Biosorption Of Cu (II) Ions Onto Base Treated
Sugarcane Bagasse

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ABSTRACT

The adsorption of Cu (II) ions from aqueous solutions using agricultural waste particularly sugarcane bagasse that have been treated with base or Chemically Treated Sugarcane Bagasse (CTSB) was performed under batch mode. Batch experiments were conducted to determine the factors affecting adsorption such as pH, initial heavy metal concentration and contact time. The batch experiment showed that pH 3-5 was the best range for the sorption of copper ions. Adsorption was fast as equilibrium was achieved within 60 minutes, and was best described by the pseudo-second order model. According to the Langmuir model, the maximum adsorption capacity of Cu (II) ions was 23.81 mg g^{-1}. The highest amount of heavy metal adsorbed occurred at pH 5 with shaking speed of 120 rpm. This study showed that CTSB can be used as good adsorbent materials for Cu (II) removal from aqueous solution.

Keywords: *Adsorption, heavy metal, sugarcane bagasse.*

Introduction

Water pollution is one of the most serious environmental problems facing modern society (Baird, 1995). The discharge of heavy metals into aquatic ecosystems is the major reason behind this occurrence and has been and still is,a focus of attention all over the world. Overall, these pollutants are introduced into the aquatic systems significantly as a result of various industrial operations; electroplating and metal finishing industries, metallurgical industries , chemical manufacturing, pigment manufacturing, fertilizer industries, battery manufacturing and tannery operations.

Copper is one of the most hazardous heavy metals and has been the world concern over a few decades due to its toxicity. Copper is constantly released into our environment (soils, rivers, lakes, and sea), causing serious environmental concerns and creating a big challenge in wastewater management. Since copper is non-biodegradable and thus persistent, it tends to accumulate to toxic levels and causes ecological damage as well as potential threat to humans. In practice, it has been found that copper consumption at high doses will be deposited in the brain, skin, liver, pancreas, and myocardium (Davis et al., 2000) which eventually leads to intestinal distress, kidney damage and anemia (Al-Rub et al., 2006). Therefore, it is mandatory that copper is removed from effluent to prevent it from reaching the waters.

Over the few decades, several methods have been devised to remove heavy metals from wastewater including ion-exchange, chemical precipitation, oxidation-reduction, reverse osmosis, membrane separation, coagulation and solvent extraction. However, in certain circumstances, these methods did not show significant effectiveness and economic advantages. Adsorption processes using agricultural waste products are becoming the trend in today's wastewater treatment because they are cheap, simple, sludge free and involve small initial cost and land investment. One of the most preferred industrial solid wastes is the waste from agricultural industry or biomass such as coconut husk, sugarcane bagasse, oil-palm trunk and etc. These plant wastes are preferred as they are highly abundant, low-cost and have various functional groups that can bind heavy metal. This type of adsorption is called biosorption.

Sugarcane bagasse is the residue from sugarcane milling that consists of the crushed stalks from which the juice has been expressed; it consists of 50% cellulose, 25% hemicelluloses and 25% lignin. For each 10 tonnes of sugarcane crushed, a sugar factory produces nearly 3 tonnes of wet bagasse. Since the bagasse is the byproduct of the sugarcane industry, the quantity of production in each country is in line with the quantity of sugarcane produced. The content of the sugarcane bagasse and the availability to get the bagasse in large amount make it a suitable adsorbent to be used in this experiment.

In addition, modification can be done to optimize the adsorption capacity of a bioadsorbent. According to Gaballah et al. (1998), treatment of lignocellulosic waste materials can extract soluble organic compounds such as lignin and hemicellulose and enhance chelating efficiency; hence higher amount of adsorbates can be achieved. Chemical treatment also results in reduction of cellulose crystallinity and an increase in surface area of an adsorbent. Amongst the numerous kinds of treatment methods, base compound treatment is chosen as the method of choice. This type of treatment has been recorded by Kumar and Bandhyopadhyay (2006) and it was found that the uptake of cadmium on rice husk increased significantly.

