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Adsorption of lead ion from aqueous solution using acetic acid modified wheat bran

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Abstract : Adsorption experiments were carried out using biosorbent (acetic acid modified wheat bran as a low cost adsorbent) to adsorb lead ion (Pb^{2+}) from synthetic solutions. The effects of various experimental parameters such as initial solution pH, contact time, initial Pb^{2+} concentration and adsorbent dosage were studied, and the optimal condition was selected. Kinetics studies showed that Pb^{2+} adsorption process obeyed pseudo-second order rate equation. The applicability of the Langmuir and Freundlich models for the data was tested. Both the models adequately describe the experimental data of the biosorption of Pb^{2+}. The maximum adsorption capacity calculated from the Langmuir model is 25.1 mg/g for Pb^{2+}. The study has shown the effectiveness of modified wheat bran in the removal of Pb^{2+} from synthetic solutions.

Keywords : Adsorption, lead ion, modified wheat bran.

Introduction

Pollution of water by toxic metals even at rather low concentrations, implies a severe risk for human health and other biological systems, due to the metals' resistance to biodegradation and accumulation in living tissues[1]. The increasing in the use of major 20 heavy metals from over the past few decades has inevitably resulted an increasing flux of metallic substances in natural source of water. The heavy metals such as lead, cadmium, copper and mercury, are among the most common pollutants found in industrial effluents[2]. These metals are of special concern due to their toxicity and persistency properties in nature. All lead compounds are considered cumulative poisons. Acute lead poisoning can affect nervous system and gastrointestinal track[3]. Hence, it is necessary to remove lead from wastewater before being discharged. Conventional technique for heavy metals removal from water and wastewater includes electroplating, evaporating, oxidation, reduction, membrane separation, ion exchange and adsorption[4]. But the addition of chemicals often incurs high operational costs and may not meet strict regulatory requirements[1]. Although reverse osmosis and ion exchange methods are effective in removing such pollutants, they are expensive in the operational procedure. These factors have limited the use of methods for the removal of lead and other heavy metals from water and wastewater especially in most of developing countries[5,6]. The adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost. Various adsorbents such as silica gel, alumina clay, synthetics polymer resins and carbonaceous materials are used in adsorption method[7]. Activated carbon, either granular activated carbon (GAC), or powdered activated carbon (PAC) is the most popular and widely used adsorbent[8-10] but it is expensive and its cost increase with the quality. In addition its regeneration with refractory technique results in a 10–15% loss of the sorbent and its uptake capacity. Thus, there has been intensive research exploring the potential of alternative low-cost materials as sorbents for heavy metals. For this purpose in recent years, investigations have been carried out for the effective removal of various heavy metals from solution using natural adsorbents which are economically viable such as agricultural wastes including sunflower stalks[11], Eucalyptus bark[12], maize bran[13], coconut shell, waste tea, rice straw, tree leaves, peanut and walnut husks[14,15]. The bran of wheat is the shell of the wheat seed and contains most nutrients of wheat. This bran is usually removed in the processing of wheat into flour. It is environmentally friendly and is nutritious to the plants. Therefore the use of wheat bran to eliminate pollution from water and wastewater is interesting. The main goal of this study lies on the modification of wheat bran through chemical functionalization to improve its performance as adsorbents of toxic metals in water, specifically for lead ion (Pb^{2+}) and study the effect of different parameters such as contact time, initial pH, adsorbent dosage and initial Pb^{2+} concentration on adsorption process. In addition, the lead adsorption equilibrium and kinetics were determined at various concentration conditions.

Materials and methods :

Preparation of adsorbent :

The wheat bran used in this study is a by-product of a flour factory in Shenyang, China. The wheat bran was washed thoroughly with water to ensure the removal of dust and ash. It was then sieved to -50 mesh size by passing the milled material through standard steel sieves to remove any large non-wheat bran solids. Then, about 4.0 g grinded wheat bran was mixed with 35 mL of 3.5 mol/L acetic acid. The mixture was stirred until homogenous and dried at 50 °C for 24 h. The modified wheat bran was subsequently washed with distilled water until neutral and dried at 50 °C for 24 h.

