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Adsorption and removal of cadmium (II) from aqueous solutions by bio-formulation

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Abstract: A novel sorbent, bio-formulation(BF), was prepared and employed for the adsorption of cadmium(Cd) ion from aqueous system. The process of adsorption follows the pseudo second-order kinetic equation and the adsorption behavior is fitted with a Freundlich isotherm. The removal rate of Cd is slightly dependent on the initial pH value over a wide range of 4-11. The addition of Zn²⁺ and Cu²⁺ ions hardly affects the Cd adsorption, whereas the coexisting Pb²⁺ ion greatly interferes with the adsorption. The adsorption mechanism is supposed as a cation-exchange process between Cd²⁺ and calcium and Mg²⁺ present on the surface of BF, and somewhat as adsorption in a hydrolyzed form. The adsorbed Cd ions are desorbed effectively by a 0.1 mol/L HCl solution.

Key words: cadmium; bio-formulation(BF); adsorption; desorption

1 Introduction

Release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems[1]. Cadmium is a metal widely used in industries such as electroplating, paint pigments, plastics manufacturing, mining and metallurgical processes[2]. It is a non-essential and non-beneficial element to plants and animals, and is extremely toxic in relatively low dosages[3]. Diseases such as renal damage, anemia and hypertension are associated with excess cadmium[4]. The main anthropogenic pathway through which cadmium enters the environment is via wastewater. At present there are a number of different technologies for treating cadmium-bearing waste streams, including chemical precipitation, filtration, exchange, ion adsorption using active carbon and membrane processes. Chemical precipitation processes have several disadvantages, which include incomplete metal removal and sludge generation[5]. The other technologies are generally expensive when cadmium is present in the wastewater at low concentrations, or when a very low

concentration of cadmium in treated water is required[6].

In the last decade, due to its potential, bio-sorption is one of the alternative means of treating wastewaters containing low levels of cadmium by various biological materials[7–8]. Recovery of cadmium from solution would be beneficial since cadmium may be cumulated by the biological materials and recovered for reusage, and release of potentially toxic metals into the environment would be restricted[9]. Bio-sorption involves the use of biomass[10] or natural substrates such as agricultural residues[11], microorganisms[12], and sugar beet pulp[13].

BF is agricultural waste modified by acid and base. In the present study, BF was used as a biosorbent for the removal of cadmium from aqueous solutions. The objective of this study is to explore the feasibility of using the BF for the removal of toxic heavy metals from wastewaters. Batch experiments were carried out to investigate metal biosorption properties of BF. The factors affecting the adsorption of cadmium, such as pH, initial concentration, contact time, coexisting ions were studied.

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2 Experimental

The agricultural waste was obtained from a local agricultural working factory located in Changsha, China. The waste was sun dried and ground to be less than 0.355 mm. Preliminary studies using the waste treated with acid and base were carried out in order to optimize the adsorption of cadmium. Maximum adsorption was obtained by treating the waste with calcium hydroxide $(Ca(OH)_2)$ saturated solution at room temperature for 10 h. And the BF was gained after the materials were dried at 80 °C.

The effect of pH on metal removal was carried out with 3 g/L of Ca(OH)₂-treated BF in 100 mL solution of cadmium. The pH of the solution was adjusted with 0.1 mol/L HCl or NaOH solution. The mixture was agitated with a magnetic stirrer in a 100 mL Bunsen beaker at room temperature ((28 ± 2) °C). Each beaker was removed after the required reaction time and the solution was filtered through qualitative filter paper, and the supernatant was analyzed for its metal ions using an atomic absorption spectrophotometer (WFX 120). Controls were also performed with untreated BF.

All other experiments were run in the solution of pH 8. The adsorption isotherm for Ca(OH)₂-treated BF was conducted with cadmium ion concentrations of 0.05–0.20 mmol/L. In the contact time experiment, samples were withdrawn at pre-determined intervals and Cd removal was analyzed.

Each removal experiment was run in triplicate and the mean values were reported.