Objectives

Overall, the main objectives of this study were to prepare and to understand the mechanism of copper ions removal onto sodium hydroxide treated sugarcane bagasse powder. The effects of several important physicochemical parameters which can affect copper adsorption such as pH, contact time and heavy metal concentration were discussed. The mechanisms of adsorption were identified by spectroscopic and quantitative analyses.

Experimental

Adsorbent preparation

Sugarcane bagasse was obtained from a night market near Universiti Teknologi MARA Pahang, Jengka, Malaysia. The leaves were washed several times with distilled water, and then dried in an oven overnight at 80°C. The dried brownish bagasse were cut into small pieces, grounded and sieved to obtain the average particle size of 180-355 μm.
Base treatment

16 g of dried sugarcane bagasse powder were mixed with 240 mL (0.5 M) NaOH solution, stirred at 500 rpm for 90 minutes, filtered and washed extensively with distilled water until no further change in pH of the effluent was observed. The sodium hydroxide treated sugarcane bagasse powder (hereafter called CSTB) was dried again in an oven overnight at 80°C.

Preparation of lead solution

The stock solution of 10000 mg L^{-1} Copper nitrate was purchased from Merck, Germany. All other chemicals were analytical reagent grade. The stock solution was further diluted with distilled water to obtain the required concentration for adsorption experiment. The pH of the copper solution was adjusted by adding drops of 0.1 M NaOH and HCl solution.

Adsorption Studies

Adsorption was carried out in a batch system in which pre-weighed CTSB was mixed with copper solution at a certain period of time. All experiments were conducted in duplicates and the results were reported as average.

The amount of Cu (II) ions adsorbed, q_e (mg g^{-1}) was computed by using the following expression:

$$q_e = \frac{C_o - C_e}{m} V$$

where C_o and C_e are copper of nickel concentrations (mg L^{-1}) before and after adsorption, respectively; V is the volume of heavy metal solution (L) and m is the weight of the adsorbent (g). The percentage of removal of heavy metal ions was calculated by the following equation:

$$removal(\%) = \frac{C_o - C_e}{C_o} 100$$

The effect of pH on the adsorption of copper and nickel ions was investigated at pH ranging from 1 to 5. The initial pH of the solutions was adjusted by adding drops of 0.10 M NaOH or HCl solution. A weight of 0.10 g CTSB was mixed with 50 mL (10 mg L^{-1}) copper solution in different conical flasks (100 mL). The mixtures were shaken at 120 rpm at room temperature for 90 minutes. The samples were filtered and the amount of copper ions in the filters was analyzed by using AAS.

Contact time is an important parameter which can give information on the adsorption equilibrium time for evaluating various kinetic models. A weight of 0.10 g CTSB was mixed with 50 mL (5, 19, and 20 mg L^{-1}) copper solution in 100 mL conical flasks. The initial pH was fixed at 5 by adding drops of 0.10 M NaOH or HCl solution. The mixtures were shaken at 120 rpm at room temperature and at different time intervals (0 to 90 minutes). After adsorption, the mixtures were filtered. The filtrates were analyzed for copper ions by using AAS.

Results and Discussion

Effect of pH

It is well known that pH plays an important role in adsorption due to its influence on the ionization state of the functional groups (carboxylate , hydroxyl, sulfate, phosphate, etc) and different ionic forms of copper. Therefore, the adsorption of Cu(II) was studied as a fuction of pH. The initial pH values were kept below 6 in order to avoid the possible removal of copper by precipitation (Kim et al., 2005). As shown in Fig.1, the S shape of the curve indicates no adsorption occurred at strongly acidic solution, pH 1, while low adsorption of copper ions at pH 2. A drastic increase in copper adsorption with the increasing pH was also called pH adsorption edge (Kumar and Bandyopahyay,2006). In this study, the pH adsorption edge is between 3-4.