Batch adsorption experiments :

Batch techniques were used to investigate Pb^{2+} adsorption, which was examined via kinetic studies and adsorption isotherms, together with the effect of some operating parameters. All the batch experiments were carried out in duplicate and the results given are the means with a relative standard deviation of less than 5%. Control experiments without sorbent was carried out to ascertain that the sorption was by the adsorbent and not the wall of the container. The adsorption capacity of modified wheat bran was determined by batch adsorption isotherms at 20 °C in aqueous solution. Lead ion was hardly adsorbed onto any of the wheat bran samples in solutions having values of pH less than 3, at values of pH higher than 7, the adsorption experiments failed as a result of precipitation of lead hydroxide. Thus, in adsorption experiments we fixed the pH values of the initial solution at 4, 5 and 6. In several glass vials, 100 mL of solution containing various Pb^{2+} concentrations (30, 50, 75, 100, 150 mg/L) were contacted with 0.7 g of modified wheat bran. The vials were placed in a water bath at 20 °C and shaken at 150 r/min for approximately 10 h, and the pH was adjusted by adding 0.1 mol/L NaOH or HNO_3 until it remained constant (± 0.10). The reaction mixture was then filtered with a polycarbonate membrane of 0.22 μm of pore diameter, and the concentration at equilibrium was determined. Initial and equilibrium concentrations were measured by an atomic fluorescence spectrometer (AFS) (PS Analytical Ltd., Kent, UK). The amount of lead ion adsorbed was calculated from the difference between the quantity of metal ion added to the modified wheat bran and the metal ion content of the supernatant with the following equation :

$$q_e = V(c_0 - c_e)/W \tag{1}$$

where q_e is the amount adsorbed (mg/g), c_0 and c_e are the initial and equilibrium lead concentrations in the solution (mg/L), respectively, V is the solution volume (L) and W is the mass of wheat bran (g).

The adsorption kinetic study was performed for Pb^{2+} in solution at pH 6.0 and room temperature (20 ± 1 °C). Several glass vials were used to hold 100 mL Pb^{2+} solution of known initial concentration (50 and 100 mg/L) and 0.7 g of adsorbent at pH 6.0, and shaken at 150 r/min for a duration ranging from 0 to 360 min. At certain period of time, each vial was removed from the shaker, and the solution was then filtered to measure the Pb^{2+} concentration. The effects of various parameters on the rate of adsorption process were observed by varying contact time (5, 10, 20, 30, 40, 50, 60, 90, 120 and 180 min), initial concentration of Pb^{2+} (10, 30, 50, 75, 100 and 150 mg/L), adsorbent dosage (2, 3, 4, 5, 6, 7 and 8 g/L) and initial pH of solution (3.5, 4, 4.5, 5, 5.5, 6 and 6.5).

Results and discussion

Effect of acetic acid modification on adsorption process :

The comparison result on the uptake of Pb^{2+} by unmodified and modified wheat bran showed that the removal rate of Pb^{2+} is 56.32% and 87.72%, respectively. It can be seen that the adsorption of Pb^{2+} was enhanced when modified wheat bran was used as the adsorbent.

The adsorption capacity of modified wheat bran for Pb^{2+} is about 1.6 times higher than that of unmodified wheat bran. The presence of carboxyl groups in modified wheat bran is believed to be primarily responsible for the adsorption of Pb^{2+}. Previous investigations have also postulated that the adsorption of positively charged species is due to the presence of binding sites such as carboxyl and hydroxyl groups on the surface[16-18].