3 Results and discussion

3.1 Effect of chemical treatment on adsorption

The effect of treatment of BF on the adsorption of Cd is listed in Table 1. Treatment with Ca(OH)₂ greatly enhances metal adsorption whereas BF treated by HCl shows lower adsorption than the control material. Ref.[14] reported that sodium hydroxide treated waste products showed greater adsorption of Cd compared with the unmodified materials. Other work[15] also showed that NaOH treated soybean and cottonseed hulls improved adsorption capacity for Zn as compared with the untreated materials. However, in our study the BF

 Table 1 Adsorption of Cd with various chemically modified
 BF

| Treatment | Untreated | HCl | NaOH | Ca(OH) ₂ |
|-------------------------|-----------|------|------|---------------------|
| Removal rate of Cd/% | 85.6 | 75.7 | 95.2 | 99.4 |

* Initial concentration of Cd is 0.1 mmol/L, and contact time is 30 min

treated by Ca(OH)₂ has adsorption capacity for Cd greater than that treated by NaOH. It can be explained by an increase in the amount of hydroxyl functional groups.

3.2 Kinetic study

Effect of time on adsorption of Cd onto BF can be seen in Fig.1(a). An aqueous solution (100 mL) of 0.1 mmol/L Cd was contacted with 0.1, 0.2, 0.3 g of BF at room temperature. It reveals that the adsorption is rapid in the first 30 min and then slows down considerably as the reaction reaches the equilibrium. The adsorption rate is found to accelerate with an increase in the amount of BF.



Fig.1 Time dependence of Cd ion adsorption onto BF: (a) Time course; (b) Kinetics curves (Cd initial concentration: 0.1 mmol/L; BF: 1, 2 and 3 g/L, respectively.)

Various adsorption kinetic equations have been used to describe the removal of metals. Recently, Ref. [16] reported that most of the adsorption systems followed a pseudo second-order kinetic equation that can be expressed as

$$\frac{t}{q_{\rm t}} = \frac{1}{k} + \frac{t}{q_{\rm e}} \tag{1}$$

where t is the contact time (min); q_t and q_e are the

quantities of sorbate sorbed at time *t* and equilibrium (mmol/g); *k* is the rate constant (mmol·g⁻¹·min⁻¹). Plots of t/q_t vs *t* for Cd-BF systems are shown in Fig.1(b). It can be seen that the adsorption process for Cd on BF follows the pseudo second-order kinetics.

3.3 Effect of pH on Cd adsorption

pH is a key parameter, along with metal concentration and solution composition, in determining biosorption levels. The objective of this study was to determine the effects of pH (2–11) on removal levels. Fig.2 shows the effect of initial solution pH on the removal of Cd^{2+} by BF. The results show excellent removal capacities for Cd^{2+} . The Cd^{2+} removal increases from 79.7% at pH 2 to 99.4% at pH 8. Then the removal keeps almost constant until pH 10. At higher values of pH cadmium ions precipitate $Cd(OH)_2[17]$. And the Cd^{2+} shows a decrease in adsorption with pH less than 3 and greater than 10.



Fig.2 Removal rate of Cd²⁺ by BF with different pH values (Cd initial concentration: 0.1 mmol/L; BF: 3 g/L; Contact time: 30 min)

The dependence of metal removal rate on pH is related to both the surface functional groups present on the biomass and the metal chemistry in solution. At low pH, the surface ligands are closely associated with the hydronium ions (H_3O^+) and restrict the approach of metal cations as a result of the repulsive force[18-19]. Furthermore, the metal ions removal rate by BF dependent on pH can also be justified by the association-dissociation of certain functional groups, such as the carboxyl and hydroxyl groups present on the biomass. In fact, it was known that at low pH value, most of the carboxyl groups were not dissociated and could not bind the metal ions in solution, although they took part in complexation reactions[20]. Based on these results, the following experiments were performed at pH 8.

