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Removal of Mercury Ions from Aqueous Solutions using *Eucalyptus Globules* Bark Carbon – A Low Cost Material Alternate to Commercial Activated Carbon

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ABSTRACT

In the present study, a low-cost adsorbent *eucalyptus globules* bark carbon (EGBG) have been prepared from naturally and abundantly available agriculture waste and it was used as replacements for the current expensive adsorbent viz., commercial activated carbon (CAC) for the removal of toxic Hg(II) ions from wastewaters. The influence of various parameters such as effect of pH, contact time, adsorbent dose, initial concentration of metal ions and temperature on the removal was examined by batch method. Langmuir and Freundlich isotherm models were tested and found to be applicable. Monolayer adsorption of Hg(II) ions occur on the surface of the adsorbents. Adsorption data are modeled with various first order kinetic equations like Natarajan-Khalaf, Lagergren and Bhattacharya and Venkobachar equations. The intra particle diffusion model is found to be applicable. This indicates that the Hg(II) ions adsorption on CAC and EGBC is first order with the intra-particle diffusion as one of the rate determining steps.

1. Introduction

Environmental pollution by heavy metals is a serious and complex problem that has been, and still is, a focus of attention worldwide. Heavy metals are among the chief pollutants of surface and groundwater. Industrial and municipal wastewaters frequently contain metal ions that can be harmful to aquatic life and human health. Waste streams containing heavy metals are often encountered in chemical process industries, such as metal, finishing and plating facilities, as well as in mining operations and tanneries. In general, heavy metals are not biodegradable and they tend to accumulate in living organisms, causing various diseases and disorders [1-4].

Mercury (Hg) is one of the extremely toxic metals in the environment that can cause irreversible neurological damage in human. Mercury and its compounds act as dangerous and insidious poisons and can be adsorbed through the gastrointestinal tract and also through the skin and lungs. After adsorption, mercury circulates in the blood and is stored in the liver, kidneys, brain, spleen and bone which can lead to several health problems such as paralysis, serious intestinal and urinary complications, disfunction of the central nervous system and, in more severe cases of intoxication, death [5]. Therefore, the removal of mercury to the acceptable concentration is a challenge in drinking water and wastewater treatment.

Treatment processes for metal contaminated wastewater include chemical precipitation, membrane filtration, reverse osmosis, ion exchange, and adsorption [6-10]. Most of these methods require high capital cost and recurring expenses such as chemicals, which are not suitable for small-scale industries. The process of adsorption is by far the most versatile and widely used technique for metal ions removal. Activated carbon has been the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater for potable use for almost three decades. Despite its prolific use in water and waste industries, activated carbon remains an expensive material. In recent years, research interest in the production of low-cost alternatives to activated carbons has grown. The use of local, natural, and cheap materials that are available in large quantities or certain waste from agricultural operations for treatment of water and wastewater containing heavy metals in developing countries like India is an area that is gaining interest.

Activated carbons from cheaper and readily available resources and various kinds of agricultural, domestic and industrial wastes have been utilized for the removal of various metal ions by adsorption. However, new economical, easily available and highly effective sorbents are still needed. The objective of this study was to investigate whether activated carbon prepared from *Eucalyptus globules* bark could be used as an alternative for commercial activated carbon for the removal of mercury ions from water and wastewater. The influence of various parameters such as pH, initial concentration of metal ion, contact time, and adsorbent dose on the removal efficiency was studied. The kinetics of metal ions adsorption onto the EGBC was analyzed by kinetic models. The experimental equilibrium adsorption data were analyzed by Freundlich, Langmuir, Dubinin–Radushkevich, and Temkin isotherm models to determine the best fit isotherm equation.

2. Experimental Methods

All the chemicals and reagents are analytical grade used as received.

2.1 Preparation and Activation of Eucalyptus Globules Bark Carbon

The *Eucalyptus globules* bark was collected from our college campus as well as Alagar kovil hill and it was carbonized, pulverized and sieved [3,4]. The particles obtained by sieving between the sieves 90, 120, 150, 180, 225 and 250 microns were used in the present study. These adsorbents were activated by digesting 200 g of carbon with 600 mL of 4 N nitric acid solution for 120 min at 80 °C. It was washed with boiling double distilled (DD) water several times to remove the acid (tested with pH paper) and metal ions present in the adsorbent (tested with Eriochrome black –T indicator) and finally with DD water. These activated adsorbents were dried in an air oven at 120 °C for about five hours. It was then stored in an airtight wide mouth reagent bottles and used for adsorption studies.