Effect of initial Pb^{2+} concentration on adsorption process :

Initial concentration is one of the effective factors on adsorption efficiency. The experiments were done with variable initial Pb^{2+} concentration (10, 30, 50, 75, 100 and 150 mg/L) and constant temperature (20 °C), pH (6.0), contact time (90 min) and 7.0 g/L of adsorbent dosage. The experimental results were shown in Fig. 1. It can be seen that the Pb^{2+} removal rate decreased with the increase in initial Pb^{2+} concentration, the percentage adsorption of Pb^{2+} on modified wheat bran decreased from 96.32 to 43.21% as the initial Pb^{2+} concentration was increased from 10 to 150 mg/L. At lower Pb^{2+} concentrations, the ratio of the available adsorption sites of adsorbent to the initial number of molecules of Pb^{2+} is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of Pb^{2+} which depends upon the initial concentration decreases.

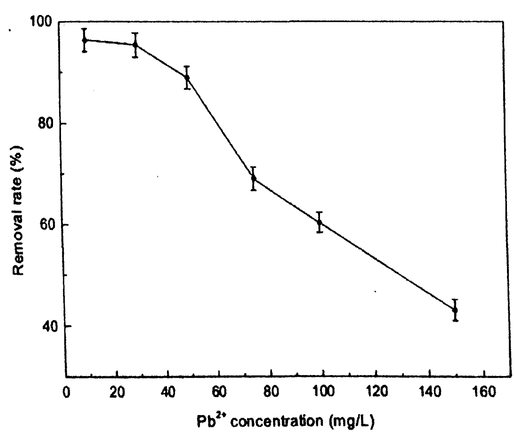

Fig. 1. Effect of initial Pb^{2+} concentration on the adsorption of Pb^{2+} (Experiment conditions employed : adsorbent dosage 7.0 g/L, solution pH 6.0, adsorption time 90 min, agitation speed 150 r/min).

Effect of adsorbent dosage on adsorption process :

The effect of adsorbent dosage in percentage adsorption of Pb^{2+} was shown in Fig. 2. The increase in adsorbent dosage from 2.0 to 7.0 g/L resulted in an increase from 25.22 to 91.3% in adsorption of Pb^{2+}. This is because of the availability of more and more adsorption sites (carboxyl groups) for Pb^{2+} adsorption during the adsorption reaction. A further increase in adsorbent dosage (>7.0 g/L) did not cause significant improvement in Pb^{2+} adsorption. This may be due to the adsorption of almost all Pb^{2+} to the adsorbent and the establishment of equilibrium between the Pb^{2+} molecules adsorbed to the adsorbent and those remaining unadsorbed in the solution. Thus 7.0 g/L of modified wheat bran was chosen for next study.

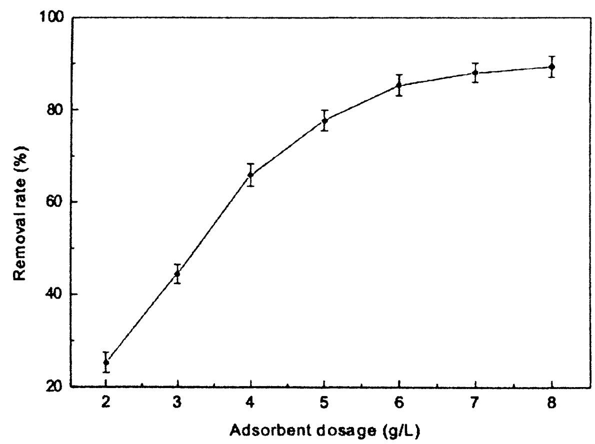

Fig. 2. Effect of adsorbent dosage on the adsorption of Pb^{2+} (Experiment conditions employed : initial Pb^{2+} concentration 50 mg/L, solution pH 6.0, adsorption time 90 min, agitation speed 150 r/min).

Effect of initial solution pH on adsorption process :

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The adsorption of Pb^{2+} on modified wheat bran was conducted at different pH values. Fig. 3 shows the percentage of Pb^{2+} removed as a function of pH values at pH 3.5~6.5.

