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Research Paper

Kinetics of Batch Adsorption of Iron (II) ions from Aqueous Solution using Activated Carbon from *Glossocardia linearifolia* Stem

C. Jayajothi[1], M.M. Senthamilselvi[2*], S. Arivoli[3], N. Muruganantham[4]
[1]Periyar E.V.R. College, Tiruchirappalli, Tamil Nadu, INDIA
[2]Department of collegiate education, Tiruchirappalli, Tamil Nadu, INDIA
[3]Department of Chemistry, Thiru. Vi. Ka., Government Arts College Thiruvarur, Tamil Nadu, INDIA
[4]Department of Chemistry, Sri Ramakirshna College of Engineering, Perambalur, Tamil Nadu, INDIA

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Abstract: *Glossocardia linearifolia Stem obtained from nearby area of pudukkottai district, was activated around 600^o C and the particle size (53–150 µm) was used as an adsorbent for the removal of Fe (II) ion from aqueous solution. The effect of various factors (temperature, adsorbent dose and Initial pH) on adsorption of Fe (II) on Glossocardia linearifolia Stem was investigated. The effect of pH shows that the amount adsorbed increased with the increase of pH of solution. The equilibrium adsorption isotherms were analyzed by Langmuir and Freundlich equations. Both Langmuir and Freundlich models can describe the adsorption equilibrium but the Langmuir model shows better agreement. The amount adsorbed increased with the increase of temperature suggests the formation of dimer in the contact region. SEM micrographs and differential molar isosteric heat of adsorption (ΔH) calculated at different surface coverage, indicate that the surface is heterogeneous having energetically different adsorption sites. Values of n calculated from Freundlich plots indicate that adsorption of Fe (II) on Glossocardia linearifolia Stem is spontaneous. At high surface coverage, the differential heat of adsorption versus surface coverage plot shows maximum value indicating the occurrence of structural rearrangement in the adsorbate. With the increase of adsorbent dose, amount adsorbed increased due to the increased surface area of adsorbent.*

Keywords: Iron, Activated *Glossocardia linearifolia* Stem Carbon (AGLS), Adsorption models, Equilibrium.
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Introduction

Water is the main component for living organisms and the increase in water pollution as a result of progress in the industrial technologies, has been reduced using many methods to treat the wastewater[1]. The choice of suitable methods is controlled by different factors such as the efficiency of removing the pollutant materials, the availability of the chemicals used and the chemistry of the contaminated materials beside the process cost[2]. It is well–known that the pollutants are the wastewater discharge from industrial effluents, sewage, sludge, pesticides, and fertilizers. The composition of the contaminated water depends on the source of the pollutant, the chemical composition of the original water whether it is surface or underground water and also the chemical reaction taking place with the soil. For example, groundwater contains one or more contaminants like iron, manganese, ammonium, methane and natural organic matter, e.g., humic acid. Hence, before using this water supply for agro-irrigation purposes, these contaminants should be removed or reduced to the acceptable levels. Iron and manganese, which are usually present in the groundwater as divalent cations, considered to be contaminants mainly due to their organoleptic properties. The maximum recommended levels of Fe in drinking water are 0.3 mg/L, respectively. There are various methods for removing Fe (II) cations from the wastewater including ion-exchange method, oxidation by oxidizing agents such as chlorine and potassium permanganate, activated carbon and/or other filtering materials, supercritical fluid extraction, bioremediation and treatment with limestone[3-9]. Some of these methods are simple and economic while the others are complicated and expensive. In oxidation treatment, oxygen, chlorine or potassium permanganate ($KMnO_4$), is generally used for Fe(II) oxidation. Adsorption using activated carbon is an effective technique to remove heavy metals from wastewater that is due to that activated carbon has a pore size distribution which controls its adsorption capacity, a chemical structure that influences its interaction with polar and non-polar adsorbate, and active sites which determine the type of chemical reactions with other molecules[10-11].