The maximum amount of copper adsorbed is at pH 5 which was 3.481 mg g^{-1}. This pH was selected for subsequent adsorption analysis. This behavior of copper adsorption could be explained by the change in ionic state of carboxyl functional group which is represented by pK_a value. A previous study indicated that the carboxylic acids generally have a pK_a value between 2 and 5 (Strelko et al., 2002). This means that at pH below 2, all the binding sites were protonated causing repulsive forces to copper ions, that eventually resulting in a very low adsorption. As the pH increased to 3, the carboxyl groups started to dissociate and carry negative charge, reducing the electrostatic repulsion and more copper ions could be adsorbed.
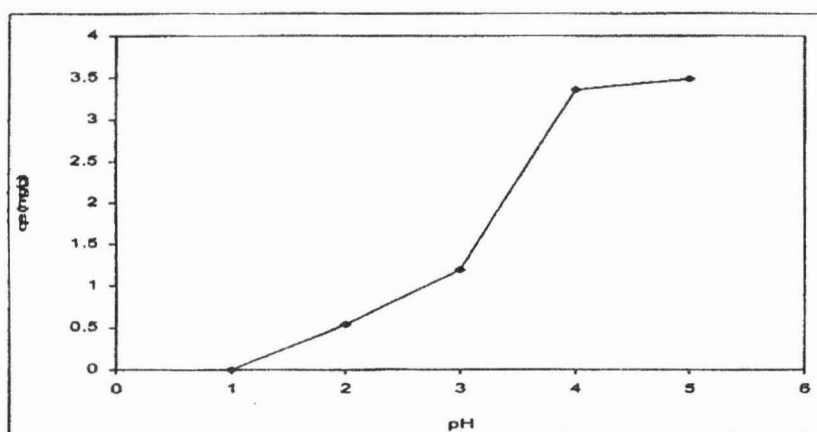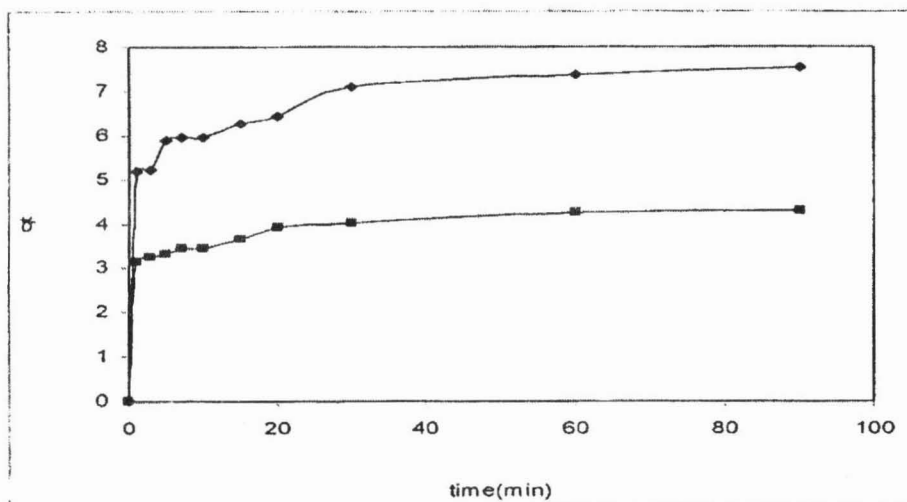

Fig.1 : Effect of pH on copper adsorption.

Effect of Concentration and Contact Time

In an adsorption study, it is also important to determine the time required to reach the equilibrium and this factor is influenced by the concentration of the adsorbate. The amount of copper adsorbed was found to increase with the same increase in concentration and contact time, Fig. 2. The shortest time to reach the equilibrium was 60 minutes, achieved by the lowest heavy metal concentration,5 mgL^{-1} and increased to 90 minutes for 10 mgL^{-1}. At low heavy metal concentration, the adsorption sites seemed to take up available copper ions much quickly due to less competition among heavy metal ions for binding sites. It is also interesting to note that CTSB was able to adsorb heavy metals ion quite rapidly for all copper concentrations as more than 60% of copper ions were adsorbed in the first 10 minutes.