2.2 Procedure for the Adsorption Studies

Stock solution of Hg(II) (500 ppm) was prepared and diluted exactly to get experimental solutions of Hg(II)ion of various initial concentration, C_i (range: Hg(II)= 100-200 ppm for CAC and 15-21 ppm for EGBC) with double distilled water to a total volume of 50 mL in 250 mL leak proof reagent bottles (with i/c stoppers). Required amount of adsorbent was weighed and transferred into each one of these bottles. The bottles were then placed in a mechanical shaker and shaken vigorously for a period of

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contact time (5-40 min) at 200 rpm agitation speed. After attaining equilibrium, the bottles were kept aside for 15 min at room temperature (30±1 °C) in order to allow the adsorbent particles to settle down. The solutions were then filtered through whatman no. 1 filter paper in a clean dry conical flask.

Exactly 10 mL of the filtrate was pipetted out into a clean conical flask and titrated against standardized solution of EDTA of known strength (0.01 M) using Eriochrome black–T indicator. The end point is the colour change from red to blue. The titrations were repeated to get concordant titre values. From the titre values, the equilibrium concentrations (C_e) of metal ions was calculated.

The percentage removal of metal ions and amount adsorbed (q, mgg^{-1}) have been calculated using the following relationships

$$\text{Percentage removal} = 100\,(C_i - C_e)/C_i \qquad (1)$$

$$\text{Amount adsorbed (q)} = (C_i - C_e)/m = x/m \qquad (2)$$

where, C_i and C_e are the initial and equilibrium concentrations (ppm) of metal ions, respectively; x is the amount of metal ions adsorbed in ppm ($x = C_i - C_e$) and 'm' is the mass of adsorbent (CAC and EGBC) in gL^{-1}.

3. Results and Discussion

3.1 Effect of Initial Concentration

Adsorption studies of Hg(II) ions on CAC and EGBC at a fixed dose of adsorbent ($4gL^{-1}$ CAC and $12gL^{-1}$ EGBC) at different initial concentrations of metal ions (range: 100–200 ppm for CAC and 15-21 ppm for EGBC) and contact time (30 min for EGBC and CAC) and at solution pH (6.1), fixed particle size for CAC and EGBC (90 micron) at a temperature 30±1 °C were carried out. The range of percentage removal of Hg(II) ions observed are 100-90.04 for CAC and 88.93-47.28 for EGBC. The effect of initial concentration of Hg(II) ions on the percentage removal by CAC and EGBC are presented in the Fig. 1.

It indicate that the increase in initial concentration of Hg(II) ions resulted in a reduction in the percentage removal. It was observed that, the percentage removal of Hg (II) ions decreases exponentially with the increase in the initial concentration of Hg(II) ions. This may be due to reduction in immediate solute adsorption, owing to the lack of available active sites on the adsorbents surface compared to the relatively large number of active sites required for high initial concentration of Hg(II) ions. At an optimum initial concentration of Hg(II) ions *viz*., for CAC is 500 ppm and EGBC is 100 ppm for Hg (II) ion, the percentage removal are noted to be maximum, hence these values are fixed as an optimum initial concentration [11-15].

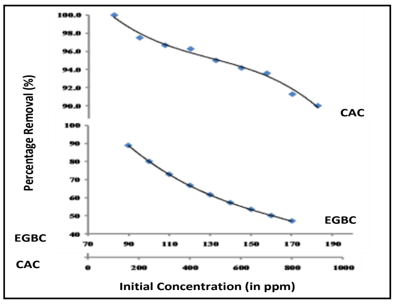

Fig. 1 Effect of Initial concentration for the removal of Hg(II) ions by adsorption onto CAC and EGBC

3.1.1 Adsorption Isotherm

The study of adsorption isotherm has been of importance and significance in the treatment of water and the waste water by the adsorption technique, as they provide an approximate estimation of the adsorption capacities of the adsorbents. The equilibrium data for the removal of Hg(II) ions by adsorption on CAC and EGBC at 30±1 °C were used in fitting the Freundlich and Langmuir isotherms.