However, in developing countries such as India, traditional activated carbon remains an expensive material for heavy metal removal. Recently, many researchers have been published in the literature including preparation of activated carbons from various cheaper and alternative materials, e.g., agricultural by-products and biomass materials, using chemical activation with H_3PO_4[12-14]. However, there is only limited research on the preparation of activated carbons from woody biomass such as sawdust for uptaking heavy metals such as Hg (II) from wastewaters[15,16].

Various authors found that the removal of iron and other heavy metals by activated carbon depends on the nature of carbon (porosity, surface area, oxygen functional groups, etc.). Within the frame of this policy, the present paper narrates the investigation of Fe(II) ions removal from aqueous solution using adsorption methods in order to determine the optimum pH for the effective removal. The adsorption was carried out using an activated carbon obtained from *Glossocardia linearifolia* Stem. The adsorption data was analyzed by using Langmuir and Freundlich isotherm models. Overall, this study was also intended to determine the efficiency and the optimum conditions in adsorption processes for removal of iron cations.

Material and Methods

Adsorbent

The natural plant material *Glossocardia linearifolia* Stem, used in the present investigations was collected from agricultural area. The stems were washed with distilled water several times to remove the dirt and dust and were subsequently dried in a hot air oven at 110^0C. Afterward, carbonization of the *Glossocardia linearifolia* Stem was done and activated at 600^0C for 1 hour in a muffle furnace. The activated carbon was thereafter Cooled to room temperature in an insert atmosphere of nitrogen and washed with hot distilled water and 0.5 N Hydrochloric and until the pH of the material reached 7.0 the activated carbon was also dried in a hot air oven at 110^0C, ground and sieved to obtain the desired particular size (150µm) and stored in desiccators for further use.

Chemicals

All chemicals used of high purity commercially available Analar grade purchased from scientific equipment company Trichy. Iron solution was prepared from $FeSO_4.7H_2O$ (2.489 g in 500 ml distilled water equivalent to one g/l). All experimental solutions were prepared by diluting the stock solution to the required concentration. The pH of each experimental solution was adjusted to the required initial pH value using dilute HCl (or) NaOH before mixing the adsorbent. The concentration of residual Iron(II) was determined with atomic absorption spectrophotometer (Perkin Elemer 2380).

Batch experiments

The effect of various parameters on the removal of Iron(II) onto AGLS was studied. Batch adsorption experiments were conducted at (30-60°C). For each experimental run, 50 ml of iron solution of known initial concentration and pH were taken in a 250 ml plugged conical flask. A 25 mg adsorbent dose is added to the solution and mixture was shaken at constant agitation speed (200 rpm). Samples were withdrawn at appropriate time intervals (10-60 min) and the adsorbent was separated by filtration. The residual solutions were analyzed to determine the Iron (II) concentration. The effect of dosage of adsorbent on the removal of Iron (II) was measured by contacting 50 ml of 50 mg/L of Iron (II) solution with 25 mg of AGLS till equilibrium was attained.

Adsorption equilibrium isotherm is studied using 25 mg of AGLS dosage per 50 ml of Iron (II) solution. The initial concentration were ranged from (25 to 125 mg/L) in all sets of experiments. The plugged conical flask was shaken at a speed of 200 rpm for 60 minutes. Then the solution was separated from the mixture and analyzed for Iron (II) concentration. The adsorption capacity was calculated by using a mass equilibrium equation as follows:

$$q_e = (C_0 - C_e)\, V/M \quad \ldots\ldots (1)$$

Where C_0 and C_e being the initial iron concentration (mg/L) and equilibrium concentration, respectively V is the experimental volume of Iron (II) solution expressed in litre [L] and M is the adsorbent mass expressed in gram [g]. The Iron (II) ions percentage can be calculated as follows:

$$\%R = (C_0 - C_t) \times 100/C_0 \quad \ldots\ldots (2)$$

The effect of pH on the rate of adsorption was investigated using iron concentration of 25 mg/L constant AGLS dosage. The pH values were adjusted with dilute HCl and NaOH solution. The adsorbent – adsorbate mixture was shaken at room temperature using agitation speed (200 rpm) for 60 minutes. Then the concentration of Iron in solution was determined.

