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Adsorption Isotherm and Kinetics Studies of Chemical Modified Waste Corn Stalk by Urea and Microwave for Removal of Lead(II)

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Corn stalk modified by urea and microwave was investigated as an adsorbent for Pb(II) removal from aqueous solution. The preparing parameters on mass percent gain of modified corn stalk are analyzed using response surface methodology. The effects of pH and modified corn stalk dose on the Pb(II) removal process were studied by batch methods. The maximum adsorption capacity of Pb(II) onto modified corn stalk was found to be 12.78 mg/L. The adsorption isotherms were analyzed using the Langmuir and Freundlich isotherms. The results showed that the adsorption process was well described by Langmuir isotherm model with correlation coefficients (R) of 0.99998 for Pb(II) adsorption. Kinetic studies revealed that the adsorption process followed pseudo second order model.

Keywords: Corn stalk, Modified, Adsorption, Lead.

INTRODUCTION

Water pollutions containing lead, cadmium, mercury and chromium *etc.* are much concern by people because of their toxicity. Heavy metals finally reach in the human body through food chain. Heavy metals can react with various enzymes and proteins in the human body, makes them inactive. They may also be enriched in certain organs of the human body. If the limits of heavy metals amount have beyond the human body can withstand, It may result in acute poisoning and great harm to the human body[1]. Lead poisoning causes damage to reproductive system, the nervous system, kidney and brain. The major sources including mining, metal plating, batteries, paints, petroleum refining, steel and glass industries, *etc.* can cause lead pollution into wastewater. Many technological methods have been used for toxic heavy metal ions removal such as chemical precipitation, ion exchange resin, membrane filtration, activated carbon adsorption, *etc.*[2]. At present the adsorption technique using agro-based waste biosorbents showed an effective removal of the toxic metal ions from water since widely sources from agriculture waste, low cost, easily modified, reusable and have high absorption capacity. The application of biosorption in environmental protection has become an important research area in recent years[3]. Agriculture waste such as rice husk, corn stalk, peanut shell, sugar bagasse and wheat stalk have polymeric groups like cellulose, hemicellulose, lignin, pectin and proteins as active centers for metal uptake. Cellulose contains a lot of hydroxyls groups and can be modified by various chemical methods. The purpose of this study is to modify the corn stalk (CS) by urea and microwave as adsorbent for removal of Pd(II) from aqueous solution. The influences of urea and microwave on modified corn stalk (MCS) preparation and the effect of pH, modified corn stalk dose, contact time, initial metal concentration and temperature on the Pb(II) removal process were studied by using batch methods. The adsorption properties of modified corn stalk were studied. Isotherm models (Freundlich and Langmuir) and kinetic models (pseudo first order and pseudo second order) were employed to describe the experimental data.

EXPERIMENTAL

Raw corn stalk, urea, $CdCl_2$, NaOH, HCl are used in this work.

Preparation of modified corn stalk: The synthesis route used to obtain modified corn stalk is shown in Fig. 1. The corn stalk was washed clean, dried and grinded to powder before preparation, Take corn stalk and urea into a beaker and mix with some distilled water. Then put the beaker in a microwave oven with power at 500-900 w for radiation and reaction. After

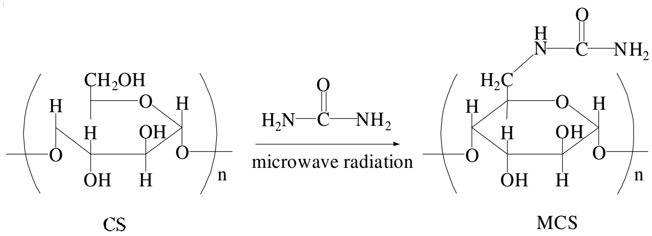

Fig. 1. Synthesis route of modified corn stalk (MCS)

reaction, cooled down to room temperature and washing with water. Then take the product into a blast oven for drying at 60 °C for 12 h, The product was modified corn stalk.

Preparation of the Pb(II) solution: The stock solution containing 1000 mg/L Pb^{2+} was prepared by dissolving $PbCl_2$ in distilled water. Pb^{2+} solutions of different concentrations were prepared for test as required.

