Utilization of Sago Waste as an Adsorbent for the Removal of Cu(II) Ion from Aqueous Solution

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Abstract: The preparation of activated carbon (AC) from sago industry waste is a promising way to produce a useful adsorbent for Cu(II) removal, as well as dispose of sago industry waste. The AC was prepared using sago industry waste with H_2SO_4 and $(NH_4)_2S_2O_8$ and physico-chemical properties of AC were investigated. The specific surface area of the activated carbon was determined and its properties studied by scanning electron microscopy (SEM). Adsorptive removal of Cu(II) from aqueous solution onto AC prepared from sago industry waste has been studied under varying conditions of agitation time, metal ion concentration, adsorbent dose and pH to assess the kinetic and equilibrium parameters. Adsorption equilibrium was obtained in 60min for 20 to 50mg/L of Cu(II) concentrations. The Langmuir and Freundlich equilibrium isotherm models were found to provide an excellent fitting of the adsorption data. In Freundlich equilibrium isotherm, the R_L values obtained were in the range of 0 to 1 (0.043 to 0.31) for Cu(II) concentration of 10 to 100mg/L, which indicates favorable adsorption of Cu(II) onto Sago waste carbon. The adsorption capacity of Cu(II) (Qo) obtained from the Langmuir equilibrium isotherm model was found to be 32.467 mg/g at pH 4 ± 0.2 for the particle size range of 125–250μ. The percent removal increased with an increase in pH from 2 to 4. This adsorbent was found to be effective and economically attractive.

Keywords: Activated carbon, Sago carbon, Adsorption, Copper removal

Introduction

Water is essential for survival. But today about 200 million people in India do not have access to safe drinking water due to water pollution[1]. Any change in physical, chemical or biological properties of water is known as water pollution. Heavy metal is important role of water pollution.

The heavy metals are continuously released into the aquatic eco system from natural process such as volcanic activity and weathering of rocks. The effluents from mining, ore processing, metal processing, metal polishing, cleaning, paint manufacturing and battery manufacturing industries and acid rain contribute for the increasing metal loads in the water bodies[2]. The heavy metal contamination of the water system is responsible for serious diseases and death. Copper is one of the few metallic elements found in the earth's crust. It constitutes 70mg/kg of the earth's crust, occurring as a constituent of several ores like, chalcopyrite ($CuFeS_2$), which is about 50% of total world copper deposits. Copper was the first metal used for men for utility purpose. Large number of important alloys contains copper as the principle element[3]. Environmental pollution due to copper arises from industrial and agricultural operations. Copper has broad industrial applications, such as alloy industries, paper and pulp; basic steel works foundries and petroleum refining industries[4]. Copper finds its way to water bodies through wastewater from copper wire mills, coal burning industries, tanning, insecticides and fungicides producing industries[5]. Copper is a trace element that is drinking water essential for most animals, including humans of that iron metabolism and maintenance of blood vessels. In India acceptable limits of Cu is 3mg/L. Higher concentration of copper is cause neuro toxicity commonly known as "Wilson's disease" due to the deposition of copper in the lenticular nucleus of the brain and liver. The other effect of copper to human includes congestion of nasal mucous membranes and pharynx, ulceration of nasal septum and metal fume fever. Eye irritation has been reported by factory workers exposed to copper dust. In some individuals, exposure to copper metal produces dermatitis[6]. Acute poisoning due to excessive amounts of copper salts may produce hematemesis, melena, coma and jaundice. Copper bound to albumin is considered to be the transport form of Cu(II) in blood. Copper deficiency causes Menke's disease[7]. Hence it is essential to remove Cu from industrial wastewater before discharging in to natural water sources to meet National Regulatory Standards as well as to protect public health. Conventional treatment methods for heavy metals containing waste water, chemical precipitation, Ferrite treatment system, sulphate precipitation, solvent extraction, evaporation, xanthate process *etc*., but due to operational demerits and the treatment cost is high .The need for cost effective and economic removal of toxic heavy metals from waste water resulted in a research for non-conventional materials and methods. Several low cost adsorbents include sawdust, orange peel, almond husk, parthenium *etc*.