Results and Discussion

The different chemical constituents of activated *Glossocardia linearifolia* Stem are given in Table 1 along with some other characteristics. X-ray spectra of both adsorbents befour and after adsorption do not show any peak indicating the amorphous nature of activated *Glossocardia linearifolia* Stem.

Glossocardia linearifolia

Adsorption studies

Batch experiments were performed to investigate the adsorption process of Fe(II) by the AGLS. For each experimental run, 50 mL of Fe(II) solution of known concentration, initial pH, ionic strength and the amount of the AGLS were taken in a 250 mL stopper conical flask. This mixture was agitated in a temperature-controlled shaking water bath at a constant speed of 200 rpm/min. For adsorption equilibrium studies, Fe(II) solutions of different concentrations were contacted with a certain amount of AGLS under certain conditions for an hr. Ensuring the achievement of equilibrium, the residual Fe(II) concentration was measured and the amount of Fe (II) adsorbed onto AGLS was calculated from mass balance. Effects of contact time, adsorbent dosage, initial Fe(II) concentration, initial solution pH, ionic strength and temperature on Fe(II) adsorption by AGLS were investigated. Adsorption kinetics was determined by analyzing adsorptive uptake of Fe(II) from aqueous solution at different time intervals[18]. The amount of Fe (II) adsorbed at time t, q_t (mg/g), was calculated using mass balance equation.

Table 1: Characteristics of the Adsorbent

Properties	AGLS
Particle size(mm)	0.015
Density (g/cc)	0.2005
Moisture content (%)	0.2527
Loss in ignition (%)	0.021
pH of aqueous solution	5.2

Table 2: Equilibrium parameters for the adsorption of iron (ii) ion onto AGLS

M_0	Ce (Mg / L)				Qe (Mg / L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	3.64	3.03	2.54	2.73	92.70	93.92	94.90	94.52	92.72	93.92	94.90	94.52
50	11.43	10.46	8.47	7.56	177.1	179.0	183.0	184.8	88.56	89.53	91.52	92.43
75	25.74	22.36	19.64	17.36	248.5	255.2	260.7	265.2	82.83	85.08	86.90	88.42
100	47.84	43.64	19.64	36.67	304.3	312.7	360.7	326.6	76.07	78.17	90.17	81.66
125	73.88	69.93	40.64	60.90	352.2	360.1	418.7	378.19	70.44	72.02	83.74	75.63

Effect of Contact Time on batch Adsorption of Iron (II) ions in Aqueous Solution

Figure 1 shows the effect of contact time on the adsorption of Iron (II) ions solution using activated arbon from *Glossocardia linearifolia* Stem. The concentrations of iron (II) ions in solution were varied from 25mg/L to 125mg/L and batch adsorption was carried out with 25mg of activated *Glossocardia linearifolia* Stem. The percentage of iron (II) ions adsorbed increased with time until equilibrium was reached for each concentration. It is therefore evident from Figure 1 that at low concentration ranges the percent adsorption is high because of the availability of more reactive sites.

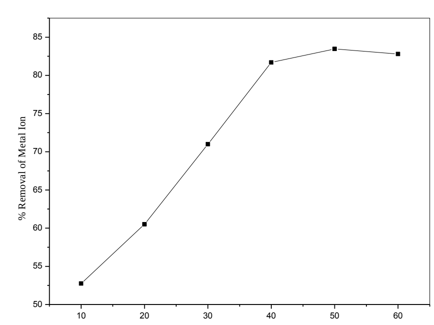

Figure 1: Effect of Contact Time on the Removal of Metal ion[M]=50mg/L, adsorbent dose=25mg/50ml, pH-6.5,Temp 30^{0}C

At higher concentration of metal ion more and more surface sites are covered, the capacity of the adsorbent get exhausted due to non-availability of active surface sites. This leads to a fall in the percentage of metal ion adsorbed at higher concentration[19]. It was observed that the percentage adsorption of iron(II) ion rapidly reached equilibrium at 30 minutes of contact for 25mg/L concentration, it increased to 100% implied that iron(II) (Fe^{2+}) ion was completely removed from aqueous solution at this concentration.

