Sugar Industry Waste as Removal of Toxic Metals from Waste Water

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Abstract Toxics metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters. Various methods available in literature but due economical point view are facing difficulties to be adopted. Some alternative methods like adsorption material bagasse, rice husk, wheat husk sawdust etc, are more popular due to efficiency as well as cost of treatment. In present study bagasse from sugarcane industry were used to remove the toxic metal from waste. Batch studies were performed to evaluate the adsorption process, and it was found that the bagasse was found to adsorb 96.4% of Cadmium (II) and 93.8% of iron (II). The rate of adsorption follows pseudo-second-order kinetics before attaining equilibrium. The desorption studies suggested that the desorption of Cadmium (II) and iron (II) was the most difficult and the desorption was zero. This work proved that bagasse can be used as an efficient adsorbent material for removal of heavy metals from water and wastewater.

Keywords: adsorption, isotherm, pH, sugarcane bagasse

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1. Introduction

In recent years the presence and removal of toxic and polluting heavy metals in wastewaters from industrial effluents, water supplies and mine waters have received much attention. It has been established that a serious health hazard result from dissolved heavy metals escaping into the environment. They tend to accumulate throughout the food chain in living tissues, multiplying their effects [1]. Thus, it is necessary to eliminate heavy metals from water and wastewater to protect public health. Different methods have been used to remove heavy metals from wastewater such as chemical precipitation, ion exchange, membrane separation, and adsorption. Among them, adsorption was found to be the most commonly used method for eliminating these contaminants, especially at low concentrations. Different adsorbents have been developed from available natural materials and used for heavy metals removal such as activated carbon [2], pine bark [3], charcoal [4] Banana Peel [5], tar sands [6], modified rice husk [7,8], zeolites [9] and moss peat [10]. Low-cost agricultural by products, such as almond shells, olive stones and peach stones was used for the removal of Zn^{2+} , Cd^{2+} and Cu^{2+} [11]. After canning process generally bagasse are used for energy generations in power plant. The ash remain are dumped in open area, which create an environment problem. In this regard's an effort has been made to utilize the waste in proper way and reduced the toxic metal with low cost adsorption.

2. Materials and Methods

2.1. Adsorbent

The raw material used in this work as an adsorbent was the sugar industrial wastes (bagasse wastes). This waste is obtained from food canning processes. Bagasse wastes were dried in an electrical oven at 60° C for 24 hours. Dried bagasse was milled to powder form in an electrical mixer. It was then sieved into particle sizes 0.5 - 4 mm. The infrared (I. R.) absorption spectrum apparatus was used to investigate the chemical structure of bagasse.

2.1.1 Infrared Spectra of the Bagasse Waste

Infrared spectra (IR) of bagasse were obtained using a Perkin-Elmer 621 spectrophotometer. The infrared spectrum of the solid substance has been recorded on in the region 400–4000 cm⁻¹ using KBr and nujol mull techniques. The observed frequencies have been assigned in terms of the fundamentals, overtones and combinations assuming D 2h point-group symmetry.

2.1.2 Chemical Analysis

The chemical analysis of bagasse waste was measured to detect its main contents using high-performance liquid chromatography (HPLC). A Shimadzu LC-6A highperformance liquid chromatography equipped with a Rheodyne Model 7125 injector and a Hitachi Model F-1050 fluorescence spectrophotometer was used. Also, Qualitative and Quantitative carbohydrate analysis of bagasse waste was measured using (HPLC).

2.2. Adsorption Process

The sorption of cadmium (II) and iron(II) ions has been studied by batch experiments. Solutions of Cd^{2+} ions (20 mg/L) and Fe²⁺ ions (20 mg/L) were prepared from 1 g/L stock solution of each salt using distilled water, respectively. When the solution volume for both cations was fixed at 100 mL, the adsorption percentage of Cd (II) and Fe (II) ions as a function of shaking time was investigated at a shaking speed of (220 ± 5) min⁻¹. After the filtration, the concentrations of Cd²⁺ and Fe²⁺ ions in filtrate water were determined by high-performance liquid chromatography-hydride generation atomic absorption spectrophotometric (HPLC-HGAAS). The adsorption percentage is determined as

$$\eta = 100 \times C_0 - C_e / C_0 \tag{1}$$

where η is the adsorption percentage of cations C_0 and C_e are the initial and the equilibrium concentrations of cations, respectively, mol/l. All experiments were carried out in triplicate and the average adsorption is reported here.

2.3 Desorption Study

Desorption experiments of the investigated metals was carried out on loaded bagasse waste adsorbent resulting from the equilibrium sorption experiments. Desorption process was studied taking into consideration the effect of unabsorbed solution remaining incorporated within the natural material sample. This solution can't be completely withdrawn, where 1 ml of clear supernatant was left in the bottle together with solid phase 9 ml of desorbed solution was added and the closed poly ethylene bottles where shaken for the descried time. The bottle was centrifuged for 15 min. and desorption was evaluated using the following formula:

$$\mathbf{D}\% = \left\{ \left(\mathbf{C_a} - \mathbf{X} \ \mathbf{C_e} \right) / \left(\mathbf{C_o} - \mathbf{C_e} \right) \right\} \ \mathbf{100}$$
(2)

Where C_a: the activity of desoprtion solution X: is the volume fraction left initially with natural material sample.