The objective of the present study is to be prepare and characterize quality evaluate the efficiency of using sago waste carbon as an adsorbent for the removal of Cu. The adsorption study was carried out systematically involving various parameters such as pH, agitation time and adsorption dose.

Experimental

Adsorbent

Sago waste was collected from the sago industry in Salem district, Tamilnadu state; India, and was used as the source of activated carbon. Sago industry waste was subjected to chemical activation by the addition of 50 % H_2SO_4 and $(NH_4)_2S_2O_8$ (0.5 % w/w with constant stirring at room temperature for 0.5 hour. The charred material was kept in hot air oven at $105 \pm 5\ ^{\circ}C$ for 12 hour and was washed with distilled water (5 times). This material was soaked in 5 % $NaHCO_3$ solution and allowed to stand overnight to eliminate the residual acid from the pores of the carbon. The material was washed with distilled water until the pH of the slurry reached 6±0.5. Then it was dried in a hot air oven at 105±5 $^{\circ}C$ for 3 hour. The dried material was ground and sieved to get a product with a particle size range of 125–250μ, which was used for this study.

Adsorbent characterization

The physico-chemical properties of the carbon were presented in Table 1. The Brunauer–Emmett–Teller (BET) surface area was determined using computer controlled nitrogen gas adsorption analyzer at –196 $^{\circ}$C. Surface functional groups on the carbon were evaluated by adsorption experiments know as the Boehm technique[12], based on the selective neutralization of surface acid groups by varying strengths of bases and basic groups by a strong acid. The pH_{ZPC} for the sorbent was determined using the pH equilibrium method described by Kadirvelu *et al*[11] and Xiaoge *et al*[13]. Elemental analysis of C, H, N, and O (by difference) in the activated carbon was carried out on a Perkin Elmer elemental analyzer. Other parameters were analyzed using standard methods[11].

Table 1. Properties of the activated carbon used for this study

Parameter	Value
pH of 1 % solution	7.1
pH ZPC	5.7
Moisture, %	4.33
Cation exchange capacity, meq/g	0.75
Carbon, %	65.0
Hydrogen, %	2.0
Nitrogen, %	3.0
Oxygen, % (by difference)	30.0
Yield, %	78.0
Ash, %	12.0
Apparent density, g/mL	0.75
Decolorizing power, mg/g	55.5
Matter soluble in H_2O, %	5.5
Matter soluble in 1M HCl, %	8.0
Porosity, %	80.0
*BET Surface area, m^2/g	625.0
Surface acid groups, meq/g	
I Carboxyl	1.20
II Lactonic	1.80
III Phenolic	0.90
IV Carbonyl	1.60
Total basic groups, meq/g	1.10
Pore volume, mL/g	0.67

* BET surface area corresponds to the particle size 125–250µm.

Batch adsorption studies

A stock solution of 1000mg/L of Cu (II) was prepared by dissolving 3.929g of $CuSO_4$ in doubly distilled water acidified with 5mL of conc. H_2SO_4 to prevent hydrolysis and diluting to 1000mL. Batch adsorption test consisted of by mixing 50 mg of adsorbent and 50mL of Cu(II) solution of a desired concentration at an initial pH 4.0±0.2 in 100mL conical flasks and agitating the flasks in a mechanical shaker at 170rpm for predetermined time intervals at room temperature (30±2 $^{\circ}$C). After the agitation the adsorbate and adsorbent were separated by centrifugation at 3000 rpm for minutes and the Cu(II) content in the   solution was estimated spectrophotometrically at 445nm. The effect of agitation time on percent removal was studied using Cu(II) concentrations of 20–50mg/L. The effect of carbon dose was tested using Cu(II) concentrations of 25 and 50mg/L by varying the carbon dose between 25 and 250 mg per 50mL of solution.