It is evident that the percentage of Pb^{2+} removal strongly depended on the solution pH. The adsorption amount increased with increasing initial pH to reach a maximum at pH 6.0. At initial pH <6.0, H^+ ions competed with Pb^{2+} ions for the surface of the adsorbent, which would restrict the approach of lead ions due to the repulsion[19]. Hence, the metal removal was the lower

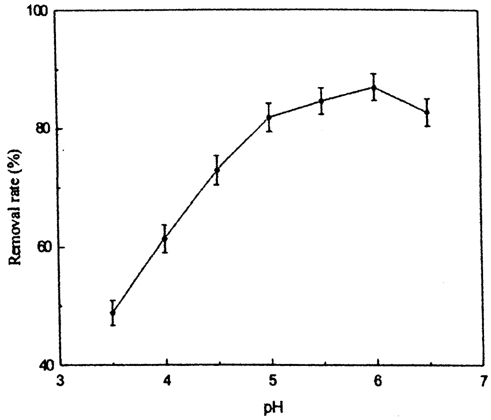

Fig. 3. Effect of pH on the adsorption of Pb^{2+} (Experiment conditions employed : initial Pb^{2+} concentration 50 mg/L, adsorbent dosage 7.0 g/L, adsorption time 90 min, agitation speed 150 r/min).

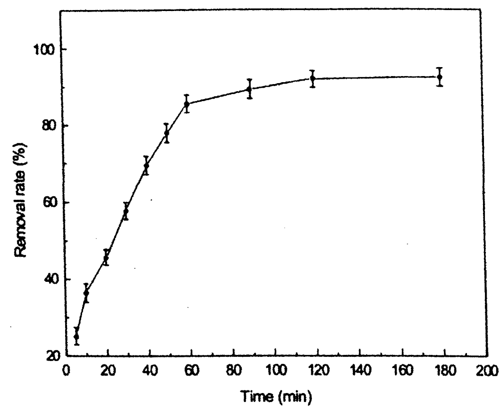

Fig. 4. Effect of contact time on the adsorption of Pb^{2+} (Experimental conditions employed : initial Pb^{2+} concentration 50 mg/L, adsorbent dosage 7.0 g/L, solution pH 6.0, agitation speed 150 r/min).

amount presumably due to the enhanced competition of proton with lead ions for ligand binding sites and complex formation. On the other hand, the adsorptive behavior of lead ion resulted pH dependent because the pH values also affected the charge on the adsorbent surface. At pH <6.0, lead ions can be repelled by the surface positive charges on the adsorbent due to the protonation of oxygen groups ($R\text{-}OH_2^+$). The adsorption of lead ions increased as the initial pH of the system increased, lead ions are attached on the surface of modified wheat bran by replacing H^+ ions of the carboxylic and phenolic ions until a maximum yield is reached. The condition of initial pH >6.0, noted in adsorption decrease, may be attributed to precipitation of the lead ions as hydroxides[20]. For this reason, the optimal pH value was selected to be 6.0.

Effect of contact time on adsorption process :

Contact time is one of the effective factors in batch adsorption process. The effect of contact time on Pb^{2+} adsorption efficiency was shown in Fig. 4. As it is shown, the adsorption was very fast and equilibrium between the aqueous solution and modified wheat bran was established within about 90 min. There was no significant change in Pb^{2+} removal rates after 15 h up to 3 h. Based on the result, 90 min was taken as the equilibrium time in adsorption experiments. The removal of Pb^{2+} from aqueous solutions by adsorption on modified wheat bran increases with contact time, till the equilibrium is attained.

Adsorption isotherms :

In the sorption technology, it is utmost essential to determine an adsorption, as it shows how the adsorption molecules are distributed in the liquid phase and with the adsorbent. For the design purpose, it is necessary to fit the isotherm data with the models. Langmuir and Freundlich isotherm equations are most widely used for the equilibrium study. Pb^{2+} adsorption isotherm obtained for modified wheat bran was shown in Fig. 5. These isotherms represent the adsorption behavior of Pb^{2+} on the adsorbent as a function of increasing aqueous Pb^{2+} concentration for a contact time of 8 h at pH 6.0. The isotherm showed that the adsorption capacity increases with increasing equilibrium concentration of Pb^{2+}.

