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Sorption equilibrium studies of iron, copper and cobalt using activated carbon prepared from morinda pubescences linn, in aqueous medium

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ABSTRACT

Morinda pubescence Linn a commonly found herbal plant was used to prepare activated carbon by physicochemical activation method. The sorption capacity of this bio-resource material to remove Fe(III), Cu(II) and Co(II) from aqueous solutions were determined by batch tests. The influences of important parameters such as contact time, dosage, pH, pH zpc, co-ions and temperature on metal adsorption process were also investigated. The equilibrium data were fitted to Langmuir and Freundlich isotherms. The batch adsorption rate for the sorption process was explained on the basis of intraparticle diffusion. Various thermodynamic parameters like ΔG^0 , ΔH^0 and ΔS^0 were analyzed to observe the nature of adsorption. The metal adsorption process on the surface of adsorbent was verified as a surface phenomenon by performing SEM and XRD analysis.

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KEYWORDS

Adsorption;
Activated carbons;
Langmuir;
Freundlich isotherm;
Intraparticle diffusion.

INTRODUCTION

Metals can be distinguished from other toxic pollutants, since they are not biodegradable and can be accumulated in living tissues, causing various diseases and disorders. Conventional methods for removing metals from industrial effluents include chemical precipitation, coagulation, solvent extraction, electrolytic processes, membrane separation, ion exchange, reverse osmosis, ultra filtration, biological systems and adsorption^[1]. Adsorption processes for removal of metals have been found cheaper and more effective than the several technologies^[2]. Numerous by products of agro-industrial productions and agricultural by-products have been studied for potential use as inexpensive sorbents^[3]. Many examples are available in the literature concerning the direct or activated use of these materials as adsorbents^[4,5,6]. This study deals with the investigation

of Fe(III), Cu(II) and Co(II) removal from aqueous solutions by adsorption on activated carbon prepared from Morinda pubescence Linn (MP).

EXPERIMENTAL

The preparation of activated carbon from MP consisted of carbonization of the plant material. Dried raw barks were cut into small pieces and the carbonization was conducted in a muffle furnace at 400°C for 2 hours. After carbonization, the carbon was ground using domestic mixie. The activated carbon obtained was kept in a desiccator and were characterized for the physical parameters which are given in TABLE 1. Adsorption equilibrium study of these metal ions was carried out in 250ml stoppered Iodine flask. The concentration of the metal ions was determined by UV/ Visible spectrophotometer (UV 240 Shimaduzu). All other water quality

TABLE 1: Characteristics of the activated carbon

S.no	Parameters	Morinda pubescence Linn
1	Particle size (mm)	0.14
2	Density (g/cc)	0.58
3	Ash content (%)	2.11
4	Moisture content (%)	1.50
5	Loss of ignition (%)	88.3
6	Water soluble matter	0.24
7	pH of aqueous solution	7.0
8	pH (zpc)	6.7
9	Iodine number (mg/g)	190

parameters were analyzed by using standard methods^[7]. The pH measurements were done with a pH electrode (Systronics) and pH_{ZPC} (pH of zero point charge) was determined by pH drift method^[8]. The surface morphology of the raw and treated activated carbons was visualized by SEM with a HITACHI-S-3000H model. XRD pattern was recorded using X¹ per PRO (model), PAN analytical (make). Computations were made using Microcal Origin, (version 6.0) software.

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time on the adsorption of iron(III), copper(II) and cobalt(II) with 50ml of 20 ppm of each metal ion solutions were studied using MP. Figure 1 shows the effect of contact time on adsorption of the adsorbent. The results show that the percentage of metal ion adsorption increased with increasing time of equilibration. This study does not claim any kinetic evaluation of adsorption process, but it has shown that the equilibrium was attained.

Effect of dose

The effect of the activated carbon MP dose on the removal of metal ions is shown in figure 2. A significant increase in percent removal with increase in dosage of activated carbons was done to bring down the metal ions level to its tolerance limit. The adsorption increased from 35 to 95 percentages with increase in adsorbent dose from 50 mg to 500mg.