Freundlich adsorption isotherm data was obtained from the studies on the effect of carbon dose on the Cu(II) removal. Initial adsorption coefficients and Lagergren adsorption rate constants were obtained from the effect of agitation time on Cu(II) removal. Different ranges of particle sizes of the adsorbent were used to obtain the percent removal in Cu(II) concentration of 20 mg/L. The effect of pH on Cu(II) removal was studied using Cu(II) concentrations of 20 mg/L, by varying the initial pH of the solutions between 2 and 9 using HCl and NaOH for pH adjustment.

Results and Discussion

Adsorbent characterization

The results of sorbent characterization experiments are summarized in Table 1. The surface morphology of the activated carbon was examined using scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained using a JSM-840 microscope (JEOL Techniques Ltd., Japan) at 2500× magnification (Figure 1). At such magnification, the activated carbon particles showed rough areas of surface within which micropores were clearly identifiable. The BET surface area was higher ($625 m^2/g$) than those of some other carbons prepared from agricultural wastes such as peanut hull ($208 m^2/g$), coir pith ($595 m^2/g$), eichhornia ($266 m^2/g$) cassava peel ($200 m^2/g$) and coconut tree saw dust carbon ($325 m^2/g$) which is more important for adsorption processes[8,10,11]. Specific acidic groups were also measured using Boehm's method and the results were comparable with those of activated carbons prepared from other agricultural wastes[8,11]. It is very important to know the distribution and concentration of functional groups present on the carbon surface in order to better understand the adsorption process mechanism. Lactonic groups are present in high concentration in activated carbon, followed by carbonyl, carboxyl basic and phenolic groups. It has been reported that carboxyl groups dissociate in the pH range 3–7. In fact, it is noted that a considerable increase in Cu(II) sorption capacity occurs at or near this pH range. This makes the present activated carbon an excellent adsorbent for treatment of Cu(II)-containing water.

Figure 1. SEM micrograph of the surface of sago waste carbon, Magnification- 2500x

Effect of agitation time and initial Cu(II) ion concentration on Cu(II) adsorption

The optimum equilibrium time was found out by using different concentrations of metal ion solution at pH 4 ± 0.5 (Figure 2). The effect of agitation time and initial metal ion concentration on adsorption of Cu(II) by sago waste carbon. The removal rate was rapid initially and then gradually diminished to attain an equilibrium time beyond which there was no significant increase in the rate of removal. The equilibrium was attained for 60 minutes for all the concentration studies. It should be noted that the contact time required for all metal ion concentrations was very short for the removal of Cu(II) which is an important parameter for economic wastewater application. At equilibrium time the amount adsorbed was 15.3, 20.08, 25.78 and 30.79 mg/g for the concentrations 20, 30, 40 and 50 mg/L respectively. Similar results have been reported for Cu(II) adsorption[14-16]. It is very clear from the results that the agitation time required for maximum uptake of metal ion by using sago carbon is less when compared to other adsorbents. The metal ion adsorption *vs* time curves were single, smooth and continuous leading to equilibrium suggesting the possibility of the formation of monolayer coverage of metal ions on carbon surface[17].
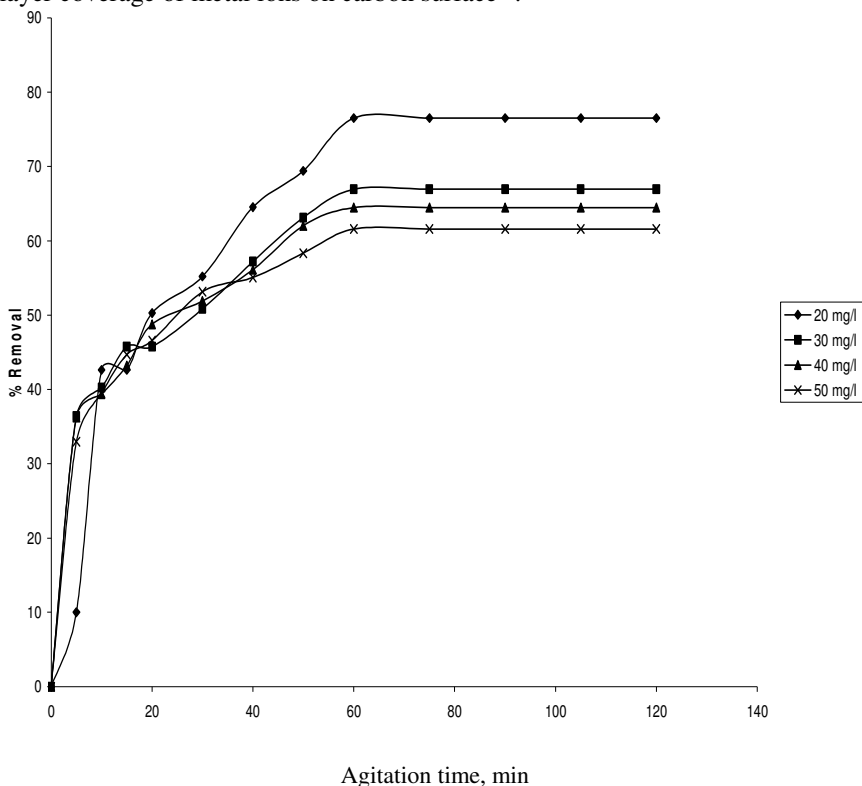