Adsorption of Pb(II) ion: Batch adsorption experiments were carried out in 200 mL flasks containing 100 mL of Pb^{2+} solutions. Throughout the experiments, pH varied between 1 to 7, contact time from 20 to 120 min, adsorbent dose from 0.5 to 2.5 g, temperature from 25 to 45 °C and initial metal concentration from 40 to 120 mg/L. The adsorption isotherm experiments were performed at 160 rpm on a shaker with 0.1 g of adsorbent in flasks containing $PbCl_2$ solution at various concentrations and at the adsorption kinetic experiments were performed at an initial concentration of 100 mg/L Pb^{2+} solution at 298 K. The Pb^{2+} concentrations in the filtrate was determined by flame atomic absorption spectroscopy.

Data evaluation: Mass percent gain (mpg) of modified corn stalk after preparation process was calculated according to eqn. 1, The amount of adsorbate adsorbed at time *t* (q_t, mg/g) and the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (q_e, mg/g) were calculated from eqns. 2 and 3. The removal efficiency (R, %) were calculated according to the eqn. 4:

$$mpg(\%) = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

where m_1 and m_0 are masses of materials after and before the modification,respectively.

$$q_t\,(mg/g) = \frac{C_0 - C_t}{m} \times V \quad (2)$$

$$q_e\,(mg/g) = \frac{C_0 - C_e}{m} \times V \quad (3)$$

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (4)$$

where C_0 and C_e (mg/L) are the initial and the equilibrium concentrations of Pb^{2+} in flasks. C_t is the concentrations of Pb^{2+} in flasks at time *t*. V is the volume of the solution (L) and m is the mass of adsorbent used (g).

Equilibrium adsorption isotherms

Freundlich isotherm model: The linearized form of Freundlich isotherm model[4]. is given as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (5)$$

where K_F and n are Freundlich constants representing the adsorption capacity and intensity of adsorption. The adsorption capacity (K_F) and the adsorption intensity (1/n) are directly obtained from the slope and the intercept of the linear plot of log q_e *versus* log C_e.

Langmuir isotherm model: The linearized form of Langmuir Isotherm Model[5]. is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (6)$$

where q_{max} is the maximum adsorption capacity and b is the equilibrium Langmuir constant related to adsorption energy. A dimensionless constant called separation factor (R_L) describing the essential characteristics of the Langmuir isotherm is calculated using the formula:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where C_0 is the initial concentration of Pb^{2+}. The R_L value indicates the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

Adsorption kinetics models: In order to present the kinetic model describing adsorption of Pb^{2+} on modified corn stalk. The pseudo-first-order and pseudo-second-order models were used to test the absorption data. The linear form of the first-order rate equation and the second-order rate equation are expressed by eqns. 8 and 9, respectively[6]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

where k_t is the rate constant (min^{-1}) of the adsorption.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where k_2 (g/mg min) is the rate constant of the pseudo-second-order sorption.

RESULTS AND DISCUSSION

Optimization of preparation: The effect of the urea concentration (10-40 g/L), Microwave power (500-900 w) and reaction time (30-120 min) on the preparation of modified corn stalk adsorbent were investigated through response surface methodology (Box-Behnken Design) by Design-Expert software. The results is shown in Figs. 2 and 3. The results suggested that the mpg was maximum (21.41 %) when the Urea concentration was 25 g/L, the microwave power was 700 w and the reaction time was 75 min.

