Adsorption of Cr(VI) from Aqueous Solution with Double Layers Calcium-Iron-Alginate Gel Beads

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Abstract-single and double layer alginate calcium iron gel beads were prepared. The adsorption property of alginate calcium iron gel ball on Cr(VI) was studied, under the existence of Fe^{3+}. The effects of the number of layers and the sequence of Fe^{3+} in gel ball on adsorption of Cr(VI) were discusses, and the adsorption kinetics of Cr(VI) were further explored. The results show that the number of layers has little effect on adsorption of Cr(VI) with alginate calcium iron gel beads, the removal rates is more than 96 % after 3 h. The effect of Fe^{3+} order in gel ball on adsorption of Cr(VI) is obvious, the sequence of adsorption quantity of Cr(VI) is @-Fe-@-Fe=@-@-Fe>@-Fe-@. The processes of alginate calcium iron gel beads adsorbed Cr(VI) fit well with quasi-two adsorption kinetics model. The order of their adsorption rates is as follow: @-Fe>@-Fe-@-Fe>@-@-Fe>@-Fe-@.

Keywords-calcium-iron-alginate gel beads; adsorption; Cr(VI); dynamics; the quasi-two adsorption kinetics

I. INTRODUCTION

Sodium alginate, a natural polysaccharide, has good gel property, film-forming performance and solution concentration ability. So it is widely used in food, medicine, cosmetics, adhesive, textile, papermaking, and coating industry. Recently, the research of sodium alginate gets more and more attention. The alginate could gel simply induced by crosslinking with most divalent or trivalent cations. The divalent or trivalent cation such as Ca^{2+}, Zn^{2+}[1], Ba^{2+}[2]and Fe^{3+}. Calcium silicate selected as crosslinking agent has also been reported [3].

The researches also focus on removal of organic or inorganic pollutants by calcium alginate ball. C. Gok adopted isotherm models and thermodynamic to study biosorption of radiostrontium ^{85}Sr by alginate beads [4]. R. Lagoa and J. R. Rodrigues evaluated the suitability of dry protonated alginate particles for biosorption applications and to examine their potential for lead uptake from aqueous solutions [5]. The Langmuir equation is the most adequate model to lead sorption. F. Wang prepared core–shell structural composite beads taking calcium silicate as shell and alginate as core with P507 involved, and researched the adsorption of rare earths [6]. The pseudo-second-order kinetics model and Langmuir isotherm equation were used to describe the adsorption process very well. S. Uzaşçı reported to remove of hexavalent chromium from aqueous solution by barium ion cross-linked alginate beads, and studied adsorption isotherm and adsorption kinetics [7].

Sodium alginate as a carrier of biological species has also been reported to remove organic or inorganic pollutants from aqueous solutions. Decolouration of azo dyes by Phanerochaete chrysosporium immobilised into alginate beads has been reported [8]. Marı´a F Bergero used Pseudomonas putida A ATCC 12633 immobilized in calcium alginate beads to degradate cationic surfactants [9]. A study on enhanced degradation of phenol by Pseudomonas sp. CP4 entrapped in agar and calcium alginate beads in batch and continuous processes has been reported[10]. J. Panda and P. Sarkar studied biosorption of Cr(VI) by calcium alginate-encapsulated enterobacter aerogenes t2, in a semi-batch plug flow process, and studied the kinetic of isotherm models [11]. A sorbent based on 2 % grape stalk wastes encapsulated in calcium alginate beads was investigated for the removal of Cr(VI) and Cr(III) from aqueous solutions [12]. Previous studies in our research group showed the removal ration of Cr(VI) by SA-Ca-Fe gel beads was 93 %. SA-Ca-Fe gel beads were prepared by adding Fe^{3+} ions onto SA-Ca, which was prepared by sodium alginate (SA) in $CaCl_2$ solution. But there is less reports about adsorption of Cr(VI) by multilayer alginate calcium iron gel beads.

In this paper, we prepare single and double layers alginate calcium iron gel beads. The adsorption property of alginate calcium iron gel ball on Cr(VI) are studied, under the existence of Fe^{3+}. The effects of the number of layers and sequence of Fe^{3+} in gel ball on adsorption of Cr(VI) with gel balls are discussed, and the adsorption kinetics of Cr(VI) are further explored.