Figure 2 Effect of agitation time on Cu(II) ion removal

Adsorption Kinetics

Lagergren Rate Equation
The kinetics of Cu(II) adsorption on Sago waste carbon follows first order rate expression given by Lagergren.

$$\log (q_e - q) = \log q_e - (K_{ad} t / 2.303)$$

Where, q_e = The amount of Cu (II) adsorbed at equilibrium (mg/g)

   Q = The amount of Cu(II) adsorbed at time t (mins)

   K_{ad} = The rate constant of adsorption of Cu(II) by sago waste carbon

The linear plots of log $(q_e - q)$ *vs* t show the applicability of the above equation for the adsorption of Cu(II) by sago waste carbon. The values of K_{ad} were calculated from the slope of the linear plots and are presented in Figure 3 for different concentration of the metal ion.
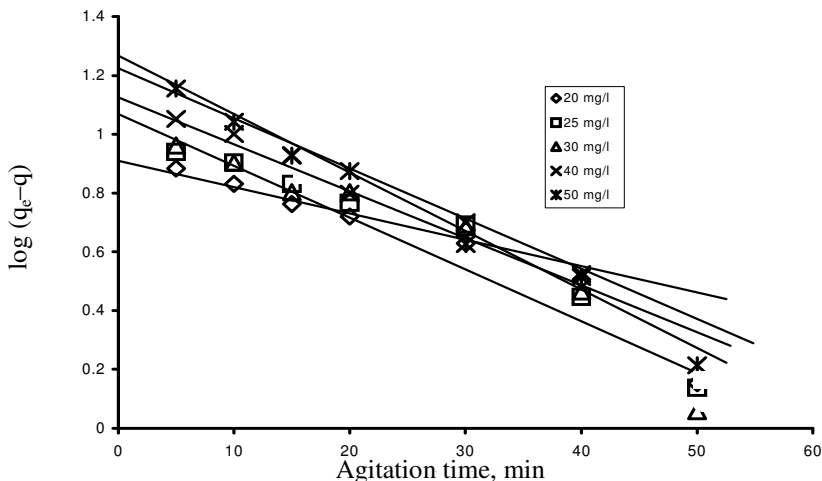

Figure 3. Lagergren plots for Cu(II) adsorption plots of log $(q_e - q)$ *Vs* time

Effect of Carbon dosage on Cu(II) Removal

Figure 4 shows that the removal of metal ions increased with increase in carbon dosage and attained a maximum after a particular carbon concentration. It was observed from the results that the complete removal of Cu(II) from 50mL of 25 and 50mg/L required a maximum carbon dosage of 175 and 225 mg respectively. The increase in the percent removal of Cu(II) with the increase in carbon dosage is due to the availability of larger surface area with more active functional groups at higher adsorbent dosage and saturation occurs as a result of non-availability of active sites on the adsorbent.