Effect of pH

The pH dependence of iron(III), copper(II) and cobalt(II) take onto MP is shown in figure 3. The pH of the aqueous solution was clearly an important parameter that controlled the adsorption process. It is well known that these metal ions undergo hydrolysis reactions in water and form insoluble complexes with in-

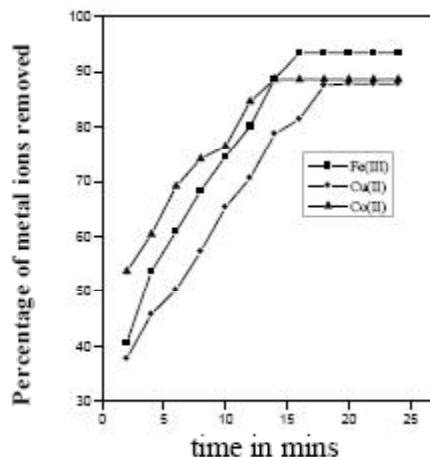


Figure 1: Effect of contact time for MP

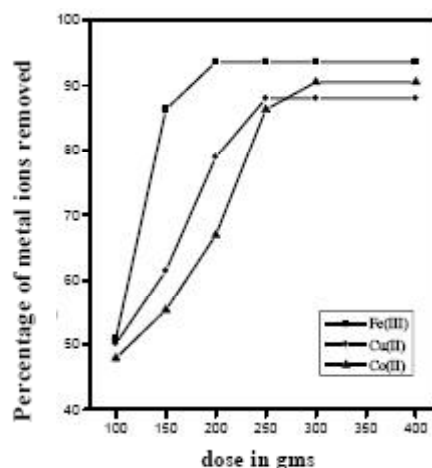


Figure 2: Effect of dose for MP

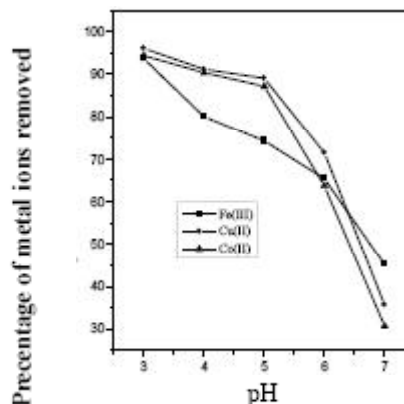


Figure 3: Effect of pH for MP

creasing pH. This phenomenon is conceded as important for understanding the adsorption behaviour of all metal ions onto these activated carbons. Up to pH 5.0 due to the presence of H⁺ ions of the acid used for adjusting pH. However, this effect causes in the pH range of 5.0-7.0^[9].

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Effect of Co-ions

The influence of other co-ions such as Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , Ca^{2+} and Mg^{2+} which are commonly present anions and cations in water was investigated viz., 200,400,600,800 and 1000 mg/L concentrations on the adsorption of iron(III), copper(II) and cobalt(II) by the adsorbent. Figure 4 gives the effect of co-ions on the adsorption of copper(II) as representative plot. In all the cases, the presence of these co-ions did not significantly alter the metal ions adsorption process by the activated carbon.

Adsorption isotherms

Equilibrium data are basic requirements for the design of adsorption systems and adsorption models are used for the mathematical description of the adsorption equilibrium of the metal ions on to the adsorbent. The results obtained on the adsorption of iron(III), copper(II) and cobalt(II) were analyzed by the well-known models given by Langmuir and Freundlich^[10].

Langmuir isotherm

The linear form of Langmuir isotherm equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (1)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption. The Langmuir curves pertaining to the Cu(II) adsorption by MP is provided in figure 5 as representative plot. The Langmuir constants b and Q_0 were calculated from equation (2) and the values are given in TABLE 2. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) which is defined by,