Effect of Initial Concentration on the Adsorption of Iron (II) Ion in Aqueous Solution

The effect of initial concentration of iron(II) ions on adsorption of iron(II) ions using *Glossocardia linearifolia* Stem activated carbon. Adsorption of iron(II) ions in solution increase significantly with reduction in the initial concentration of iron(II) ions in solution. The initial concentration of adsorbate varied from 25mg/L to 125mg/L. The rate of adsorption decreased from 92% - 70% as the concentration of iron(II) ions increased from 25mg/L to 125mg/L within 30 min of adsorption. This is attributed as the initial concentration of metal ion increases, the available reactive sites on AGLS decreases.

Effect of Carbon Dosage on the Batch Adsorption of Iron (II) Ions in Aqueous Solution

Iron(II) ions in aqueous solution of known concentration was adsorbed using different carbon dosage of activated *Glossocardia linearifolia* Stem ranging from 25mg – 125mg in 50 ml of stock solution of iron(II) ions. The effect of carbon dosage on the adsorption of iron(II) ions using activated carbon from waste *Glossocardia linearifolia* Stem is presented in Figure 2.

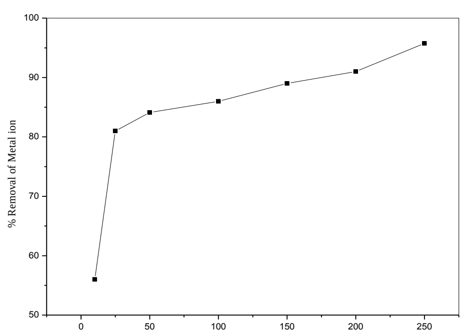

Figure 2: Effect of adsorbent dose on the removal of Metal Ion [M]=50mg/L: Contact time=60 min: pH=6.5: Temp 30^{0}C

There was significant increase in the adsorption of iron (II) ions in solution as carbon dosage increased within adsorption time of 30min[14]. This is due to the increased availability of active adsorption sites arising due to the increase in effective surface area resulting from the increases in dose of adsorbent or due to conglomeration of the adsorbent. Further, it was found that the optimum uptake of iron(II) ions requires about 250 mg of activated carbon from *Glossocardia linearifolia* Stem to adsorb 100% iron(II) ions in aqueous stock iron(II) solution.

Effect of Particle Size on the Batch Adsorption of Iron (II) ions in Aqueous Solution

Effect of particle size of activated carbon produced from waste *Glossocardia linearifolia* Stem on the batch adsorption of iron(II) ions in aqueous solution was studied. The adsorption of iron(II) ions increased with reduction in particle size[19]. This study revealed that particle size of activated *Glossocardia linearifolia* Stem carbon has significant effect on the adsorption of iron(II) ions in aqueous solution. Smaller particle size ($\leq$ 150 μm) adsorbed the highest amount of iron(II) ions within 30 mins of adsorption.

Effect of pH on the Batch Adsorption of Iron (II) Ions in Aqueous Solution

The pH of the wastewater is one of the imperative factors governing the adsorption of the metal ions. The effect of pH was studied from a range of 2 to 6 under the precise conditions (at optimum contact time of 60 min, 200 rpm shaking speed, with 25mg of the adsorbents used, and at a room temperature of 30^{o}C). When activated carbon from *Glossocardia linearifolia* Stem was used as an adsorbent, it was observed that with increase in the pH (2-6.5) of the wastewater, the percentage removal of iron(II) ions increased up to the pH 6.5 as shown in figure 3. At pH 6.5, maximum removal was obtained for metal ions, with 92.72% removal of Fe(II). The increase in percentage removal of the metal ions may be explained by the fact that at higher pH the adsorbent surface are deprotonated and become negatively charged. Hence attraction between the positively metal cations occurred[20].