Adsorption Isotherm

Several mathematical models, such as those derived by Langmuir and Freundlich, are capable of describing the distribution of metal ions between the liquid phase and the solid phase. It is very important to have a satisfactory description of the equilibrium state between the two phases in order to successfully represent the dynamic behaviour of any adsorbate from solution to the solid (carbon) phase.

The Langumir isotherm was applied for adsorption equilibrium of Cu(II) onto sago waste carbon.

$$C_e / q_e = (1 / Q_0 b) + (C_e / Q_o)$$

Where, C_e = Concentration of Cu (II) at equilibrium (mg/L).

   q_e = Amount of metal ion adsorbed at equilibrium time (mg/g).

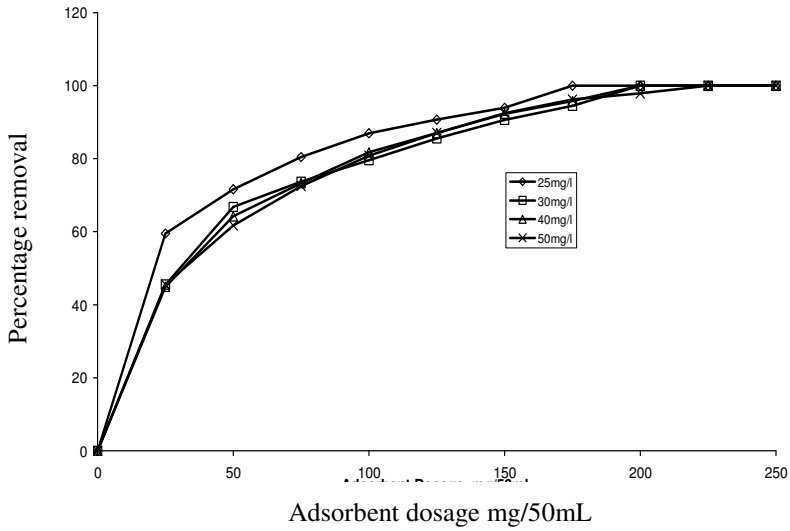 Q_0 = Adsorption capacity (mg/g).

   B = Langmuir constant.

Figure 4. Effect of carbon dosage on Cu(II) removal

Linear plot of C_e/q_e *vs* C_e shows that the adsorption follows Langmuir isotherm model (Figure 5). The values of Q_o and b were determined from the slope and intercept of the plot and were found to be $Q_0 = 32.467$ mg/g and b = 0.2173 L/mins. The applicability of Langmuir isotherm suggests the monolayer coverage of Cu(II) on the surface of activated carbon prepared from sago waste.
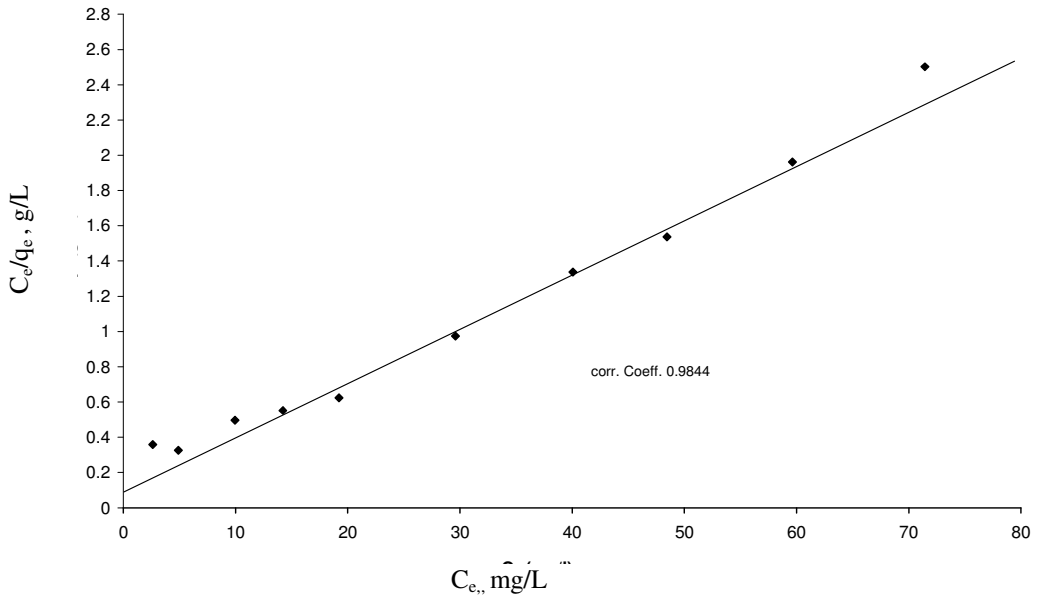