$$\text{Freundlich isotherm} = \log (x/m) = \log K + 1/n \log C_e \qquad (3)$$

$$\text{Langmuir isotherm} = C_e/q_e = 1/Q_o b + C_e/Q_o \qquad (4)$$

Where, Freundlich constants K and 1/n are the measures of adsorption capacity and intensity of adsorption, respectively; q_e is the amount of Hg^{2+} ions adsorbed per unit mass of the adsorbent (in mgg^{-1}) at equilibrium *ie.,* $q_e = (x/m)$; $x=(c_i - c_e)$, C_i and C_e, initial and final equilibrium concentration of metal ions, respectively in ppm, m=mass of adsorbent, in gL^{-1}, Q_o is the monolayer adsorption capacity in (mgg^{-1}) and b is the Langmuir constant related to the energy of adsorption (in Lmg^{-1}). The data obtained from the adsorption experiments by varying the initial concentration were fitted with Freundlich and Langmuir isotherms (Fig. 2). These two isotherms plots are found to be linear (as evidenced from the values which are close to unity Table 1) indicating the applicability of these two adsorption isotherms for the removal of Hg(II) ions by adsorption on CAC and EGBC and a formation of monolayer of Hg(II) ions on the surface of the adsorbents.

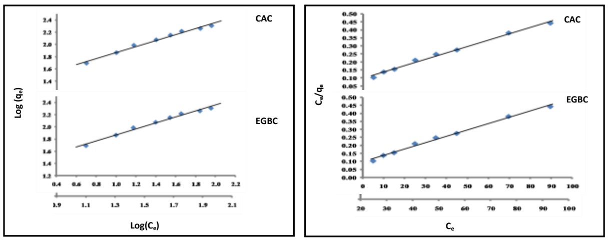

Fig. 2 (A) Freundlich and (B) Langmuir adsorption isotherm plots for the removal of Hg(II) ions by adsorption onto CAC and EGBC at 30±1 °C

The results of correction analysis of adsorption data *viz.,* correlation coefficient and the Freundlich and Langmuir constants and adsorption capacity (Q_o, (1/n) log K, b and R_L) are given in Table 1. The results of statistical analysis of adsorption data reveal that both the Freundlich and Langmuir adsorption isotherms are applicable and the correlations are statistically significant. The values of R_L observed are found to be fraction, in the range of 0 to 1 (0.077 for EGBC and 0.080 for CAC) indicating that the adsorption process is favourable [11-15].

Table 1 Results of correlation analysis of adsorption data for the removal of Hg (II) ions by adsorption on CAC and EGBC

Correlation Analysis	CAC	EGBC
Freundlich isotherm		
Correlation coefficient (r)	0.993	0.944
Slope (1/n)	0.492	0.227
Intercept (log K)	1.375	1.078
Δq (%)	0.143	0.114
Langmuir isotherm		
Correlation coefficient (r)	0.945	0.991
Slope (1/n)	0.004	0.249
Intercept (log K)	0.098	1.856
Q_o (mgg^{-1})	252.01	4.014
b value (Lmg^{-1})	0.041	0.134
R_L	0.080	0.077
Δq (%)	17.89	12.25

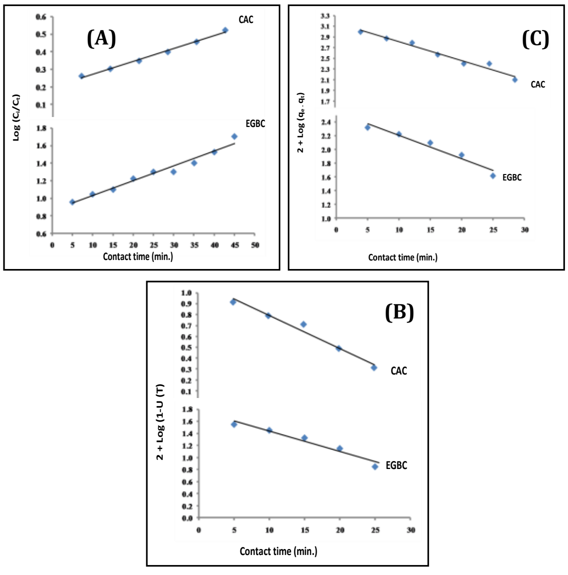

Fig. 3 (A) Natarajan-Khalaf; (B) Lagergren and (C) Bhattacharya-Venkobachar Kinetic equations for the removal of Hg(II) ions by adsorption onto CAC and EGBC at 30±1 °C