II. EXPERIMENTAL

A. Materials

Sodium alginate, Calcium chloride, ferricchloride, Potassium dichromate, Liquid paraffin and polysorbate 80 are purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China)

B. Preparation of single lay alginate calcium-iron gel beads

3 g sodium alginate was slowly poured into 100 mL distilled water, and stirred until sodium alginate completely dissolved, the solution was vacuum dehydrated for 30 min. Sodium alginate solution (SA, 3 %, w/v) was dropped into 500 mL calcium chloride solution ($CaCl_2$, 5 %, w/v) by 10 mL syringe without needle (the distance of the syringe bottom to liquid level was 25 cm), immersed in water for 12 h. These beads were removed from the solution and washed the residual $CaCl_2$ with distilled water. Then the prepared beads were immersed in $FeCl_3$ solution (2.5 %, w/v) for 12 h, and washed the residual $FeCl_3$ with distilled water to get single lay alginate calcium iron gel beads (@-Fe).

C. Preparation of double layers alginate calcium-iron gel beads

According to the reference [13], the prepared beads mentioned above were immersed in 100 mL SA solution (3 %, w/v) for 5 min, the volume ratio of gel ball to solution was 1:3. Then the SA solution with prepared beads was poured into oil phase mixed with 95 mL liquid paraffin and 5 mL Tween 80, while stirring (500 rpm) for 10 min. The $CaCl_2$ solution (5 % w/v) was added to the mixture and mixed for another 30 min. Then the beads were removed from the mixture and rinsed with distilled water. The prepared beads were immersed in $FeCl_3$ solution (2.5 % w/v) for 12 h to prepare double layers alginate calcium - iron gel beads (@-@-Fe).

The double layers of outside contained iron of calcium alginate iron gel beads (@-@-Fe), the double layers of inside contained iron of calcium alginate iron gel beads (@-Fe-@), and the double layers of both inside and outside contained iron of calcium alginate iron gel beads (@-Fe-@-Fe) were prepared as the same method.

D. Adsorption experiments

The prepared beads (7 g) mentioned above were immersed in Cr(VI) solution(10 mg/L, 100 mL), while stirring for 10 min. After adsorption a certain time, 1 mL test solution was took to a 25 mL volumetric flask, then adding 10 drops mixed acid (sulfuric acid: phosphoric acid: distilled water=15:15:70), shaking, while adding 1 mL DTP (indicator), diluting with distilled water to volume, standing for 5 min. Using distilled water as the reference, the absorbance was measured under the wavelength of 540 nm. The removal rate of Cr(VI) was calculated with the equation as follow:

$$\text{The removal rate} = (C_0 - C_t)/C_0 \times 100\% \qquad (1)$$

where C_0 is the initial concentration of Cr(VI) solution, C_t is the concentration of Cr(VI) solution after adsorption was carried out for a period of time.

E. Adsorption kinetics

The quasi-two adsorption kinetics equation used is:

$$\frac{t}{Q} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \qquad (2)$$

where Q_e and Q are the amounts of solute adsorbed at equilibrium and at any time, respectively, per unit weight of adsorbent (mg/g), k_2 is the second-order rate constant at equilibrium ($g\cdot mg^{-1}\cdot min^{-1}$). t/Q vs t gives the straight line with slope $1/Q_e$ and $1/(k_2 Q_e^2)$ as intercepts.

III. RESULTS AND DISCUSSION

A. IR analysis

The sodium alginate and calcium-iron-alginate gel beads were characterized with a NicoleET5700 FTIR instrument. IR spectra of sodium alginate and calcium-iron-alginate gel beads are presented in Fig. 1.

There is absorption peak at 3500 cm^{-1} in the IR spectra curve a, which is ascribed to the vibrations of -OH groups in sodium alginate, absorption peaks at 1600 cm^{-1} and 1400 cm^{-1} are ascribed to the symmetric and asymmetric stretching vibrations of -COO-. The peak at 1150 cm^{-1} is ascribed to the stretching vibration absorption of C-O in C-O-(H), the peak at 1350 cm^{-1} is ascribed to the bending vibration absorption of C-O-H. The results shown that sodium alginate has lots of random coil structure. In addition, the absorption peaks at 3500 cm^{-1}, 1000~1200 cm^{-1} and 1600 cm^{-1} are broad with introducing of Ca^{2+}, Fe^{3+} as seen in curve b. This may be due to Ca^{2+} and Fe^{3+} can combine with the -COOH in alginate molecules.