Fig 2 : Effect of copper concentration and contact time (5 and 10mg/L)

Adsorption Isotherm

Adsorption isotherm is an expression that shows the relationship between the amount of adsorbate adsorbed per unit weight of adsorbent (q_e, mg L^{-1}) and the concentration of adsorbate in bulk solution (C_e, mg L^{-1}) at a given temperature under equilibrium conditions. Adsorption equilibrium is established when the amount of adsorbate being adsorbed is equal to the amount being desorbed from the adsorbent. At this stage, the equilibrium concentrations in both phases are constant. Adsorption isotherm is very useful in giving information on adsorption mechanisms, surface properties and affinity of an adsorbent towards heavy metal ions (Ho et al., 2002).

The two most common adsorption isotherm models, Langmuir and Freundlich models were applied to understand the adsorbate-adsorbent interaction.

Langmuir isotherm

Langmuir isotherm assumes that adsorption occurs at specific homogeneous site on the adsorbent (Langmuir, 1916). This model was successfully used in monolayer adsorption process.

The Langmuir equation is given by (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}}$$

where qe is the adsorption capacity at equilibrium (mg g-1), Qmax is the maximum adsorption capacity (mg g-1) based on Langmuir isotherm and b is a constant (L mg-1 or L mol-1) related to energy of adsorption which quantitative reflects the affinity between adsorbent and adsorbate. The experimental adsorption isotherm data of copper ions on CTSB is shown in Fig.1
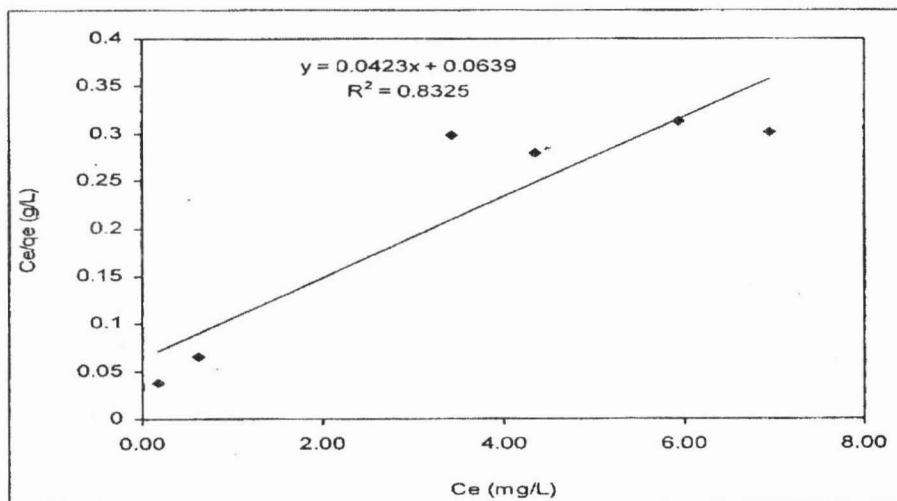

Fig. 3 : Langmuir plot of copper adsorption onto CTSB at 10 mg L^{-1}

Freundlich isotherm

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. It also assumes that the stronger adsorption sites are occupied first and the binding strength decreases with the increasing degree of site occupation.

The Freundlich equation is given by (Freundlich, 1906):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