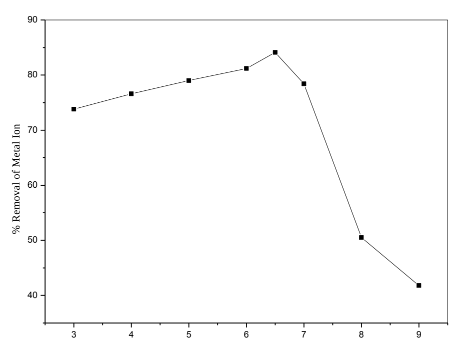

Figure 3: Effect of Initial pH on the removal of Metal Ionb[M]=50mg/L: Contact time=60 min: dose=25mg/50ml

Adsorption Models

The adsorption equilibrium data were further analyzed into two well known isotherm models via Freundlich and Langmuir models.

Freundlich model

The Freundlich model which is an indicative of surface heterogeneity of the adsorbent is described by the following equation.

$$\text{Log } q_e = \log k_f + 1/n + \log Ce \quad (3)$$

Where q_e is the amound of Fe(II) ions adsorbed per unit weight of the adsorbent (mg/l). K_f and 1/n are Freundlich constants associated with adsorption capacity and adsorption intensity respectively, The Freundlich plots between log q_e and log C_e for the adsorption of Fe(II) were drawn. It was found that correlation Co-efficient values were less than 0.99 at all the temperature studied indicating that Freundlich model was not applicable to the present study.

Langmuir model

The adsorption isotherm was also fitted to Langmuir model. The Langmuir equation which is valid for monolayer adsorption on to a surface is given below.

$$1/q_e = 1/q_m + 1/q_{mb}C_e \quad (4)$$

Where q_e (mgg^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mol L^{-1}), q_m (mgg^{-1}) is the Langmuir constant representing the maximum monolayer adsorption capacity and b (L mol^{-1}) is the Langmuir constant related to energy of adsorption. The plots $1/q_e$ as a function of $1/C_e$ for the adsorption of Fe (II) was found linear, suggesting the applicability of Langmuir model in the present adsorption system. The correction coefficient (R^2 = 0.9926 and 0.9932 at 30 & 60°C respectively for Langmuir model) confirm good agreement between both theoretical models and our experimental results. The values of the monolayer capacity (q_m) and equilibrium constant (b) have been evaluated from the intercept and slope of these plots and given in Table 3.

Table 3: Langmuir and freundlich isotherm parameters for the adsorption of iron (ii) ion onto AGLS

Temp. (°C)	Langmuir Parameters		Freundlich Parameters	
	Q_m	b	K_f	n
30°C	414.34	0.0662	1.748	2.2700
40°C	419.07	0.0766	1.791	2.3217
50°C	565.63	0.0634	1.758	1.8187
60°C	437.88	0.0931	1.833	2.2802

These facts suggest that Fe (II) is adsorbed in the form of monolayer coverage on the surface of the prepared adsorbent[21]. Satisfactory fitting of the Langmuir model to the adsorption of Fe(II) on activated *Glossocardia linearifolia* Stem adsorbent was noted.

Table 4: Dimensionless seperation factor (r_l) for the adsorption of iron (ii) ion onto AGLS

(C_i)	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.2318	0.2068	0.2395	0.1768
50	0.1311	0.1153	0.1360	0.0969
75	0.0914	0.0799	0.0950	0.0668
100	0.0701	0.0612	0.0730	0.0509
125	0.0569	0.0495	0.0592	0.0411

Kinetics study

The Kinetic adsorption data were evaluated to understand the dynamics of the adsorption reaction in terms of the order of the rate constant. Batch experiments were conducted to explore the rate of Fe(II) adsorption by *Glossocardia linearifolia* Stem as described in adsorption isotherms section at pH 6.5. Three kinetic models were applied to the adsorption kinetic data in order to investigate the behavior of adsorption process of Fe(II) onto the adsorbents. These models include the pseudo first order kinetics (reversible or irreversible), the pseudo – second – order and the intra particle diffusion models. The linear form of reversible pseudo – first – order model can be formulated as:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 x\ t \quad (5)$$