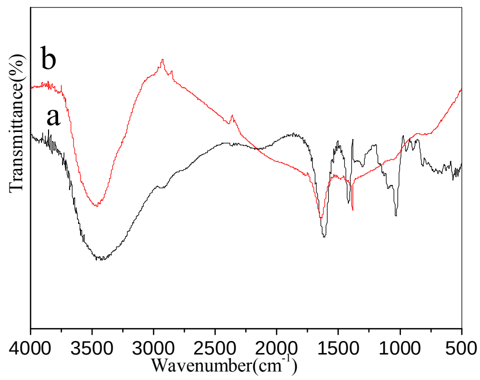

Figure 1. IR spectra of sodium alginate(a) and calcium-iron-alginate gel beads(b)

B. The morphology of calcium-iron-alginate gel beads

The morphologies of @-Fe and @-Fe-@-Fe show in Fig. 2. The average diameter of @-Fe is 1.72 mm after drying. The double layers structure of @-Fe-@-Fe can be seen clearly in Fig. 2c and Fig. 2d. The inside is a dense gel ball, the outside is an orange gel layer, and gel ball diameter is 2.50 mm.

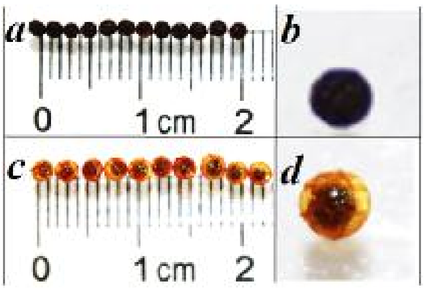

Figure 2. The morphologies of calcium-iron-alginate gel beads (a,b: @-Fe-@-Fe, c, d: @-Fe)

C. Influence of layers on the adsorption properties

In order to study the adsorption properties of different layers gel balls, the single and double alginate calcium iron gel beads are selected for adsorption of Cr(VI), the results show in Fig. 3.

The removal rate of Cr(VI) is 95.9 % and 89.6 %, respectively, after adsorbing by @-Fe and @-Fe-@-Fe for 60 min. Thus, the adsorption speed of @-Fe on Cr(VI) is faster than @-Fe-@-Fe. But both of the removal rates are 99.3 % after adsorption for 120 min, so the final adsorption effects are the same. This may be due to the outside gel in double layers of alginate calcium iron gel beads (@-Fe-@-Fe) was thin, and the complex Fe^{3+} is less, so the adsorption rate of Cr(VI) is slow. Furthermore, Cr(VI) is prevented entered in the outside layer of gel, the reaction of Cr(VI) and Fe^{3+}, which is on the inside gel ball, is slow. The structure of @-Fe is more closely than @-Fe-@-Fe, Fe^{3+} on the surface of @-Fe can complex with Cr(VI) directly, so the adsorption velocity of Cr(VI) is fast.

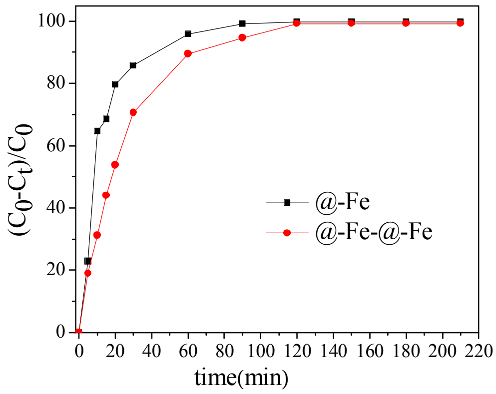

Figure 3. Adsorption of Cr(VI) with different layers gel beads ($K_2Cr_2O_7$ 10 mg/L, 50 mL, gel ball 7 g, 27 °C)

D. The effects of Fe^{3+} order

By the early studies, we know the removal rate of Cr(VI) from the SA-Ca gel balls is almost 0, the adsorptions of Cr(VI) by three kinds of double layers gel ball, which contained different sort of iron, are researched under the condition of Cr(VI) 10 mg/L 50 mL, gel ball 7 g, 27 °C, the results shown in Fig. 4. The removal rate of Cr(VI) is 99.3 %, 96.2 % and 70.2 %, respectively, after adsorption of Cr(VI) with @-Fe-@-Fe, @-@-Fe and @-Fe-@ gel balls for 180 min. The adsorption capacity of @-Fe-@-Fe is strongest; followed by @-@-Fe gel balls, the worst is @-Fe-@.

This may be due to the both inside and outside layers of @-Fe-@-Fe gel balls contain Fe^{3+}, the Fe^{3+} can easy complex with Cr(VI), therefore the adsorption ability of Cr(VI) is strongest. The @-@-Fe gel balls contain Fe^{3+} on outside layer, while inside layer do not contain Fe^{3+}, so the inside layer can not adsorb Cr(VI), adsorption of Cr(VI) mainly depends on the outside layer. The structure of the @-Fe-@ gel balls is that Fe^{3+} is in insider layer, while outsider layer has little Fe^{3+}, it is difficult for Cr(VI) to penetrate the outside gel film into the inside layer and to combine with Fe^{3+} at inside layer. Therefore, the amount of adsorbed Cr(VI) is less.