3.2 Effect of Contact Time

3.2.1 Kinetics of Adsorption

In order to study the kinetics of adsorption of Hg(II) ions, the batch type adsorption experiments were carried out by varying contact time at optimum initial concentration of Hg(II) ions and fixed dose of adsorbent 4 g/L of CAC and 12 g/L of EGBC at 30 °C. The boundary layer resistance which affect the rate of adsorption. Increase in contact time will reduce the mobility of the adsorbate [Hg(II) ions] in the adsorption system. In order to find out the nature and order of kinetics of adsorption in the present study, the applicability of various first order kinetic equations such as Natarajan-Khalaf, Lagergren and Bhattacharya –Venkobhachar equations was tested. The kinetic plots (Fig. 3) observed to be linear and the computed *r* (correlation coefficient) values which are very close to unity (range of *r* values: 0.986-0.990) as shown in Table 2 indicate the applicability of these first order kinetic equations and the first order nature of the adsorption process of metal ions.

The minimum and maximum values of first order rate constants (k, min^{-1}) are noted for Hg(II)–CAC (3.344-6.251 min^{-1}) for Hg(II) – EGBC (2.209-6.074 min^{-1}) system, respectively. This indicates that the removal of Hg(II) ions by EGBC is maximum and CAC is minimum [16-20].

Table 2 Kinetics and dynamics of adsorption of Hg (II) ions by CAC and EGBC

Parameter	CAC	EGBC
Natarajan Khalaf Equation		
Correlation coefficient (r)	0.986	0.990
10^2 k (min^{-1}.)	3.344	2.209
Δq (%)	34.49	27.22
Lagergren Equation		
Correlation coefficient (r)	0.978	0.991
k (min^{-1}.)	6.251	6.074
Δq (%)	17.00	10.69
Bhattacharya and Venkobachar equation		
Correlation coefficient (r)	0.978	0.991
k (min^{-1}.)	6.251	6.074
Δq (%)	18.96	19.66
Intra – Particle diffusion model		
Correlation coefficient (r)	0.988	0.992
K_p (mgg^{-1} $min^{-0.5}$.)	2.395	0.615
Δq (%)	39.63	8.535
Intercept	106.15	2.309
Log(%R) vs Log (Time)		
Correlation coefficient (r)	0.988	0.985
Δq (%)	115.59	101.06

3.2.2 Intra–Particle Diffusion Model

In diffusion controlled adsorption process, the amount of solute adsorbed is calculated using the following equation.

$$(x/m) = K_p t^{1/2} + C \quad (5)$$

Where, C=constant (intercept); K_p = intra- particle diffusion coefficient ($mgg^{-1}min^{-1}$)

The plots of (x/m) *vs* $t^{½}$ and Log (% removal) *vs* log (T) are showed in linear curve (Fig. 4). It indicates that the intra particle diffusion is the significant rate limiting step in the adsorption process, under the given set of experimental conditions. The minimum and maximum values of intra particle diffusion rate constant (K_p, mgg^{-1} min^{-1}) are noted for Hg(II)– CAC and for EGBC as 2.395 and 0.615, respectively.

The minimum and maximum values of intercept (C) of intra particle diffusion plots are noted for Hg(II) – EGBC (2.309) and Hg(II) – CAC (106.15) systems. The correlations of the values of log (% removal) and log (time) for CAC is 0.988 and for EGBC is 0.985.

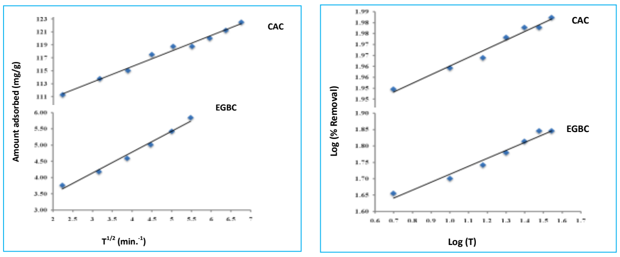

Fig. 4 Intra-particle diffusion model (A) Amount adsorbed *vs* $t^{1/2}$ ($min.^{-1}$) and (B) Log (% Removal) *vs* Log (T) for the removal of Hg(II) ions by adsorption onto CAC and EGBC at 30±1 °C

3.3 Effect of Dose of Adsorbent

The adsorption data for the removal of Hg(II) ions by adsorption on CAC and EGBC with different doses of adsorbents (range 3-4.8gL^{-1} for CAC & 2-20 gL^{-1} for EGBC) at constant optimum initial concentration of Hg(II) ions and contact time and constant initial pH are presented Fig. 5. The percentage removal of Hg(II) ions is found to increase with the increase in dose of adsorbent, which may be due to the increase in availability of active adsorption sites. This may be due to the increase in the increase in effective surface area resulting from the conglomeration of adsorbent particles, especially at higher doses of adsorbents [21-23]. The optimum values of dose of adsorbents are 4 gL^{-1} for CAC and 12 gL^{-1} for EGBC.

