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Evaluation of Chemical Modified Sugarcane Bagasse for Cadmium Removal in Aqueous Environment

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Abstract. This study evaluated the adsorption capacity of chemically modified sugarcane bagasse with citric acid (CAS), sodium hydroxide (SHS) and peroxide hydroxide (PHS) for cadmium ion adsorption in aqueous environment. The sugarcane bagasse (NS) and activated sugarcane bagasse are characterized using scanning electron microscopy (SEM) and IR analysis. The surface area analyzed by SEM indicated that the pores of the adsorbents were relatively high, with well-developed pores. The removal of Cd (II) from aqueous solution using the modified sugarcane bagasse is studied in batch experiments, the influences of time, pH and adsorption isotherms were investigated. The results showed that the adsorption fits well with Langmuir isotherm model and the maximum adsorption capacities were 80.3 mg/g for SHS and 90.9 mg/g for CAS and PHS at optimum pH 6.5 and 60 minutes equilibrium time.

Keywords: cadmium removal, cellulosic materials, and adsorption

1. Introduction

The removal of cadmium, Cd (II) ions has become a matter of great concern from both environmental and economical perspective due to its highly toxic impacts on humans, animals, and plants. This metal is serious hazardous because of its non-degradable characteristics and therefore persistent. The major sources of cadmium are products of industries such as metal plating, cadmium-nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, metallurgy, ceramics, photograph, textile printing, lead mining, sewage sludge, alkaline batteries, and electroplating [1].

Agricultural waste materials are now becoming viable alternatives since they are abundantly available, much cheaper and have various functional groups such as carboxylic acid, ester, carboxylate, hydroxyl, phenolic and amino groups that can act as adsorption sites for heavy metal ions [2]. In general, chemically modified plant wastes exhibit higher adsorption capacities than unmodified equivalents. Many methods to modified cellulose extracted from sugarcane bagasse were studied, such as using acids or base to change surface of cellulose, using several agent such as hydrogen peroxide, EDTA to oxidize cellulose, using organic acid to change functional groups in biological polymers, from hydroxyls to esters, or acid [2]. The aim of this work was to compare the performance of sugarcane bagasse (SB) as an alternative material for Cd (II) removal from aqueous solutions by using chemical treatments with sodium hydroxide (SHS), citric acid (CAS) and hydroxide peroxide (HPS).

2. Materials and Methods

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2.1. Materials

Sugarcane bagasse (SB) was first washed with distilled water several time to remove the dust particles and then dried at 105oC for 24 hours. The material was ground to smaller particles and sieved to desired particle size no larger than 0.5mm-2mm. Then, sugarcane bagasse was washed with distilled water, and dried at 105 ℃ taken within 24 hours before chemical modification.

SB were treated by alkali (NaOH), citric acid ($C_6H_8O_7$), hydroxide peroxide (H_2O_2) in stirring 30 minutes – 2 hours at a speed of 150rpm with alkali and citric acid; and boiling for 2 hours at 85 ℃ with hydroxide peroxide. The treated SBs was washed by distilled water to remove excess soluble substances until neutrality and then dried at 80 ℃ within 24 hours before used as adsorbent.

2.2. Methods

Microstructure and surface morphology of the adsorbent samples were characterized by a 10 kV HITACHI S-4800 NIHE scanning electron microscope (SEM).

Adsorption studies were mainly carried out by batch technique at temperature room to obtain rate and equilibrium data. The batch studies were conducted by mixing 0.1 g of adsorbent with 50 ml of solution of varying Cd (II) concentration range 10, 50, 100, 200, 300, 400 or 500 mg/L. The initial pH value of the solutions was adjusted with either HCl or NaOH solutions the concentrations of which are 0.02N to determine the optimum pH for optimum adsorption. The samples were shaken at 150 rpm at varying time intervals (10, 30, 60, 90, 120, 150 and 180) minutes to determine the equilibrium time. At the end of the contact time, the mixture was then centrifuged for 10 min at 5000 rpm.