Analysis and comparison of the results in Fig. 3 and Fig. 4, the adsorption capacity of four kinds of calcium-iron-alginate gel on Cr(VI) followed an order: @-Fe = @-Fe-@-Fe = @-@-Fe>@-Fe-@.

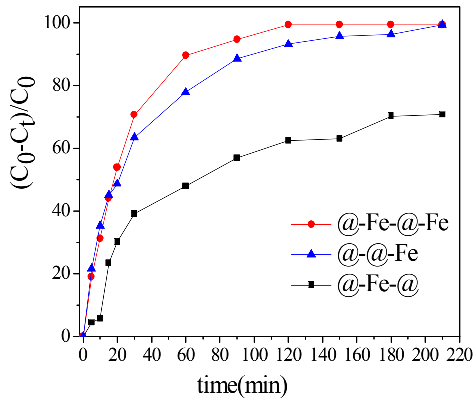

Figure 4. Adsorption of Cr(VI) with double layers of calcium-iron-alginate gel ($K_2Cr_2O_7$ 10 mg/L 50 mL, gel ball 7 g, 27 °C)

E. Adsorption kinetics

Adsorption kinetics is one of the most important parameters for a certain adsorption system. Quasi-two adsorption kinetic equation is applied to fit the experimental data, which are from the processes that adsorption of Cr(VI) on alginate calcium iron gel beads, the fitting results show in Fig. 5. The processes fit well with quasi-two adsorption kinetics model. The linear correlation coefficients R^2 are close to 1.

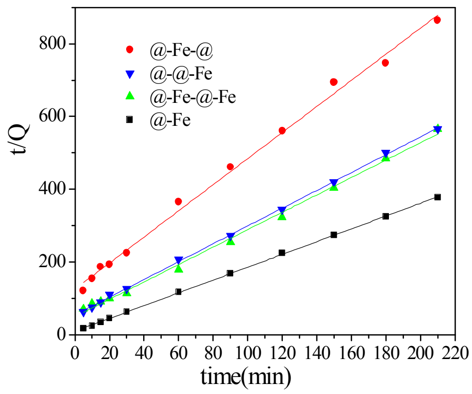

Figure 5. Fitting curve with quasi-two adsorption kinetics

The dynamics equation and rate constants k_2 as shown in table 1. The rate constants R^2 of adsorbing Cr(VI) on @-Fe, @-Fe-@-Fe, @-@-Fe and @-Fe-@ gel balls are

0.0342, 0.0035, 0.0031 and 0.0006 g $mg^{-1}\cdot min^{-1}$, respectively. Comparison of rate constant k_2, it is indicated that the order of their adsorption rates is as follow: @-Fe>@-Fe-@-Fe>@-@-Fe>@-Fe-@.

TABLE I. THE KINETICS AND RATE CONSTANT K_2 OF CR(VI) ADSORPTION BY GEL BEADS

the kind of gel balls	quasi-two adsorption kinetics equation	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2
@- Fe	t/Q=1.76017t+9.46	0.0342	0.9980
@-Fe-@	t/Q=3.58742t+125.31	0.0006	0.9950
@-Fe-@-Fe	t/Q=2.39224t+49.44	0.0035	0.9963
@-@-Fe	t/Q=2.45059t+53.77	0.0031	0.9944

IV. CONCLUSIONS

Four kinds of gel balls @-Fe, @-@-Fe, @-Fe-@, @-Fe-@-Fe are prepared, adsorption properties of Cr(VI) on gel balls are studied.

After adsorption of Cr(VI) on @-Fe and @-Fe-@-Fe for 120 min, the both removal rates reach 99.3 %.

The number of layers has little effect on adsorption of Cr(VI) with alginate calcium iron gel beads, the removal rates is more than 96 % after 3 h.

The effect of Fe^{3+} order in gel ball on adsorption of Cr(VI) is obvious, the sequence of adsorption quantity of Cr(VI) is @-Fe-@-Fe=@-@-Fe>@-Fe-@.

The processes of alginate calcium iron gel beads adsorbed Cr(VI) fit well with quasi-two adsorption kinetics model. The order of their adsorption rates is as follow: @-Fe>@-Fe-@-Fe>@-@-Fe>@-Fe-@.

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