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

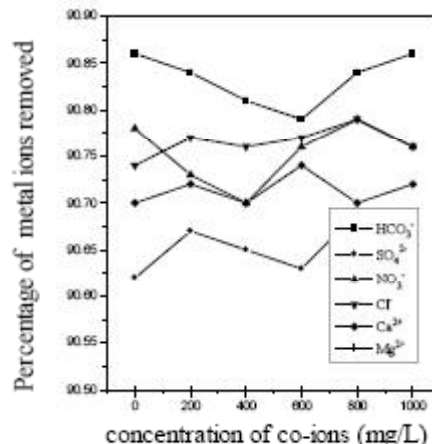


Figure 4: Effect of co-ions for MP

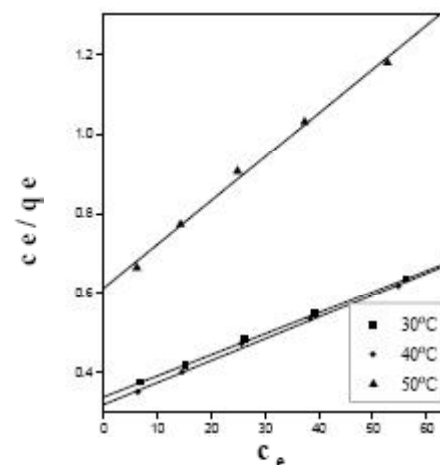


Figure 5: Langmuir plot for Cu(II)

where b is the Langmuir constant and C_0 is the initial concentration (mg/L). The value of R_L indicates the type of the isotherm to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The value of R_L was found to be less than one and this again confirmed that the Langmuir isotherm model was favourable for adsorption of metal ions onto the activated carbon under the conditions used in this study.

Freundlich isotherm

TABLE 2: Langmuir and Freundlich constants

Metal ions	Langmuir constants				Freundlich constants			
	Temperature	Q_0	b	R^2	R_L	$1/n$	K_f	R^2
Fe(III)	303	1.546	0.304	0.998	0.910	0.743	3.526	0.997
	313	1.557	0.3621	0.999	0.976	0.750	3.718	0.998
	323	1.569	0.4031	0.999	0.905	0.757	3.996	0.998
	303	1.181	0.157	0.999	0.968	0.742	3.554	0.998
Cu(II)	313	1.188	0.164	0.999	0.968	0.746	3.705	0.998
	323	1.194	0.180	0.999	0.965	0.754	3.967	0.999
	303	1.574	0.132	0.997	0.815	0.887	3.071	0.999
Co(II)	313	1.636	0.159	0.998	0.834	0.836	3.264	0.999
	323	1.762	0.168	0.999	0.853	0.811	3.697	0.999

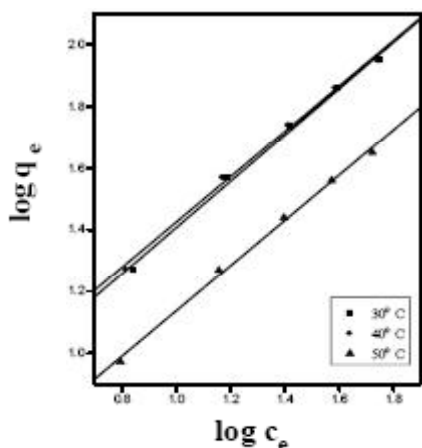


Figure 6: Freundlich plot for Co(II)

TABLE 3: Thermodynamic parameters for sorption of metal ions at 20 ppm

Metals	ΔG^0 (KJmol ⁻¹)			ΔH^0 (KJmol ⁻¹)	ΔS^0 (KJmol ⁻¹)
	303K	313K	323K		
Fe(III)	-2.50	-2.68	-2.94	+5.25	0.059
Cu(II)	-2.44	-2.26	-2.70	+4.89	0.073
Co(II)	-1.66	-1.26	-1.70	+9.57	0.084

The well-known logarithmic form of Freundlich isotherm is given by the following equation,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L) and q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). K_f and n are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively. The values of K_f and $1/n$ were obtained from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero^[11]. Freundlich constants K_f and n values were calculated and listed in TABLE 2 and a representative plot is given in figure 6.

Thermodynamic parameters

Thermodynamic parameters with the adsorption viz., standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated using the equation below and the values are given in TABLE 3.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where the ΔG^0 is the free energy of adsorption, T is the temperature and R the Universal gas constant. The adsorption distribution coefficient K_o for the adsorption reaction was determined from the slope of the plot $\ln(q_e/c_e)$ against C_e at different temperature and extrapolating to zero C_e according to method suggested by Khan and Singh (12). The adsorption

distribution coefficient may be expressed in terms of enthalpy change (ΔH^0) and entropy change (ΔS^0) as a function of temperature,

$$\Delta G^0 = -RT \ln K_o \quad (5)$$

Where the values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the plot of $\ln K_o$ against $1/T$ ^[13].