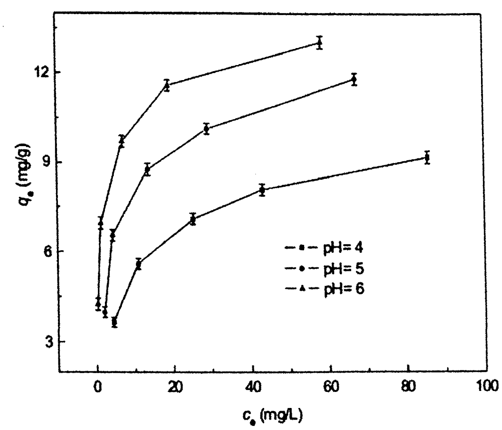

Fig. 5. Adsorption isotherms for Pb^{2+} by modified wheat bran (Experimental conditions employed : adsorbent dosage 7.0 g/L, adsorption time 8 h, agitation speed 150 r/min).

The results of Pb^{2+} adsorption on modified wheat bran (Fig. 5) were analyzed by using the Langmuir model to evaluate parameters associated to the adsorption behavior. The linear form of Langmuir equation at a given temperature is represented by :

$$q_e = q_m \cdot b \cdot c_e / (1 + b \cdot c_e) \quad (2)$$

where c_e is the aqueous phase Pb^{2+} equilibrium concentration (mg/L), q_e is the amount of Pb^{2+} sorbet onto 1 g of the considered adsorbent (mg/g), b is the adsorption constant (L/mg) related to the energy of adsorption and represents the affinity between the adsorbent and adsorbate, q_m is the maximum adsorption capacity (mg/g).

Eq. (2) can be rearranged to obtain :

$$c_e/q_e = 1/(b \cdot q_m) + c_e/q_m \quad (3)$$

Experimental isotherm data acquired at different initial pH were correlated with the linear form of Langmuir model. The isotherm parameters related to the model were listed in Table 1. It could be seen that both q_m and b increased with increasing initial pH from 4.0 to 6.0. The maxima adsorption capacities (q_m) were 16.06, 21.54 and 13.31 mg/g at pH values 4, 5 and 6, respectively. High values of b were reflected in the steep initial slope of an adsorption isotherm, indicating desirable high affinity. Therefore, modified wheat bran performed well in Pb^{2+} adsorption at initial pH 6.0 compared to other initial pH values examined.

The Freundlich isotherm model is also used to analyze the results of Pb^{2+} adsorption on modified wheat bran (Fig. 5). The Freundlich model can be expressed by the following equation :

$$q_e = k_f \cdot c_e^{1/n} \quad (4)$$

where k_f and n are constants related to the adsorption capacity and affinity, respectively. The equation is conveniently used in the linear form by taking the logarithm of both sides as :

$$\lg q_e = \lg k_f + (1/n) \lg c_e \quad (5)$$

Experimental isotherm data acquired at different pH were fit with the linear form of Freundlich model and the isotherm parameters related to the model were listed in Table 1. The data showed that the k_f constant was increased with the increase of initial pH values, at initial pH 6.0, k_f reached its corresponding maximum value, and $1/n$ value at initial pH 6.0 was smaller than that at other initial pH values. These implied that the affinity between the adsorbent and Pb^{2+} molecules was also higher than other initial pH values. The correlation coefficients (R^2) given in Table 1 also showed that the Langmuir equation gave a better fit than Freundlich equation to the adsorption isotherms.

Table 1. The parameters of Langmuir and Freundlich equation

Initial	Langmuir equation			Freundlich equation		
pH	q_m (mg g^{-1})	b (L mg^{-1})	R^2	$1/n$	K_f	R^2
4.0	10.06	0.1105	0.9992	0.3068	2.5076	0.98321
5.0	12.54	0.1983	0.9988	0.2918	3.7528	0.9623
6.0	13.31	0.6004	0.9991	0.2012	6.2111	0.9877

Kinetic study :