Figure 5. Langmuir Plot for Cu (II)

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless separation factor or equilibrium parameter R_L that is defined by,

$$R_L = 1 / 1 + b\ C_o$$

Where, C_o = Initial Cu (II) concentration (mg/L)

   b   = Langmuir constant (L/mg)

   The parameter, R_L indicates the shape of the isotherm as follows.

R_L Value	Type of Isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$C_o < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The R_L values obtained were in the range of 0 to 1 (0.043 to 0.31) for Cu(II) concentration of 10 to 100mg/l, which indicates favourable adsorption of Cu(II) onto Sago waste carbon.

Freundlich Isotherm

The Freundlich equation can be derived by assuming that the free energy of adsorption decreases logarithmically as adsorption density increases. The Freundlich equation is used for heterogeneous surface energies. The linear form of Freundlich equation is given by the following expression

$$\log (x/m) = \log K_f + 1/n\ \log C_e$$

Where,

   X = Amount of Cu (II) adsorbed at equilibrium (mg).

   M = Weight of the adsorbent used (g).

   C_e = Equilibrium metal ion concentration (mg/L).

   K_f and n = Freundlich constants.

Linear plots of $\log_{10} x/m$ *versus* $\log_{10} C_e$ shows that the adsorption follows Freundlich isotherm model. K_f and n values were calculated from the intercept and slope of the plots (Figure 6).
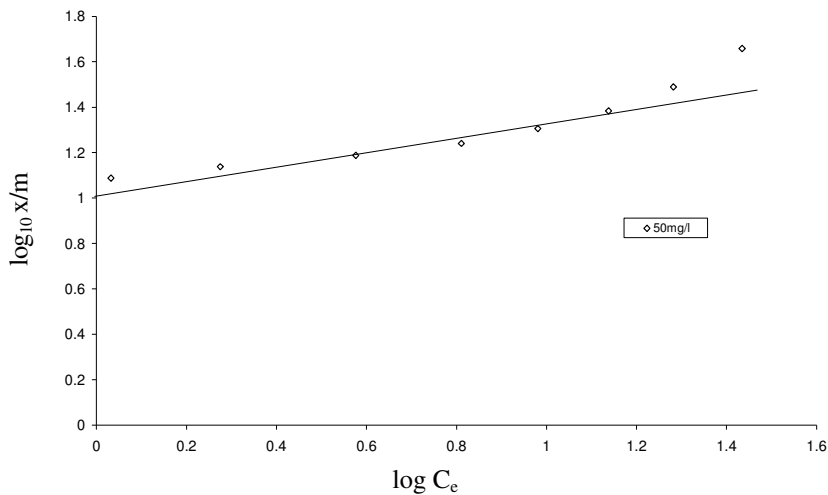

Figure 6. Freundlich plot for Cu (II) adsorption

Since the 'n' values in the range of 1 to 10 indicate beneficial adsorption, the values of n suggest that sago waste carbon may consider as an effective adsorbent.