Intraparticle diffusion

From a mechanistic point of view, to interpret the experimental data, production of the rate-limiting step is an important factor to be considered in the sorption process. Though kinetic and equilibrium isotherm studies help to identify the adsorption process, predicting the mechanisms is required for design purpose. For a solid - liquid sorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. This is determined by plots of the amount of metal adsorbed against the square root of time, $t^{1/2}$ for three different temperatures. According to Weber, an intraparticle diffusion coefficient is defined by the equation.

$$q_t = K_p t^{1/2} \quad (6)$$

q_t = the amount of metal ions adsorbed per unit mass of adsorbents at any time t , $t^{1/2}$ =square root of time, K_p = Intraparticle diffusion rate constant

The plots of intraparticle diffusion curves shows initial curved portion followed by linear portion and a plateau. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption where the intraparticle diffusion is rate controlled. The third portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentration in solutions^[15]. The values of K_p are given in TABLE 4 and figure 7 shows Cu(II) intraparticle diffusion by MP as representative plot.

Instrumental analysis

SEM images of the activated carbon before and after of iron(III) sorption are shown in figure 8 as representative images. Comparison of these micro graphs before and after iron(III) sorption shows that the surface texture and porosity of the adsorbents has holes and small openings, which constitute the contact areas facilitating pore diffusion during adsorption of metal ions on the surface of the activated carbon. XRD patterns of the treated adsorbents showed significant changes.

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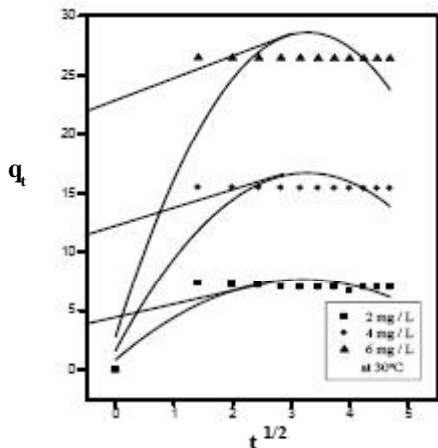


Figure 7: Effect of Intraparticle diffusion for MP

TABLE 4 : Values of K_p

Concentration of metal ions in ppm	Values of K_p		
	Fe(III)	Cu(II)	Co(II)
2	2.58	4.88	6.48
4	3.66	6.11	7.65
6	5.78	7.06	8.00

(a)



(b)



Figure 8(a): SEM for MP before treatment b) SEM for MP after treatment

The XRD data of the treated activated carbon provided evidence of decrease in the peak intensity at 2θ values which shows that adsorption of iron(III) on the surface of the adsorbent and at the same it dose not alter the crystalline structure of the material^[16]. Figure 9 indicate the decrease in the peak intensity values after adsorption of iron(III) on MP as representative.

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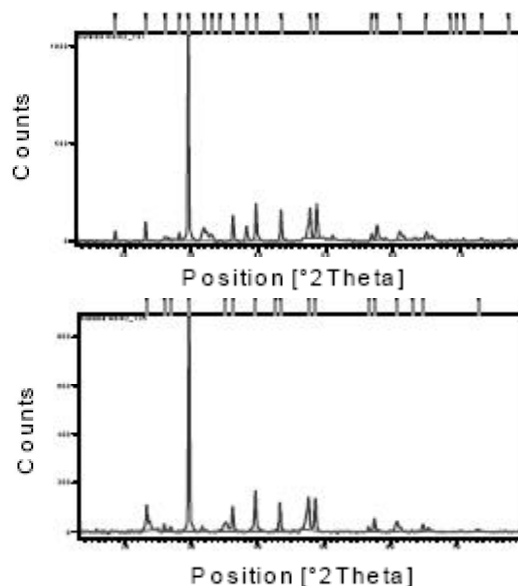


Figure 9(a): XRD for MP before treatment b) XRD for MP after treatment

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