Where q_e (mol/g) and q_t (mole/g) are the amount of Fe (II) adsorbed at equilibrium and at time t, respectively and K_1 (min^{-1}) is the rate constant. K_1 values were evaluated from the linear regression of $\ln(q_e$-$q_t)$ versus data. Linear form of irreversible pseudo first order model can be formulated as:

$$\ln\left(C_o/C_t\right) = K \times t \quad (6)$$

Where C_o (mg/l) is the initial concentration of Fe (II) and C_t (mg/l) is equilibrium concentration of Fe (II) at time't' respectively, and K(g min^{-1}) is the rate constant Evaluation of data has been done using linear plot of ln (C_o/C_t) versus time. The Linear form of pseudo – second – order equation can be formulated us.

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (7)$$

Where q_e and q_t are surface loading of Fe(II) at equilibrium and time 't' respectively and K_2 (g/mg/min) is the second – order rate constant, The Linear plot of t/q_t as a function of provided not only the rate constant K_2, but also an independent evaluation of q_e. The fitting of experimental data to the pseudo – first – order and the pseudo – second- order equation seemed to be quite good and the calculated correlation coefficients (R^2) have almost the same values.

Table 5: Thermodynamic parameters for the adsorption of iron (ii) ion onto AGLS

(C_0)	ΔG^o				$\Delta H°$	$\Delta S°$
	30°C	40°C	50°C	60°C		
25	-5786.1	-6346.5	-6702.7	-6972.1	6.11	39.51
50	-4319.1	-4798.5	-5878.6	-6068.4	14.96	63.61
75	-3485.4	-3821.6	-4392.9	-4953.7	11.56	49.47
100	-2250.9	-2459.8	-5293.1	-3194.0	15.58	59.39
125	-1289.8	-1613.2	-3613.3	-2199.3	13.52	49.38

The Elovich equation and intra-particle diffusion model

The Elovich model equation is generally expressed as

$$dq_t / d_t = \alpha \exp(-\beta q_t) \qquad (8)$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation. Chien and Clayton (1980)[24] assumed $\alpha\beta t >> t$ and by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq.(10) becomes:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \qquad (9)$$

If Fe(II) ions adsorption fits with the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of (1/β)and an intercept of (1/β)ln (αβ).
The Elovich model parameters α, β, and correlation coefficient (γ) are summarized in Table 6.