In order to obtain the adsorption kinetic information of Pb^{2+} on the modified wheat bran adsorbent, the change of Pb^{2+} concentration with adsorption time was recorded for an initial concentration of 50, 100 mg/L and a fixed pH solution of 6.0, adsorbent dosage 7.0 g/L (Fig. 6). It could be seen that the adsorption of Pb^{2+} increased rapidly with time as well as with the increase of the initial Pb^{2+} concentrations. However, the time to reach the adsorption equilibrium took longer with an increase in the concentration. The adsorption of Pb^{2+} reached to equilibrium state after about 60 min reaction at initial Pb^{2+} concentration of 50 mg/L. For the initial Pb^{2+} concentration of 100 mg/L, the adsorption time reached to equilibrium state was about 120 min.

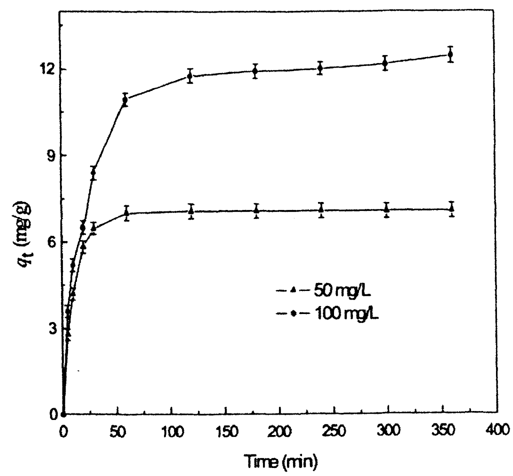

Fig. 6. Adsorption kinetics of Pb^{2+} by modified wheat bran (Experimental conditions employed : pH 6.0, adsorbent dosage 7.0 g/L, agitation speed 150 r/min).

To investigate the mechanism of adsorption, the pseudo-second order rate equation model was applied to experimental data. The pseudo-second order kinetic equation could be derived as[20] :

$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (6)$$

Separating the variables in eq. (6) gave :

$$-d(q_e - q_t)/(q_e - q_t)^2 = k_2 \cdot dt \qquad (7)$$

Integrating both sides for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gave the integrated rate law for a pseudo-second order reaction,

$$1/(q_e - q_t) = 1/q_e + k_2 \cdot t \qquad (8)$$

Eq. (8) could be rearranged to obtain :

$$t/q_t = 1/(k_2 \cdot q_e^{\,2}) + t/q_e \qquad (9)$$

The kinetic constant, k_2, could be determined by plotting of t/q_t against t.

The kinetic experimental data of Pb^{2+} on the modified wheat bran was simulated by pseudo-second order rate eq. (9). The results were listed in Table 2. Remarkably, the kinetic data could be described well by the pseudo-second order rate equation which was based on the assumption that the rate limiting step may be chemical sorption or chemisorptions involving valency forces through sharing or exchange of electron between adsorbent and adsorbate[21]. It could also be seen that the values of the pseudo-second order rate constant decreased with increasing the initial Pb^{2+} concentrations.

Table 2. Kinetic parameters for Pb^{2+} adsorption by modified wheat bran

C_0 (mg L^{-1})	q_e (mg g^{-1})	k_2 (L mg^{-1} min^{-1})	R^2
50	7.21	3.01×10^{-2}	0.9998
100	12.87	5.37×10^{-3}	0.9995

Conclusions

The modification of wheat bran by acetic acid significantly improved its adsorption capacity due to its concentration of carboxylic groups, and made this material a suitable adsorbent to remove Pb^{2+} from synthetic solutions. The adsorption capacity of modified wheat bran for Pb^{2+} is about 1.6 times higher than that of unmodified wheat bran. The amount of Pb^{2+} adsorbed was found to vary with initial solution pH, adsorbent dosage, contact time and initial Pb^{2+} concentration. The overall adsorption rate was illustrated by the pseudo-second order kinetic model. The equilibrium data obtained from this study was well presented by Langmuir model. As wheat bran is readily available in great abundance in China, it can be considered as an attractive alternative to the more expensive technologies used in wastewater treatment containing dye.

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