where KF is maximum adsorption capacity (mg g-1) based on Freundlich model and n (unitless) is related to adsorption intensity. If the value of n is greater than unity, this is an indication of a favourable adsorption. The higher the n value, the stronger the adsorption intensity. A plot of log qe versus log Ce will give a straight line of slope $\frac{1}{n}\frac{1}{n}$ and intercept KF. The Freundlich plot of copper is shown in Fig. 2. The maximum adsorption capacities (KF) of copper and nickel ions, the adsorption intensity values (n) and correlation coefficients are given in table 3. The entire n values however lies in the range 1 to 10, an indication of favourable adsorption process (Li et al., 2009).
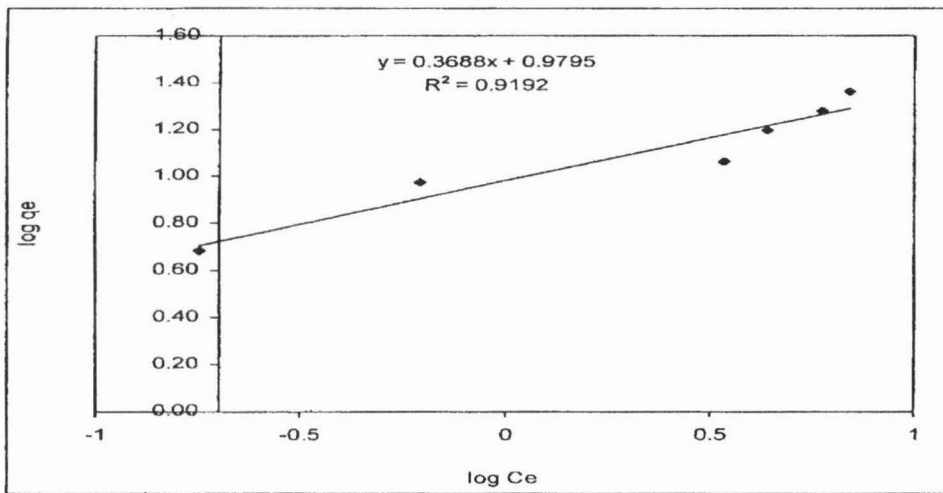

Fig. 4 : Freundlich plot of copper adsorption onto CTSB at 10 mg L^{-1}

Based on Table 1, the highest adsorption capacity of Cu (II) ions was recorded as 23.81 mg g^{-1} and the value is recorded as the highest value as compared to the other adsorbents that have been used before as in Table 5.

Table 1 : Langmuir and Freundlich isotherm constants and their correlation coefficients

Langmuir			Freundlich		
Q_{max} (mg g^{-1})	b (L/mg)	R^2	K_F	n	R^2
23.81	0.67	0.832	9.528	2.72	0.919

Table 2 : A comparison of maximum adsorption capacities for copper ions by different adsorbents

Adsorbent	Q_{max} (mg g^{-1})	pH	T (K)	Reference
Sphagum peat moss	12.60	5	298	Ho and McKay 2004
Neurospora crassa	12.30	5	298	Kiran et al. 2005
SoHIC	11.64	5	310	This study
Saccharomyces cerevisiae	10.72	6	298	Lale et al. 2005
Cercis siliquastrum leaves	9.35	4	N/A	Salehi et al. 2008
Activated carbon	9.22	N/A	293	Ferro-Garcia et al. 1998
Modified carrot residue	8.74	5.25	293	Güzel et al. 2008
Puracite C-104 ion-exchange resin	7.92	4.5	298	Sengorur et al. 2006
Herbaceous peat	4.84	5.5	294	Gündoğan et al. 2004
Modified oak sawdust	3.60	4	313	Argun et al. 2007
Potato peels	0.38	6	303	Aman et al. 2008
Periwinkle shell carbon	0.07	8	N/A	Badmus et al. 2006

Conclusion

This study showed the potential of base treated sugarcane bagasse, CTSB, as an adsorbent for copper aqueous solutions. Adsorption was more favourable at pH 5 with pH 3-5 recorded as the best range for the sorption of copper ions. The pseudo-second-order model was best fitted indicating the chemisorptions type of adsorption. Equilibrium data also fitted well to Langmuir isotherm equation and showed great potential as an adsorbent as the maximum adsorption capacities of Cu (II) ions was 23.81 mg g^{-1}, which is comparable with other adsorbents that have been studied before. Since sugarcane bagasse is highly abundant and it can be modified easily at relatively low cost, this waste material could be applied as a potential adsorbent for removing copper ions from aqueous solutions.

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