3. Results and Discussion

3.1 Characterization Studies

Fig. 1 shows the surface morphology of sugarcane bagasse before and after modification. There are significant changes to the surface morphology of the adsorbents. SB had a smooth and less porous structure texture. While SHS, CAS and HPS had high well-developed pores in surface and appeared many small pieces in the adsorbent surface which shows a potential possibility for Cd (II) to be adsorbed [3].

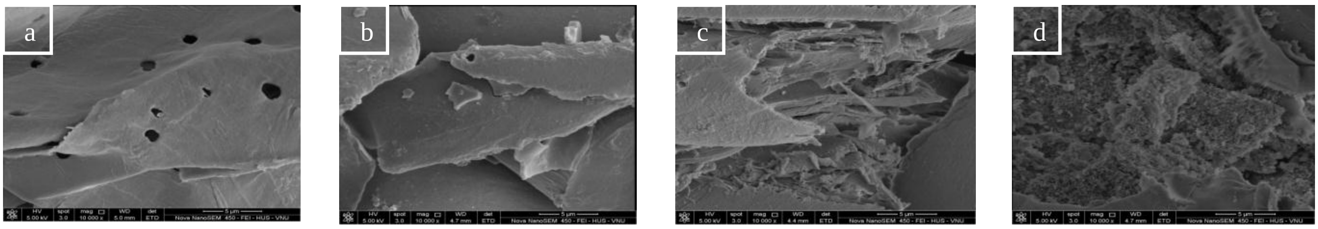

Fig. 1: The SEM images of adsorbents: (a) SB – Original sugarcane bagasse; (b) SHS – Sugar cane bagasse treated by alkali, (c) CAS - Sugar cane bagasse treated by citric acid and (d) HPS - Sugar cane bagasse treated by hydroxide peroxide

3.2 Effect of Contact Time

The effect of time on the removal of cadmium was investigated at different types of chemical modified sugarcane bagasse, at initial concentration of 100 mg/L, and at optimum pH values of 6.5. The removal of Cd (II) versus time was illustrated in Fig. 2. The amount of the adsorbed cadmium onto CAS and HPS increases with time and at some point in time after 60 minutes, reached a constant value. Hence, the equilibrium time of cadmium removal by CAS and HPS is 60 minutes. However, for SHS, the amount of Cd (II) adsorbed after 60 minutes was changed slightly, it may be due to blinding forces between SHS and Cd (II) are weak which proved that the adsorption system between CAS and HPS with Cd (II) is better than SHS.

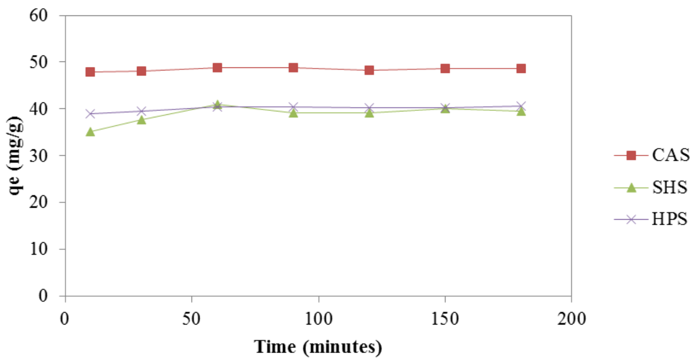

Fig. 2: Effect of time on cadmium uptake by modified sugarcane bagasse, q_e - The cadmium concentration retained in the adsorbent phase, SB – Original sugarcane bagasse; SHS – Sugar cane bagasse treated by alkali, CAS - Sugar cane bagasse treated by citric acid and HPS - Sugar cane bagasse treated by hydroxide peroxide