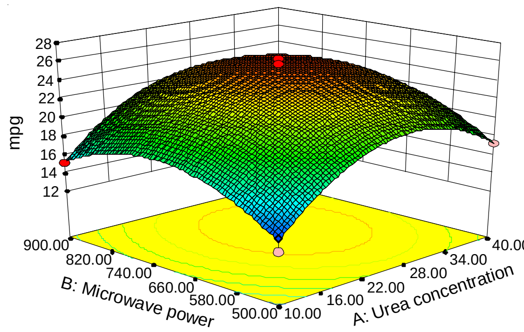

Fig. 2. Effect of microwave power and urea concentration on mass percent gain

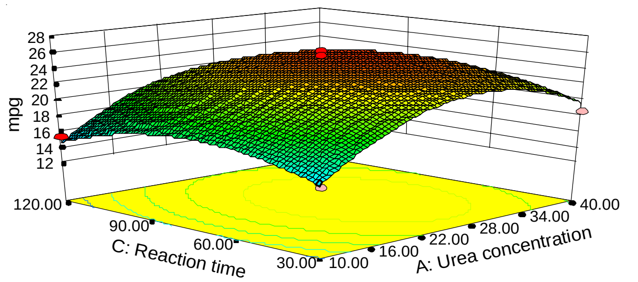

Fig. 3. Effect of reaction time and urea concentration on mass percent gain

Effect of pH: pH has been identified as the most important factor affecting metal adsorption onto the adsorbent. This may be because of the fact that H^+ themselves are strongly competing with the adsorbate. H^+ competes with metal cations for the available adsorption site whereas activate at higher pH value. When Pb^{2+} aqueous solution concentration was at 100 mg L^{-1} and volume was 100 mL, contact time was 100 min, The effect of pH on adsorption capacities was investigated in the range 1-7. The results suggested that when pH of aqueous solution was at 4, The removal capacity was maximum.

Effect of modified corn stalk dose: The removal efficiency and adsorption capacity of modified corn stalk adsorbent for Pb^{2+} was studied by changing the dose of adsorbent from 2 to 16 g/L while the concentration of Pb^{2+} was 100 mg/L and the volume was 100 mL without change. The results show that the removal efficiency of modified corn stalk increase with increasing of the amount of adsorbent at first. And when the dose of adsorbent was 10 g/L, the removal efficiency was maximum, it was 90.21 % and the experimental equilibrium adsorption capacity was 11.37 mg/g.

Adsorption isotherms: Freundlich isotherm for Pb(II) adsorption is shown in Fig. 4 and the related parameters of the isotherm are given in Table-1. Langmuir isotherm for Pb(II) adsorption is shown in Fig. 5 and the related parameters of the isotherm are given in Table-1.

By comparing the correlation coefficients (R), it can be concluded that Langmuir isotherm provides a good model for the sorption system, which describes a monolayer adsorption onto the surface of the adsorbent with finite number of identical sorption sites[7]. The maximum adsorption capacity of Pb found was 12.78 mg/g, the value of the dimensionless parameter R_L (0.33) indicates that the adsorption is favorable ($0 < R_L < 1$).

Adsorption kinetics: The adsorption kinetic data of Pb(II) are analyzed using the pseudo-first-order model and pseudo-second-order equation, as shown in Figs. 6 and 7. The kinetic parameters are given in Table-2. It was found that the calculated

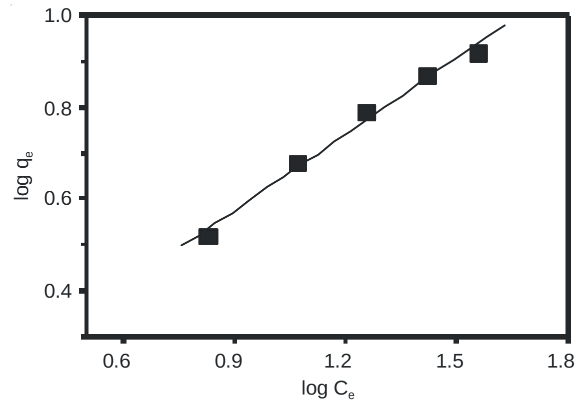

Fig. 4. Fitting of adsorption data with Freundlich isotherm (plot of log q_e *versus* log C_e)

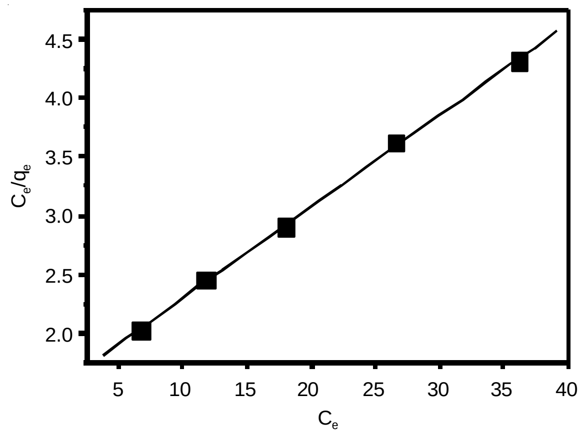

Fig. 5. Fitting of adsorption data with Langmuir isotherm (plot of C_e/q_e *versus* C_e)