3.4 Adsorption capacity

In order to investigate the adsorption capacity, the adsorbent BF concentration of 3 g/L was agitated with the aqueous solution of Cd varied from 0.05–0.20 mmol/L at room temperature for 30 min. After removal of the adsorbent, the Cd²⁺ concentration was determined. It is found from the results that the adsorption rate decreases with the increase of the Cd²⁺ concentration. The data for the Cd²⁺ concentration of 0.05–0.20 mmol/L were analyzed in the light of the Freundlich mode of adsorption. The Freundlich isotherm was tested with the following linear form:

$$\lg q_{\rm e} = \lg K + \left(\frac{1}{n}\right) \lg c_{\rm e} \tag{2}$$

where q_e is the amount of Cd²⁺ adsorbed at equilibrium (mmol/g); c_e is the equilibrium concentration of Cd²⁺ in solution (mmol/L); *K* and 1/n are the Freundlich constants.

As shown in Fig.3, with very high regression correlation coefficients (0.999 9), the plot of $\lg q_e$ vs $\lg c_e$ gives straight lines for BF, which supports the applicability of the Freundlich isotherm model to the present study. The values of Freundlich constants *K* and 1/n represent the adsorption capacity (mmol/g) and adsorption intensity of these sorbents, respectively. The constants *K* and 1/n are evaluated from the intercept and the slope of the straight lines using a least-square fit program and are found to be 0.328 mmol/g and 0.997 for BF.



Fig.3 Adsorption capacity of Cd^{2+} by BF (pH value: 8; Cd initial concentration: 0.05–0.20 mmol/L; BF: 3 g/L; Contact time: 30min)

3.5 Influence of coexisting cations upon adsorption

Fig.4 shows the influence of coexisting cations upon the adsorption capacity of Cd, which was tested by batch operation at various initial molar ratios of these cations to Cd ions. All Cd^{2+} solutions with initial

concentrations of 0.1 mmol/L were used. The initial molar ratio varies between 0 (no coexisting cations) and 20. In the binary metal solutions, lead ion dominates the competitive binding. The addition of zinc, copper ions hardly affects the Cd adsorption.



Fig.4 Cd adsorption capacity Q(Cd) at different initial molar ratios of coexisting cations to Cd ion by BF (Coexisting cations: Pb, Zn, Cu; pH: 8; BF: 3 g/L; Contact time: 30 min)

3.6 Desorption of Cd and regeneration of BF

As shown in Fig.2, low adsorption for Cd is presented in extremely pH range especially in strong acidic pH, which implies that adsorbed Cd ion can be desorbed from BF by both acidic and alkaline media. Therefore, desorption tests were carried out using sodium hydroxide and hydrochloride acid solution in batch operation. As demonstrated in Table 2, 0.1 mol/L HCl appears to be the most suitable desorption agent. After desorption operation, the adsorption rate of Cd onto the BF is reduced to about 73%. However, the adsorption capacity of BF is favorably restored to 96% by regeneration operation, that is, it is loaded again with Ca(OH)₂ saturated solution.

3.7 Adsorption mechanism study

The Fourier transform infrared spectroscopy(FTIR) has been considered as a kind of direct means for investigating mechanisms of metals adsorption on biomass. FTIR of BF unmodified, modified by Ca(OH)₂

and after Cd binding adsorption at pH 8 are shown in Fig.5. The absorption at 3 700–3 000 cm⁻¹, found in the three spectra, is —OH associated with hydrogen bond stretch vibration or amide, but the three adsorption bands are all broad, which is not accord with the rule of adsorption peak amide[21–22]. On the other hand, the —OH associated with hydrogen bond stretch vibration in the three spectra indicates that —OH is always on the BF, so the adsorption mechanism may be cation exchange effect.