3.3 Effect of Initial Concentration

The effects of initial metal concentration on the adsorption of Cd (II) ions onto adsorbents are shown in Fig. 3. The selected adsorbents were used at initial concentration ranging from 10 to 500 mg/L in a batch adsorption technique. From Fig. 3, the amount of metal ion adsorbed by SHS, CAS and HPS increased with increasing initial metal concentration. For example, when the concentration of Cd (II) increased from 0 to 400 mg/l, the amount of Cd (II) adsorbed onto SHS, CAS and HPS increased from 4.19 to 70 mg/g, from 4.95 to 85.25 mg/g and 4.94 to 78 mg/g, respectively. However, when Cd (II) initial concentration was increased from 300 to 500 mg/l, the amount Cd (II) adsorbed was unchanged because higher energy sites of adsorbents were saturated. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in adsorption capacity almost unchanged after energy site are saturated [4].

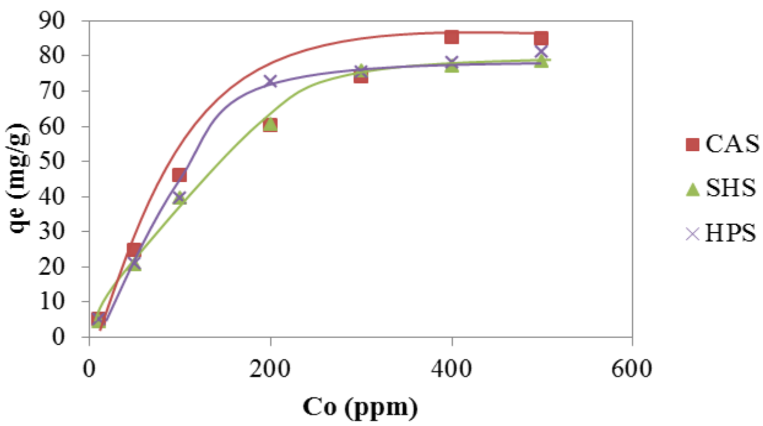

Fig. 3: Effect of initial concentration on cadmium uptake by modified sugarcane bagasse, q_e - The cadmium concentration retained in the adsorbent phase, C_o - the cadmium concentration measured before adsorption, SB – Original sugarcane bagasse; SHS – Sugar cane bagasse treated by alkali, CAS - Sugar cane bagasse treated by citric acid and HPS - Sugar cane bagasse treated by hydroxide peroxide

3.4 Adsorption Isotherms

Adsorption isotherm models have been used to describe the distribution of metal ions between the solid phase (adsorbent) and liquid phase (solution) when equilibrium was reached. The Freundlich and Langmuir isotherm models have been widely used to describe the interaction between metal ions in solution and adsorbents. The Langmuir isotherm is assumed the sorption process at specific homogeneous sites for monolayer adsorption. The Langmuir isotherm [5], [6] can be expresses in the Eq. 1 is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \tag{1}$$

where C_e (mg/L) is the equilibrium concentration; q_e (mg/g) the amount of cadmium adsorbed at equilibrium, q_m (mg/g) the adsorption for a complete monolayer; K_a (L/mg) is the adsorption equilibrium constant. When C_e/q_e is plotted against C_e and the data are regressed linearly, q_m and K_a constants are calculated from the slope and the intercept. The linear form of the Freundlich isotherm [7], [8] is given by Eq. 2:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \qquad (2)$$

The constant K_F (mg/g) is related to the adsorption capacity of adsorbents; 1/n is related to the surface heterogeneity. When log q_e is plotted against log C_e and the data are analyzed by linear regression, 1/n and K_F can be determined from the slope and intercept [8].

The Langmuir and Freundlich isotherms were plotted as a function of different types of sugarcane bagasse (in Fig. 4, Fig. 5) and the value of isotherm constants and correlation coefficients were calculated for both isotherm models (in Table 1) by using the data obtained from these figures. The correlation coefficient of four types of chemical modified sugarcane bagasse always above 0.98 showed that the Langmuir model fitted the results better than the Freundlich model (R^2 about 0.88) for both phases. The maximum adsorption capacities (q_m) estimated from the Langmuir isotherm model of adsorbents are found in ranged 83.33 to 90.9 mg/g. Comparing the Cd (II) removal efficiency of the chemical modified sugarcane bagasse, the following order: SHS<CAS<HPS was given. This might be due to compatibility of size between the Cd (II) molecules and the pores of the SHS [9], [10].