Table 6: The kinetic parameters for the adsorption of iron (ii) ion onto AGLS

C_0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	K_2	γ	h	α	β	γ	K_{id}	γ	C
25	30	99.490	0.0018	0.994	19.52	818.20	0.0916	0.9959	1.7335	0.9981	0.1291
	40	100.17	0.0016	0.991	20.90	1203.6	0.0951	0.9968	1.7504	0.9975	0.1225
	50	100.73	0.0014	0.992	20.87	1901.9	0.1004	0.9982	1.7651	0.9969	0.1145
	60	100.07	0.0014	0.991	22.10	2783.7	0.1052	0.9948	1.7738	0.9973	0.1092
50	30	190.41	0.0021	0.992	34.85	1260.1	0.0468	0.9961	1.7045	0.9989	0.1329
	40	192.37	0.0020	0.991	35.97	1460.5	0.0471	0.9987	1.7145	0.9928	0.1302
	50	195.86	0.0018	0.993	38.53	1968.7	0.0478	0.9967	1.7332	0.9941	0.1251
	60	197.17	0.0017	0.991	40.57	2144.5	0.0477	0.9989	1.7400	0.9948	0.1242
75	30	266.65	0.0022	0.992	51.10	2109.2	0.0341	0.9959	1.6825	0.9952	0.1296
	40	273.50	0.0022	0.994	52.60	2279.9	0.0334	0.9984	1.6953	0.9983	0.1286
	50	280.24	0.0021	0.991	55.94	2501.0	0.0328	0.9967	1.7095	0.9960	0.1276
	60	282.68	0.0020	0.992	47.44	4605.9	0.0362	0.9983	1.7245	0.9940	0.1143
100	30	329.80	0.0024	0.994	54.09	1150.9	0.0248	0.9943	1.6127	0.9946	0.1472
	40	338.49	0.0024	0.995	56.28	1394.5	0.0248	0.9982	1.6317	0.9988	0.1429
	50	343.90	0.0011	0.997	59.50	1673.6	0.0249	0.9972	1.6468	0.9954	0.1393
	60	351.13	0.0023	0.999	66.09	2414.7	0.0254	0.9969	1.6716	0.9990	0.1324
125	30	385.32	0.0022	0.998	57.66	839.01	0.0199	0.9981	1.5570	0.9987	0.1600
	40	392.62	0.0025	0.997	61.02	1034.8	0.0201	0.9948	1.5764	0.9967	0.1545
	50	405.44	0.0016	0.998	58.86	843.37	0.0188	0.9994	1.5756	0.9961	0.1609
	60	410.50	0.0025	0.992	65.92	1286.2	0.0197	0.9972	1.6052	0.9952	0.1499

The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicate that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second–order kinetics models[22]. This may be due to increase in the numbers of pores or active sites on the AGLS adsorbent.

For adsorption of Fe (II) on to *Glossocardia linearifolia* stem the obtained results represent more conformity to pseudo-second order model (R^2 =0.95). Kinetic data for the adsorption of Fe(II) were also analyzed according to intra-particle diffusion model, which can be formulated as[25].

$$Qt = k_{pt} \, 0.5 \qquad (10)$$

Where q_t is the amount of Fe (II) adsorbed (mg/g) at time t, and k_p (mg/g $min^{0.5}$) is the rate constant for intra – particle diffusion. Results are shown in Table 6. Usually the plot of qt versus $t^{0.5}$ may be distinguished in two or more steps taking place during adsorption process including instantaneous adsorption stage by external mass transfer (first sharper portion), intra-particle diffusion which is the rate controlling stage (second portion as the gradual adsorption stage) and the final equilibration of stage where the intra – particle diffusion starts to slow down due to extremely low solute concentration in solution (the third portion).

Adsorption Thermodynamics

The thermodynamic parameters for the adsorption of Fe(II) ions by activated *Glossocardia linearifolia* Stem were determined using the following equations:

$$K_D = q_e/C_e \qquad (11)$$

$$\Delta G^o = -RT \ln K_D \qquad (12)$$

$$\ln K_D = (\Delta S^o/R) - (\Delta H^o/RT) \qquad (13)$$

Where K_D is the distribution coefficient for the adsorption in g/L, ΔG^o is the Gibbs free energy in J/mol, R is the universal gas constant in J/mol K, T is the absolute temperature in K, ΔS^o is the entropy change in J/mol K and ΔH^o is the enthalpy change in kJ/mol[23]. The values of Gibbs free energy change (ΔG^o) for various temperatures were calculated from the experimental data.

The values of enthalpy change (ΔH^o) and entropy change (ΔS^o) were estimated from the slope and intercept of the plot of ln K_D Vs 1/T. The estimated thermodynamic parameters were tabulated and shown in Table 5. The negative values of Gibbs free energy change (ΔG^o) obtained for the adsorption of Fe(II) ions by activated *Glossocardia linearifolia* Stem at various temperatures had shown the spontaneous nature of the adsorption process.

