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REMOVAL OF MERCURY (II) BY ADSORPTION ONTO SILK COTTON HULL ACTIVATED CARBON

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ABSTRACT

Activated carbon prepared from silk cotton hull was investigated for removal of mercury (II) from aqueous solution by adsorption technique. Batch mode adsorption studies were carried out under varying conditions of agitation time, metal ion concentration, adsorbent dose and pH. Adsorption equilibrium was obtained in 150 min for 10, 20, 30 mg/L of Hg (II) concentration. Adsorption followed Langmuir isotherm. The percent removal increased with increase in pH from 2 to 5 and remains static from pH 5 to 10. Desorption studies were performed with dilute hydrochloric acid solution. Silk cotton hull carbon was found to be effective in removal of Hg (II) from aqueous solution and economically viable.

INTRODUCTION

Mercury is one among of the most toxic metals found in the environment. The major anthropogenic sources of mercury pollution in aquatic systems include industrial and urban discharges, atmospheric deposition, agricultural materials, mining and combustion (Wang et al. 2004). India imports over 250 tonnes of mercury every year and 220 tonnes leak into the environment. The major industrial culprits are chlor-alkali plants and thermal power plants. Mercury pollution in India is substantial, when considered medical waste from thermometers and blood pressure monitors of which the country produces over 10 million each year (Rajgopal 2003). The toxic potency of mercury varies depending on the chemical nature and the route of entry into human body. Mercuric (divalent) salts are usually more toxic than are mercurous (monovalent) salts (Goyer 1991). Mercury is also known to induce hypersensitivity reactions such as contact dermatitis and acrodynia (Mathesson et al. 1980).

High toxic potency of mercury has necessitated the global need for the removal of Hg (II) from wastewaters before its discharge in aquatic environment. Conventional methods for the removal of Hg (II) from wastewater include sulphide precipitation, ion exchange, alum and iron coagulation, and adsorption on activated carbon (Patterson 1995). In spite of various treatment technologies, cost effective removal of Hg (II) from wastewaters resulted in a quest for non-conventional adsorbents like fly ash (Kapoor & Viraraghavan 1994), unburned carbon from fly ash (Li et al. 2002), fruit shell of *Terminalia catappa* (Inbaraj & Sulochana 2006), polymerized saw dust and agricultural waste (Kadirvelu et al. 2003).

However, no notable attempts have been made on adsorption characteristics of activated carbon prepared exclusively from silk cotton hull to remove Hg (II) ions. India being one of largest producers of cotton in the world, enormous quantity of silk cotton hull is generated in the region. In India,

Coimbatore area encompasses highest number of cotton textile processing industries. Textile processing units in Coimbatore dispose off the pod of white silk cotton as a waste material, which can be carbonized and used for the process of adsorption technique. The objective of this study was to investigate the feasibility of using this carbon for the removal of Hg (II) from water by adsorption.

MATERIALS AND METHODS

Adsorbent

Silk cotton hull (SCH), collected from silk cotton processing industries, was cut into smaller pieces and dried in sunlight for 24 hours. The dried matter was used for carbon preparation by chemical activation method. SCH was mixed with concentrated H_2SO_4 acid and kept in a hot air oven at 100°C for 12h. The carbonized material was washed with distilled water to remove free acid. Then it was soaked in 1% sodium bicarbonate solution overnight to remove any residual acid. The material was washed with distilled water and dried at 100°C for 12 h. After cooling, the material was ground and sieved to obtain particles ranging 125-250 µm. Physico-chemical characteristics of carbon are presented in Table 1.

Batch Mode Adsorption Studies

A stock solution of 1000 mg/L of Hg (II) was prepared by dissolving 1.3540 g of $HgCl_2$ in double distilled water acidified with 5 mL of concentrated HNO_3 to prevent hydrolysis and diluted to 1000 mL. Batch adsorption test consisted of mixing 50 mg of adsorbent and 50 mL of Hg (II) solution of a desired concentration at an initial pH 5.0 in 100 mL conical flasks and agitating the flasks in a mechanical shaker at 170 rpm for predetermined time intervals at room temperature (30 ± 2°C). After agitation, the adsorbate and adsorbent were separated by centrifugation at 6000 rpm for 10 min and the Hg (II) content in the solution was estimated spectrophotometrically at 565 nm using Rhodamine 6G (Ramakrishna et al. 1976). The effect of agitation time on percent removal was studied using Hg (II) concentrations of 10-30 mg/L. The effect of carbon dose was tested using Hg (II) concentrations of 30 mg/L by varying the carbon dosage. Initial adsorption coefficients and Lagergren adsorption rate constants were obtained from the effect of agitation time on Hg (II) removal. The effect of pH on Hg (II) removal was studied using Hg (II) concentrations of 10 and 20 mg/L by varying the initial pH of the solutions between 2 and 10 using HCl and NaOH for pH adjustment.