3. Results and Discussions

3.1. Infrared Analysis

The amount of information that can be obtained from the IR spectrum of bagasse is rather limited. The spectra are reported principally for any future identification, since the absorption bands for such complex compounds are usually broad and diffuse [1]. It was observed from the Figure 1 that chemical groups corresponding the wave number of bonds cm⁻¹ Apart from the usual bands for hydroxyl (3500 cm⁻¹) and ester carbonyl (1730 cm⁻¹) groups, Nitrogen of protein (1550 cm^{-I}), amide deformation (1630 cm^{-I}) and ether group (1220 cm^{-I}) can be distinguished. The bagasse was has a high. percentage of [O" H], [C=O"], [N"], [C-"O"- C] and [C=C]. Lone pair of electrons (..) that exist at oxygen and nitrogen atom represent a high negative charge. Hence, bagasses become highly negatively charged and capable to absorb the positively charged metals of cadmium (II) iron (II) and zinc (II).



Figure 1. FTIR study of sugarcane bagasse

3.2. Chemical Analysis

The results of the chemical analysis of bagasse waste are useful in giving a hint of relative proportions of the different components. The contents of cellulose , protein and minerals are given in Table 1 for the bagasse waste. So, the main constituent of bagasse are α - cellulose and protein. This could indicate a high adsorption capacity of bagasse waste which referred to the –ve N and O of α -cellulose and protein that absorb +ve metal.

Table 1. Chemical Characteristics of the investigated Bagasse waste

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S. No	Characteristic	Percentage
1	α- cellulose	56.54 %
2	Protein	15.47 %
3	Liginin	10.75 %
4	Ash	4.87%
5	Magnesium	0.08 %
6	Calcium	1.40 %
7	Potassium	0.07 %
8	Phosphorus	2.86 %

3.4. Adsorption Process

The adsorption of investigated metals by bagasse could be attributed to the cellulose, protein, lignin and sugars component of the bagasse waste where site- binding adsorption might be occurring. This could be due to the surface complexation phenomenon of functional groups present in the bagasse Figure 1. The removal of Cd (II) and Fe(II) ions, therefore is probably due to the mixed effect of ion exchange and surface complexation on the surface of bagasse. The effects of shaking time on the adsorption Cd^{2+} and $Fe2^{+}$ ions are shown in Figure 2, which indicates that the removal of cation by bagasse waste is improved with increasing shaking time. The adsorption reaches equilibrium at about 90 minutes on bagasse waste and the maximum adsorption percentage is 96.4% and 93.8% for Cd (II) and Fe (II) respectively. These preliminary experiments for adsorption of metal ions on the bagasse showed a high relatively ion exchange capacity. This is due to the fact that bagasse was had a high sugar, cellulose, lignin and protein contents, (containing higher percentage of N, P and O). Hence, bagasse becomes highly negatively charged to absorb the positively charged metals.

3.5. Adsorption Kinetics

According to Figure 2, the adsorption rate of Cd^{2+} and Fe^{2+} ions increases sharply in 60 min., and then reaches

equilibrium gradually at about 90 min. Quantifying the changes in sorption with time requires that an appropriate kinetic model is used and, traditionally, The pseudo-first order equation [2,3], is generally expressed as eqn 3and 4:

$$\mathbf{dq}_{\mathbf{e}} / \mathbf{d}_{\mathbf{t}} = \mathbf{k} \left(\mathbf{q}_{\mathbf{e}} - \mathbf{q}_{\mathbf{t}} \right) \tag{3}$$

Where:

 q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mgg¹). K_{ad} is the rate constant of pseudo-first-order adsorption (min⁻¹). After integration and applying boundary conditions t = 0 to t = t and $q_t = 0$ to qt = qt, the integrated form of equation (3) becomes:

$$\log(\mathbf{q}_{\mathbf{e}} - \mathbf{q}_{\mathbf{f}}) = \log(\mathbf{q}_{\mathbf{e}}) - \mathbf{t} \mathbf{x} \mathbf{K}_{\mathbf{ad}} / 2.303 \tag{4}$$

A plot of $log(q_e-q_l)$ vs. time should give a straight line to confirm the applicability of the kinetic model, and a derivation of the constant. Figure 3 (a) shows a plot of log(qe - qt) vs. t for the 5 mg/\ell metal adsorption on bagasse. The value of K_{ad} for the adsorption of the various metal onto bagasse was found to be 0.0056/h and 0.0043/h for Cd^{2+} , and Fe^{2+} .



Figure 2. Effect of shaking time on adsorption of cadmium and iron ions



Figure 3. (a): Effect of time on Adsorption kinetic. (b): Second order kinetic adsorption of Cadmium and iron by bagasse

Recently, a pseudo-second-order equation has been suggested as being more appropriate for describing this type of adsorption [4]:

$$t/qt = 1/2k qe^{2} + t/qe$$
 (5)

In this equation, the initial rate of adsorption, h, is given by:

$$\mathbf{h} = 2\mathbf{k} \, \mathbf{q_e}^2 \tag{6}$$

The data for both metals at concentrations of 5 mg/l were, therefore, tested against both models. The results showed that the second-order equation was the more appropriate and it was, therefore, used to analyze the data for all the sorption/time trials, which is shown Figure 3(b).

3.6. Desorption

Desorption experiments of $Cd2^+$, and $Fe2^+$ from the loaded bagasse was investigated. It is understood in these experiments, that the sorption of the respective compounds is supposed to take place mainly by electrostatic attraction between the bagasse surface as a negative charges and the metal ions as a positive charges. The percent desorption for metal ion from bagasse was very low and can be equal to zero.

4. Conclusion

The results clearly show that the low cost adsorbent (bagasse) is a better adsorbent for Cd^{2+} and Fe^{2+} . The most explanation of the highly sorption capacity of bagasse is that the negative charge of bagasse that make it capable to absorb the positively charged metals of for Cd^{2+} and Fe^{2+} . From the kinetic model analysis using coefficient of determination, the pseudo-second order model was the most fitting for the description of Cd^{2+} and Fe^{2+} transport from the bulk solution onto the surface of bagasse adsorbents.

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