Effect of pH on the adsorption of Cu(II)

Figure 7 presents the effect of initial pH on the removal of Cu(II) ions from aqueous solution by sago waste carbon.
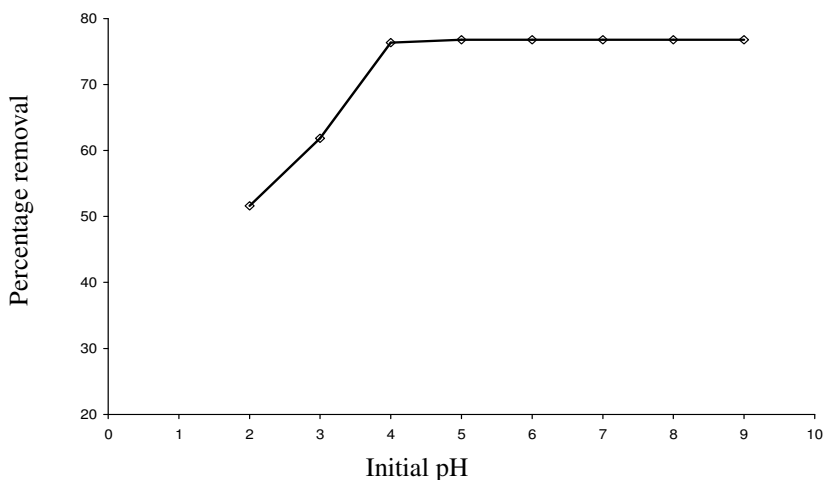

Figure 7. Effect of pH on Cu(II) adsorption

Adsorption of Cu(II) ion increases with increase in pH value from 2 to 4 and the removal is constant for further increase in pH. Adsorption of metal ion depends upon the nature of the adsorbent surface and species distribution of the metal ion. Species distribution mainly depends on the pH of the system. The influence of pH on Cu(II) removal may be acidic pH conditions; both adsorbent and adsorbate are positively charge (M^{2+} and H^+) and therefore the interaction is that of electrostatic repulsion[8,18]. Beside, the higher concentration of H^+ ions for the surface adsorbing sites results in decrease in the removal of Cu(II). The concentration of Cu(II) remains constant resulting in increase in the removal of Cu(II). The significant adsorption of metal ions is observed below pH 4.5. At pH >5 precipitation of $Cu(OH)_2$ takes place. Hence it was decided to maintain the pH at 4 ± 0.5 for all other studies.

Conclusion

Activated carbon prepared from sago waste can be used as an adsorbent for the effective removal of Cu(II) from aqueous solution. Analysis of SEM images showed that the sago waste surface was rough and possessed micropores. Adsorption depends on the solution pH, the initial Cu(II) concentration, the carbon dose employed and the particle size of the adsorbent. Adsorption of Cu(II) increased with increasing agitation time, carbon concentration and decreased with increasing pH and Cu(II) concentration. Adsorption equilibrium was reached with in a short period of time (60 minutes). The adsorption was found to obey Lagergren equation and the Lagergren rate constant for adsorption of Cu(II) was found to be constant for various initial concentrations of Cu(II), which implies that adsorption follows first order kinetics. Adsorption of Cu(II) from aqueous solution increased with decreasing particle size of the adsorbent and increased with increasing carbon concentration. Adsorption of Cu(II) onto activated carbon obeyed both Langmuir and Freundlich model. The maximum adsorption capacity (Q_o) calculated from Langmuir Isotherm was found to be 32.407 mg/L for the particle size of 125-250μ. Freundlich adsorption capacity was found to be 5.260. Freundlich constant and R_L values (0.0439-0.315)

from Langmuir Isotherm indicate that the adsorption process is favorable for the removal of Cu(II) by sago waste carbon. The present investigation shows that the sago waste activated carbon can be employed as an effective adsorbent for the removal of Cu(II) from aqueous solution. Since the raw material used in the preparation of activated carbon is available abundantly, the resulting carbon is expected to be economically viable.

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