Table 1: Characteristics of activated carbon.

Parameter	Value
pH 1 % solution	7.69
Moisture content (%)	2.86
Ash content (%)	1.987
Decolorizing power (mg/g)	22.5
Ion-exchange capacity (equi/g)	0.0415
Surface area (m^2/g)	156.0
Apparent density (g/L)	0.86
Particle size (µm)	125-250
Volatile matter (%)	12.0
Fixed carbon (%)	83.15
Calcium (mg/g)	16.0
Sodium(mg/g)	7.0
Potassium (mg/g)	13.0
Water-soluble matter (%)	2.0
HCL soluble matter (0.25 N) (%)	7.0

Table 2: Lagergren rate constant for Hg (II) adsorption.

Metal ion concentration (mg/L)	Rate constant K_{ad} × 10/min
10	0.124
20	0.0319
30	0.0177

Desorption Studies

After adsorption experiments with 20 mg/L solution of Hg (II) and 50 mg of carbon, the Hg (II) laden carbon was separated out by filtration and the filtrate

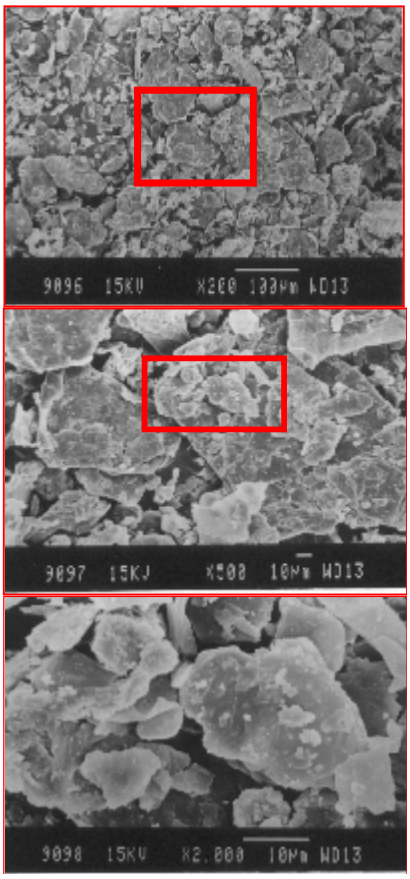

Fig. 1: SEM photograph of silk cotton hull activated carbon at various magnifications (x200, x500 and x2000).

was discarded. The carbon was given a gentle wash with double distilled water to remove the unadsorbed metal ions. Desorption studies were carried out using 50 mL of HCl of various strengths (0.25–2.00 M). The desorbed metal ions in the solution were separated by centrifugation and analyzed.

RESULTS AND DISCUSSION

Adsorbent Characterization

Characteristics of activated carbon prepared from silk cotton hull are depicted in Table 1. The determined surface area of silk cotton hull activated carbon (SCHAC) was 228 m^2/g and is comparable to various low cost adsorbent namely peanut hull carbon (Namasivayam & Periasamy 1993) (208 m^2/g). The moisture content of the carbon was found to be 2.4%. The surface morphology of silk cotton hull activated carbon was visualized in scanning electron microscopy (SEM), and corresponding SEM micrographs being obtained using a JSM-840 JEOL microscope of JEOL Techniques LTD, Japan at 2000x magnification (Fig. 1). Examination of SEM micrographs of the SCHAC particles showed rough areas of surface of the carbon and the microspores were identifiable. The activation process of SCHAC by adopting sulphuric acid treatment leads to corrode the surface of carbonaceous material and introduce micro, macro and meso pores. The X-ray Diffraction studies of SCHAC were carried out using Rotoflux X-ray Diffractometer 20KW/20A, Model 10.61 with a microprocessor recorder. The amorphous nature of the SCHAC sample was determined by using intensity of the observed rays with respect to scattering angle (2q). The XRD pattern of the SCHAC sample is shown in the Fig. 2.

Effect of Agitation Time and Initial Concentration on Hg (II) Adsorption

Effect of agitation time on Hg (II) adsorption by SCH activated carbon is shown in Fig. 3. Adsorption of Hg (II) increases with an increase in agitation time and attains equilibrium in 150 min for 10-30 mg/L Hg (II) respectively. The contact time required for the metal ion removal is very short. This result is interesting because equilibrium time is one of the important parameters for economical wastewater treatment applications. According to the results, the contact time was fixed at 150 min for rest of the batch experiments to make sure that equilibrium was reached in all the cases. This indicates that SCH activated carbon requires lesser contact time for complete removal of Hg (II) compared to commercially available activated carbon made from waste newsprint fiber is 16 h for 100 mg/L of Hg (II) (Aoyama et al. 2000). This is due to higher surface area and more functional groups present in the SCH activated carbon (Table 1).

