°C; shaking speed: 250 r/min; contact time: 60 min; pH: 8.25)

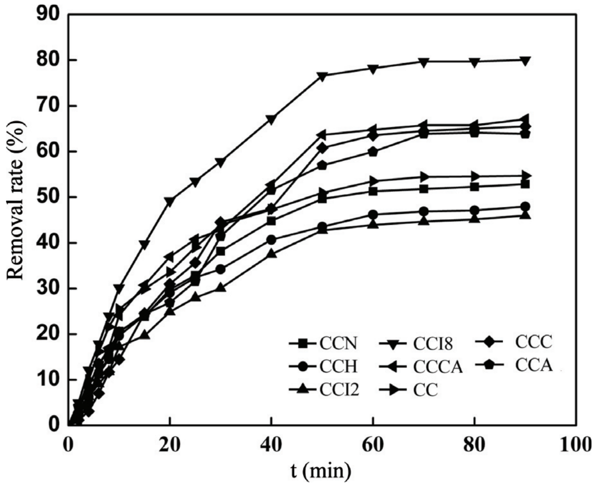

Fig. 4. Adsorption isotherms of bromate by native and modified corncob (BrO_3^- concentration: 40 mg/l; adsorbent dose: 0.20 g/200 ml; temperature: 30°C; shaking speed: 250 r/min; contact time: 90 min; pH: 8.25)

3.5. Adsorption isotherm studies

With the data in Fig. 1, the Langmuir and Freundlich models were used for analyzing the adsorption isotherms of BrO_3^-. The linear form of the Langmuir equation [26] is as follows:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m \tag{3}$$

where C_e (mg/l) is the concentration of BrO_3^- solution at equilibrium, q_e (mg/g) is the amount of BrO_3^- adsorbed at equilibrium, Q_m is the maximum adsorption capacity and a is Langmuir constant. The linear plots of C_e/q_e vs C_e indicated that the adsorption follows the Langmuir isotherm (Fig. 5-A). The isotherm constants of Q_m and a values and correlation coefficients (R^2) are shown in Table 1. The maximum adsorption capacity (Q_m) obtained from the Langmuir was 101.01 mg/g.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L [27] given by equation:

$$R_L = 1/(1 + aC_0) \tag{4}$$

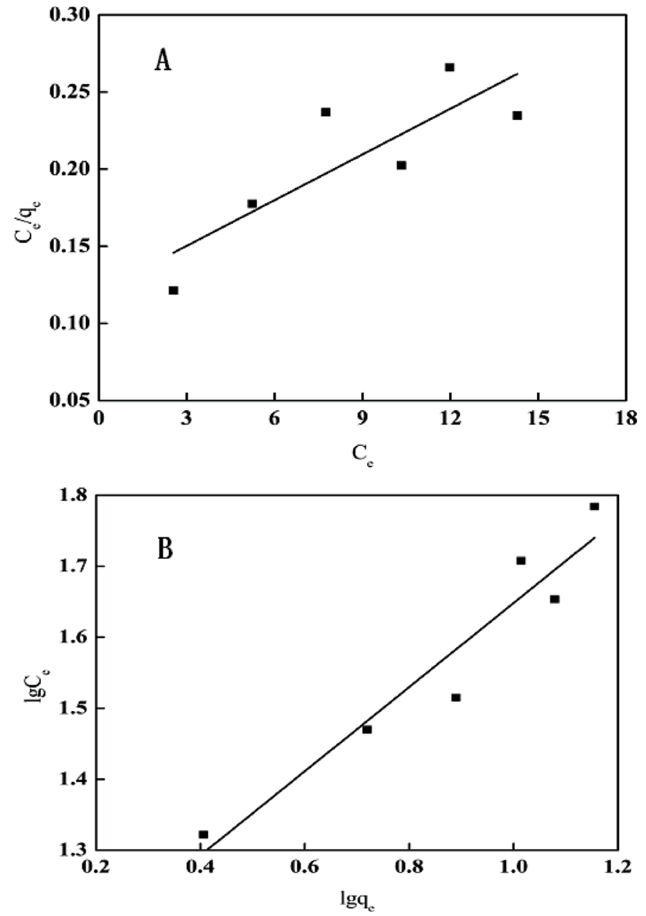

Fig. 5. Langmuir isotherms (A) and Freundlich isotherms (B) for BrO_3^- adsorption onto corncob.

where C_0 (mg/l) is the initial concentration of BrO_3^- and a (l/mg) is Langmuir constant. The parameter R_L (Table 2) indicates the nature of shape of the isotherm accordingly:

R_L values between 0 and 1 at different concentrations indicate favourable adsorption of BrO_3^- onto corncob (Table 3).

The linear form of the Freundlich equation [24] is as follows:

$$\text{In } Q_e = \text{In } K + (1/n) \text{ In } C_e \tag{5}$$

where Q_e is the amount of BrO_3^- adsorbed at equilibrium, C_e is the concentration of the BrO_3^- solution at equilibrium, K and 1/n are empirical constants and indicate adsorption capacity and intensity, respectively. The linear plots of ln Q_e vs ln C_e shows that the adsorption follows Freundlich isotherm model as well (Fig. 5-B). The isotherm constants of K and 1/n values and correlation coefficients (R^2) are shown in Table 1.