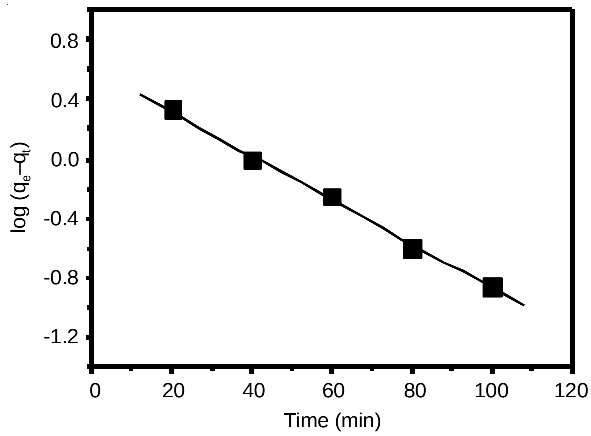

Fig. 6. Pseudo-first-order kinetic plot for Pb(II) adsorption

TABLE-1
PARAMETERS OF ADSORPTION ISOTHERM MODELS

Freundlich isotherm			Langmuir isotherm			
n	K_F	R	q_{max}(m/g)	R_L	b	R
1.19	1.81	0.9947	12.78	0.33	0.052	0.9997

TABLE-2
PARAMETERS OF ADSORPTION KINETIC MODELS

Pseudo-first-order				Pseudo second order			
K_1	R	q_e(cal.)	q_e(exp.)	K_2	R	q_e(cal.)	q_e(exp.)
0.034	0.99839	4.117	9.500	0.014	0.99998	10.06	9.500

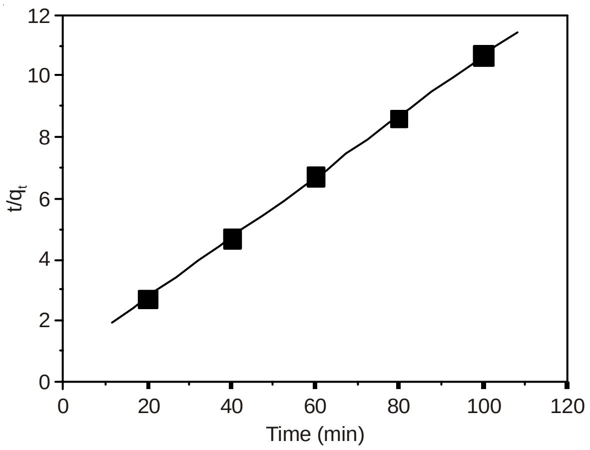

Fig. 7. Pseudo second order kinetic plot for Pb(II) adsorption

values q_e (cal) of pseudo-second-order kinetic model was more agree with the experimental values of q_e (exp), and The values of correlation coefficient (R) for the second-order kinetics model obtained were above 0.9999. The results indicated that the modified corn stalk adsorption process was more appropriately described by the pseudo-second-order kinetic model. This confirms that the chemisorption is the rate determining step[8]

Comparison studies: The adsorption capacity of modified corn stalk and corn stalk adsorbent for removal of Pd(II) ion from aqueous solutions was investigated in this study with a fixed condition (1 g adsorbent for 100 mL of 100 mg/L Pb(II) ion solution at room temperature with pH of 4 and contact time of 100 min). The results suggested that the maximum adsorption capacity of raw corn stalk increased from 6.53 to 11.37 mg/g after modification.

Conclusion

From the present work, it can be concluded that modified corn stalk adsorbent has a good adsorption capacity for Pb^{2+} from aqueous solutions. The removal efficiency of Pb^{2+} was more than 90 % and the max equilibrium adsorption capacity was 12.78 mg/g, compared with the similar adsorbent[9], the adsorption capacity was improved obviously. The obtained results showed that the Langmuir isotherm model is the best fitting model with the experimental data with high R value. Kinetic study showed that the adsorption process of metal ions can be explained with pseudo-second order model.

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