Adsorption Kinetics

The rate constant of Hg (II) adsorption on SCH activated carbon was derived from the first order rate expression given by Lagergren & Svenka (1898).

$$\text{Log}_{10}(q_e - q) = \log_{10} q_e - K_{ad}\, t/2.303$$

Where, q and qe are the amount of Hg (II) adsorbed by 1g of carbon at time t and at equilibrium time, respectively, and K_{ad} is the rate constant of adsorption (min^{-1}). The fairly linear plots of $\text{Log}_{10}(q_e - q)$ versus t at different initial Hg (II) concentrations (Fig. 4) confirm the applicability of the above equation for Hg (II) adsorption onto SCH activated carbon. The values of K_{ad} were calculated from the slope of these linear plots (Fig.4) and are presented in Table 2 for different Hg (II) concentrations.

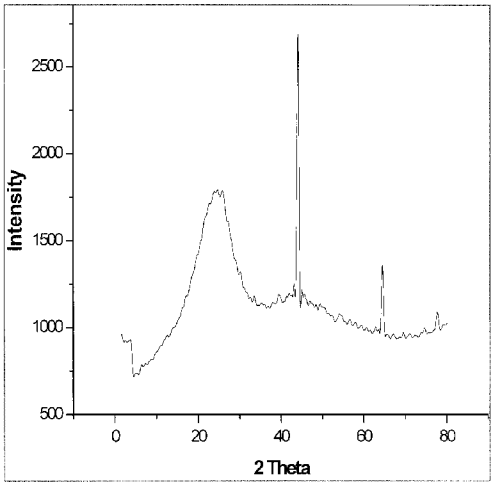

Fig. 2: X-ray diffraction pattern for silk cotton hull activated carbon.

Effect of Carbon Concentration

The effect of carbon concentration on Hg (II) adsorption is shown in Fig. 5. The figure shows that the removal of Hg (II) increases with increasing carbon concentration, with complete removal being attained at a particular carbon concentration. This is due to the availability of more surface area with more functional groups at higher carbon dosages. For the complete removal of Hg (II) from 1000 mL of 30 mg/L, a maximum carbon concentration of 1.60 g/L is required. In the case of a commercial carbon, about 5.0 g/L is required, which is three times higher when compare to the SCH activated carbon (Kadirvelu et al. 2000).

Adsorption isotherm

The Langmuir isotherm model was applied to analyze the adsorption equilibrium of Hg (II) onto SCH activated carbon.

$$C_e/q_e = 1/Q_o b + C_e/Q_o$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed (mg/g), and Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. The linear plot of C_e/q_e versus Ce shows that the adsorption follows the Langmuir isotherm model for Hg (II) adsorption (Fig.6). The values of Q_o and b were calculated from the slope and intercept of the plot, and the values obtained were Q_o = 27.96 mg/g and b = 0.296 l/g respectively. Adsorption capacity is higher compared to commercial activated carbon (12.38 mg/g) (Namasivayam & Periasamy 1993). Thus, it may be concluded that the higher Hg (II) adsorption capacity of silk cotton hull carbon is due to availability of a large surface area with active functional groups than on other compared adsorbents.

Effect of pH on Hg (II) Adsorption

The effect of pH on Hg (II) removal by adsorption is shown in Fig.7. The adsorption of Hg (II)

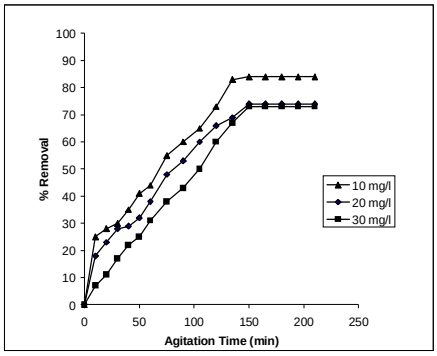

Fig. 3: Effect of agitation time on Hg (II) adsorption.