Table 1: Parameters of the Freundlich and Langmuir adsorption isotherm for adsorption materials

Adsorbents	Langmuir			Freundlich		
	q_m(mg/g)	b(L/mg)	R^2	K_F(mg/g)	n	R^2
SHS	83.33	0.03834	0.991	5.30115	1.96464	0.894
CAS	90.9	0.08594	0.99	16.7936	3.25733	0.899
HPS	90.9	0.06145	0.99	12.9747	2.93255	0.854

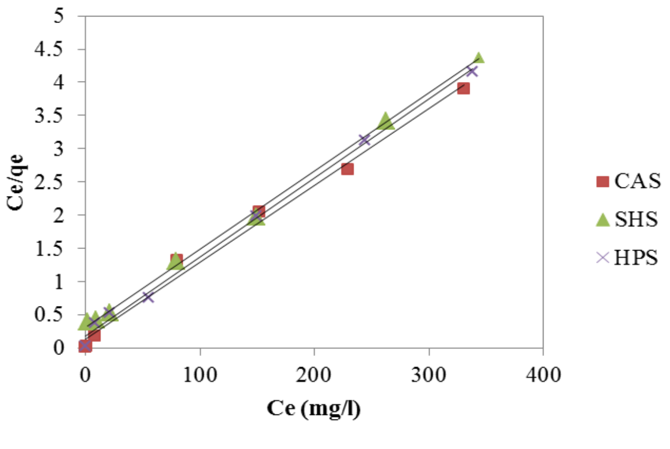

Fig. 4: The Langmuir linear for adsorbents, SB – Original sugarcane bagasse; SHS – Sugar cane bagasse treated by alkali, CAS - Sugar cane bagasse treated by citric acid and HPS - Sugar cane bagasse treated by hydroxide peroxide

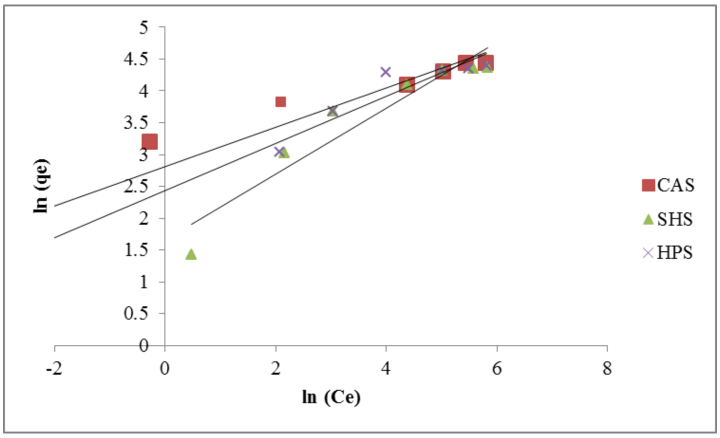

Fig. 5: The Freundlich linear for adsorbents, SB – Original sugarcane bagasse; SHS – Sugar cane bagasse treated by alkali, CAS - Sugar cane bagasse treated by citric acid and HPS - Sugar cane bagasse treated by hydroxide peroxide

4. Conclusion

Chemical modified sugarcane bagasse was explored as adsorbents for cadmium removal. The surface area of the pores of the adsorbents was relatively high, with well-developed pores. The adsorption properties of adsorbents depended on pH values and optimum pH is 6.5 for the cadmium removal. The equilibrium data were fitted to Langmuir isotherms. The SB modified with citric acid and peroxide hydroxide showed the greatest adsorption capacity of 90.9 mg/g at pH 6.5 while SHS presented 83.33 mg/g at the same conditions.

5. Acknowledgements

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