Wavenumber/cm⁻¹ Fig.5 FTIR spectra of unmodified BF (a), BF modified by

Fig.5 FTIR spectra of unmodified BF (a), BF modified by $Ca(OH)_2$ (b) and modified BF after Cd adsorption (c)

From the curves (b) and (c) of Fig.5, the wave number shifting from 3 310 cm⁻¹ to 3 440 cm⁻¹ implies that the hydroxyl group maybe changes from high aggregate to low one. This illustrates that the adsorption of Cd lowers the aggregate of hydroxyl group, which maybe supplies more opportunities for Cd²⁺ to bond with hydroxyl group.

In order to understand the cadmium trend of adsorption on BF, consideration of the types of associations among adsorbing metal ions and Ca—OH functional groups may be helpful.

$$Ca \longrightarrow OH + M^{n+} \longrightarrow M \longrightarrow OH^{(n-2)+} + Ca^{2+}$$
(3)

Heavy metal cations M^{n+} may also hydrolyze in aqueous solution and adsorb in a hydrolyzed form according to the following reaction:

$$M^{n+}+H_2O \rightarrow M \longrightarrow OH^{(n-1)+}+H^+(Hydrolysis)$$
(4)

| Tabla | 2 D | acorntion | and | regeneration | of BE |
|--------|-----|-----------|-----|--------------|-------|
| rable. | 4 D | esorbuon | anu | regeneration | UI DF |

| | Desorption agent | | | | | |
|--|--|------|------|---|------|------|
| Item | $c(\text{HCl})/(\text{mol}\cdot\text{L}^{-1})$ | | | $c(\text{NaOH})/(\text{mol}\cdot\text{L}^{-1})$ | | |
| | 0.05 | 0.10 | 0.20 | 0.05 | 0.10 | 0.20 |
| Desorption/% | 50 | 95 | 98 | 41 | 78 | 89 |
| Adsorption after desorption/% | 46 | 73 | 59 | 43 | 37 | 26 |
| Adsorption after desorption and regeneration/% | 54 | 96 | 89 | 52 | 77 | 82 |

BF: 3 g/L; c(Cd): 0.1 mmol/L, 100 mL; Contact time: 30 min; Adsorption for virgin BF: about 99%; Volume desorption agent: 50 mL; Desorption time: 20 min

And from Fig.4, it can be seen that the sorption of lead is superior to that of cadmium. The reason of higher value for Pb^{2+} is that BF adsorbs it a bit strongly as Pb^{2+} can easily be hydrolyzed in water[23], which in turn favors its chemisorptions on BF. It is, therefore, can be deduced that adsorption and hydrolysis are somewhat correlated. If the heavy metal ion is easily hydrolysable, its sorption on BF is relatively higher as that in the case of Pb^{2+} .

Spectral energy distributions of the modified BF before and after Cd adsorption are shown in Fig.6. By comparison of the two figures, the concentration of calcium and magnesium falls after Cd adsorption. The adsorption peaks of the two substances are almost absence, and a peak of cadmium appears. From this, the cation-exchange adsorption occurs at the adsorption process of Cd on BF. That is also confirmed by Eqn.(3).



Fig.6 Spectral energy distributions (Accelerating voltage: 20 kV; Light spot: 52; Working range: 11 mm.): (a) Modified BF before Cd adsorption; (b) Modified BF after Cd adsorption

4 Conclusions

1) BF is an effective adsorbent for the removal of

Cd(II) from aqueous systems like drinking water. Cd(II) ion adsorption on BF follows pseudo second-order kinetics and the adsorption mode is of a Freundlich isothermal nature. The adsorption of Cd(II) is just slightly dependent on the initial pH over a wide range (4-11) and the BF can be directly and effectively employed to common water systems without pH adjustment.

2) BF presents a quite high Cd(II) adsorption ability, and seems to be especially suitable for removal of Cd(II) in low concentration. BF is quite selective towards Cd(II). The coexisting cations, except lead, hardly interfere with the adsorption of Cd(II) ions. The adsorbed Cd(II) ions are effectively desorbed by a 0.1 mol/L HCl solution.

3) In order to realize its full potential as a commercial sorbent, removal of metals under continuous condition with industrial wastewater containing such toxic metals must be evaluated. Currently such an investigation is being undertaken.

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