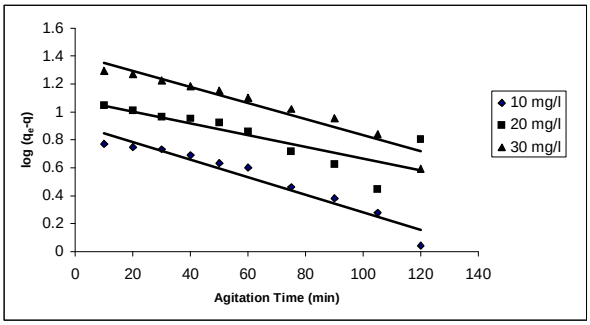

Fig: 4: Lagergren plots for adsorption of Hg (II) ions from aqueous solution.

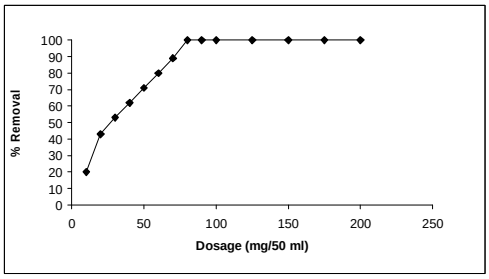

Fig. 5: Effect of carbon dosage on Hg (II) ions (30 mg/L) adsorption.

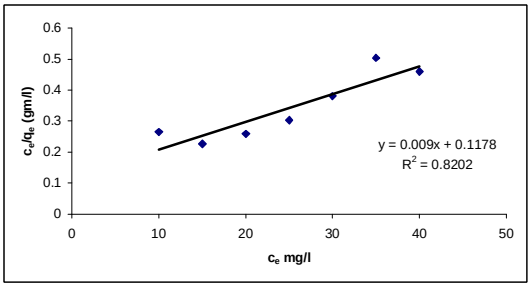

Fig. 6: Langmuir plot for Hg (II) adsorption.

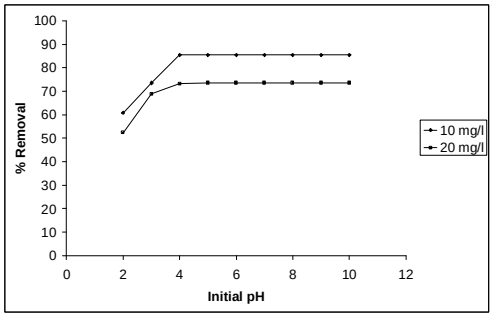

Fig. 7: Effect of pH on Hg (II) adsorption.

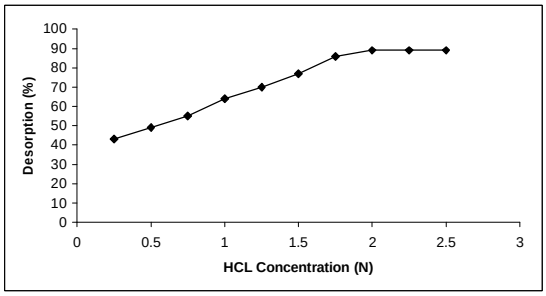

Fig. 8: Effect of HCL concentration on desorption of Hg (II).

depends on the nature of the adsorbent surface and the species distribution of Hg (II) in solution, which mainly depends on the pH of the system. The Hg (II) removal by carbon was observed over a range of initial pH values between 2 and 10. The percent of mercury removal by SCH carbon increases with increasing initial solution pH. The influence of initial pH on Hg (II) removal may be explained as follows: In the acidic condition, both the adsorbent and the adsorbate are positively charged and therefore, the net interaction is that of electrostatic repulsion (Langmuir 1918). Besides, the higher concentration of H^+ ions present in the reaction mixture competes with the positively charged Hg (II) ions for the surface adsorbing sites, resulting in a decrease in the removal of Hg (II).

Desorption Studies

Desorption helps to understand mechanism of adsorption and to regenerate the adsorbent, as well as to recover Hg (II) from the spent adsorbent apart from protecting the environment from solid waste disposal problems. Attempts were made to desorb Hg (II) from the metal loaded carbon using various ionic strengths adjusted with NaOH. The maximum desorption of Hg (II) with NaOH was found to be 99% (Fig.8). Other mechanisms, such as hydrolysis/precipitation, chemisorptions, or redox process might also be responsible for the adsorption of Hg (II) on the carbon (Kadirvelu 1998). The relative price of the material used in the present study is very much lower than that of commercial activated carbons.

CONCLUSION

The results obtained show that carbon preparation from silk cotton hull can be used effectively for the removal of mercury from aqueous solution. In batch mode studies, the adsorption was dependent on solution pH, initial Hg (II) concentration and carbon dosage. The pH effect on metal ion removal was high, and was more noticeable at pH values between 2 and 5 in particular. The results show that the liquid-phase adsorption on carbon is governed either by electrostatic attraction or ion exchange.

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