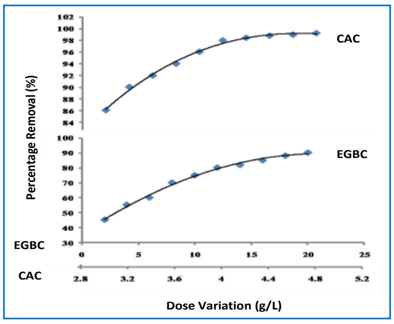

Fig. 5 Effect of Dose of adsorbent for the removal of Hg(II) ions by adsorption onto CAC and EGBC

Effect of adsorbent dose on adsorption rate was also studied and found that, the rate of adsorption of metal ions depends on the driving force per unit area and in this case since, initial concentration of metal ions is constant, the increase in the dose of adsorbent increases the surface area for adsorption and hence the rate of adsorption of metal ion is also increased. This suggests that the adsorbed metal ions may either blocked the access to the internal pores or caused particles to aggregate there by reducing the active sites availability [21-23].

3.4 Effect of Initial pH

The adsorption of Hg(II) ions on CAC and EGBC at different initial pH values at constant optimum initial concentration of Hg(II) ions dose of adsorbent, contact time was also studied, in order to find out the variation in adsorption potential of CAC and EGBC as a function of initial pH in adsorbing the metal ions. The process of adsorption of Hg (II) ions is found to be pH dependent. The variation in percentage removal of Hg(II) ions by adsorption on CAC and EGBC with initial pH are shown in Fig. 6.

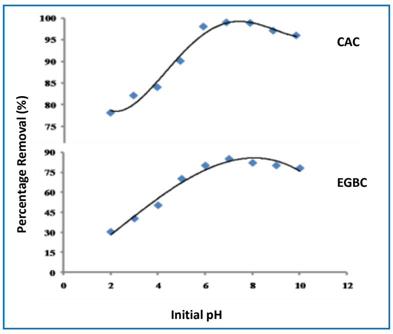

Fig. 6 Effect of Initial pH for the removal of Hg(II) ions by adsorption onto CAC and EGBC at 30±1 °C

It was observed from the figure that the removal of Hg(II) ions is maximum in slightly basic medium there after it decreases with increase in initial pH. After pH 7.6, the precipitation starts and hence percentage removal decreases. Hence, the optimum pH was fixed as 7 for both CAC and EGBC. The pH affects the charge on the surface of the adsorbent, altering its capability to adsorb adsorbate molecules or ions adsorbate molecules or ions/ species. The slightly basic medium is highly favorable for the removal of Hg (II) ions [24, 25].

4. Conclusion

The present study deals with the removal of Hg(II) ions on commercially activated carbon and *Eucalyptus globules* bark carbon by batch adsorption technique. The percentage removal of Hg(II) ion on these adsorbents (CAC and EGBC) is found to decrease with increase in initial concentration of metal ions , which is due to the lack of available sites. Langmuir and Freundlich Isotherm models were tested and found to be applicable. Monolayer adsorption of Hg(II) ions occur on the surface of the adsorbents. Monolayer adsorption capacity was determined and found to be maximum in CAC. Adsorption data are modeled with various first order kinetic equations like Natarajan-Khalaf, Lagergren and Bhattacharya and Venkobachar equations. The intra particle diffusion model is found to be applicable. This indicates that the Hg(II) ions adsorption on CAC and EGBC is first order with the intra-particle diffusion as one of the rate determining steps. The percentage removal of Hg(II) ions by adsorption exponentially increases, while the amount of Hg(II) ions adsorbed per unit mass of adsorbent . The process of removal of Hg(II) ions by adsorption on CAC and EGBC is found to be highly pH dependent. The results of the present study concluded that from the economic point of view, EGBC is better cost–effective adsorbent, even though its adsorption capacity is slightly lesser than CAC.

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