Table 1
Langmuir and Freundlich isotherm constants and correlation coefficients for adsorption of BrO_3^- onto corncob adsorbent

Adsorbent	BrO_3^-					
	Langmuir isotherm			Freundlich isotherm		
	Q_m	α	R^2	K	n	R^2
corncob	101.01	0.082	0.6962	2.875	1.688	0.9201

Table 2
Parameter R_L for isotherm

R_L value	Tape of isotherm
R_L>1	Unfavourable
R_L=1	Linear
0<R_L<1	Favourable
R_L=0	Irreversible

Table 3
Data for Langmuir isotherm

Q_m (mg/g)	α (l/mg)	Initial BrO_3^- concentration C_0(mg/l)	R_L
101.01	0.082	20	0.3788
		40	0.2336
		60	0.1689
		80	0.1323
		100	0.1087
		120	0.0923

3.6. Adsorption kinetics studies

With the data in Fig. 1, Pseudo-first-order, second-order models and intraparticle diffusion model were applied to analyze experimental data and thus elucidated the kinetic adsorption process. A linear form of pseudo-first-order model was described by Lagergren [20].

$$Ig(q_e - q_t) = Ig\ q_e - K_{ad}t/2.303 \tag{6}$$

where q_e is the amount of BrO_3^- adsorbed at equilibrium(mg/g), q_t is the amount of bromate adsorbed at time t (mg/g), and Kad is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}). The value of Kad for BrO_3^- adsorption by corncob was determined from the plot of lg(q_e–q_t) against t. The parameters of pseudo-first-order model are summarized in Table 4. The high values of correlation coefficients showed the data conformed well to the pseudo-first-order rate

Table 4
Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constant and calculated and experimental qe value obtained at different initial BrO_{3-} concentrations

C_0(mg /l)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	q_e(mg /g)	K_{ad}(min^{-1})	R^2	q_e(mg /g)	K(g/mg min)	R^2
20	2.842	0.0267	0.4263	28.49	0.0012	0.9776
40	4.101	0.0279	0.5213	39.84	0.0009	0.9555
60	6.816	0.0428	0.7174	42.55	0.0011	0.9758
80	8.276	0.0288	0.6352	68.03	0.0006	0.9838
100	7.954	0.0366	0.6776	62.89	0.0005	0.9861
120	10.399	0.0371	0.6161	92.59	0.0003	0.9592

kinetic model over the initial stage of the adsorption processes. The increase in values of the initial adsorption rates with an increase in the initial BrO_3^- concentration could be attributed to the increase in the driving force for mass transfer, allowing more BrO_3^- molecules to reach the surface of the adsorbents in a shorter period of time [28].

Also, a linear form of pseudo-second-order model is as follows [20]:

$$t/q_t = 1/(Kq_e^2) + t/q_e \qquad (7)$$

where K (g/mg min) is the second-order rate constant. The q_e and K can be calculated from the slope and intercept of the plots t/q_t versus t. The parameters of pseudo-second-order model are also summarized in Table 4. All the correlation coefficients (R^2) from pseudo-second-order kinetic model are generally greater than that from pseudo-first-order kinetic model for all initial concentrations, so the adsorption of BrO_3^- on corncob can be best described by the pseudo-second-order kinetic.

The kinetic results were further analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism [29]:

$$q_t = K_{id} t^{\frac{1}{2}} \qquad (8)$$

where K_{id} is the intraparticle diffusion rate constant (mg/g $min^{1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ (Fig. 6). For intraparticle diffusion plots, the first region is the instantaneous adsorption or external surface adsorption and the second region is the gradual adsorption stage where intraparticle diffusion is the rate limitation. As seen from Fig. 6, the plots were not linear over the whole time range, implying that more than one process affected the adsorption: the first one represents surface adsorption at the beginning of the reaction and the second one is the intraparticle diffusion at the end of the reaction [20].

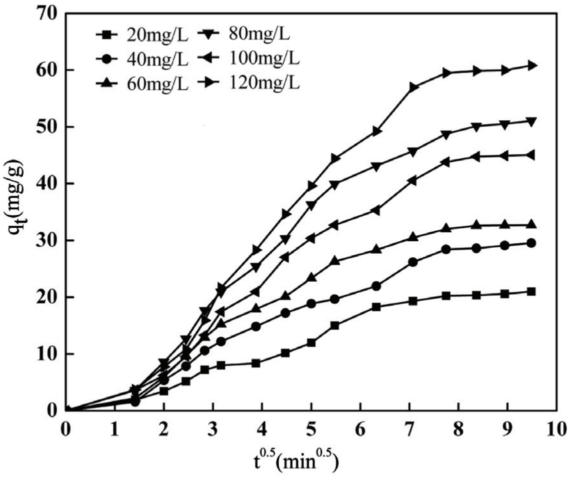

Fig. 6. Intraparticle diffusion plot for the adsorption and different initial bromate concentrations.

4. Conclusions

Various modifed and nature corncob materials were studied as adsorbents for the removal of bromate from aqueous solutions. The adsorption capacity of corncob modified by 80% isopropyl alcohol was significantly higher than nature corncob, corncob ash and corncob carbon at the same conditions. The best conditions for the removal of bromate were at the medium with low ion concentration and the kinetics behavior followed the Freundlich-second-order model very well. The conditions of obtaining the maximum adsorption capacity were 101.01 mg/g for 0.2 g/200 ml CC concentration at initial pH 9.00 and equilibrium achieved within 80 min, respectively. Effect of the solution pH on the adsorption of bromate on natural corncob was assessed, and bromate was almost not adsorbed at pH less than 2. The adsorption capacity was increased three times with the solution pH increasing from 3 to 9. Results indicate that the study can provide an effcient and cost-effective technology for eliminating bromate from wastewater and effuent solutions by the nature and chemically modifed corncob.

Acknowledgements

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