The positive values of enthalpy change ($\Delta H°$) obtained for the adsorption of Fe(II) ions by activated *Glossocardia linearifolia* stem at various temperatures indicated that the adsorption reactions were endothermic. The positive values of entropy change ($\Delta S°$) for the adsorption of Fe(II) ions by activated *Glossocardia linearifolia* Stem at various temperatures showed the increased randomness at solid liquid interphase during the sorption processes of Fe(II) ions on the adsorbent AGLS. This is a direct consequence of (i) opening up of structure of adsorbent beads (ii) enhancing the mobility and extent of penetration within the adsorbent beads and (iii) overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion[25].

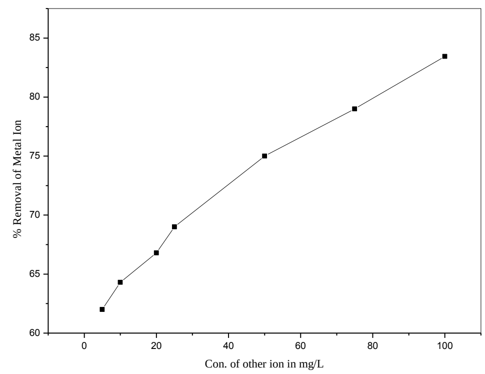

Figure 4: Effect ionic strength on the adsorption of Metal ion [M]=50 mg/L, Contact time=60 min, Dose=25 mg/50 ml

The adsorption of Fe(II) ions by Activated *Glossocardia linearifolia* Stems lightly increased when temperature was raised up to 60°C. It might be due to the generation of new active sites on the adsorbent surface and also due to the increased rate of pore diffusion. But when the temperature was further raised, adsorption processes had decreased largely. It showed that the adsorption processes of Fe(II) ions by activated *Glossocardia linearifolia* Stem were exothermic and physical in nature which involved the weak forces of attraction between the sorbate-sorbent molecules.

SEM Images of APSNC

The SEM images of AGLS (Figures 5a and 5b) shows the SEM micrographs of AGLS sample before and after dye adsorption. It is clear that AGLS has considerable numbers of heterogeneous layer of pores where there is a good possibility for Fe(II) ions to be adsorbed. The surface of metal-loaded adsorbent, however, clearly shows that the surface of AGLS is covered with metal ions.

Figure 5(a): SEM image of AGLS before adsorption

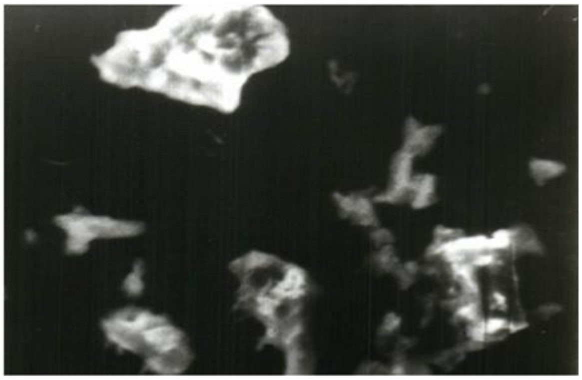

Figure 5(b): SEM image of AGLS after the adsorption of Fe (II) ions

Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. If the adsorbed metal ions can be desorbed using neutral pH water, then the attachment of the metal ion of the adsorbent is by weak bonds. The effect of various reagents used for desorption studies were studied. The results indicate that hydrochloric acid is a better reagent for desorption, because more than 92% removal of adsorbed metal ion was noticed. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the pH dependent results obtained. These desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the AGLS through physisorption as well as by chemisorptions mechanisms[20].

Conclusion

Kinetics of batch adsorption of iron (II) ions from aqueous solution using activated carbon from waste *Glossocardia linearifolia* Stem has been investigated. The amount of iron (II) ions adsorbed was found to vary significantly with process parameters such as particle size, carbon dosage, and initial concentration of adsorbate and contact time. The adsorption process follows Langmuir and Freundlich isotherms but a better sorption fit using Langmuir isotherm model was obtained indicating a monolayer formation over a surface of the material. The monolayer saturation capacity of 166.7 mg of iron (II) ions adsorbed per g of *Glossocardia linearifolia* Stem activated carbon was obtained and found to be higher than monolayer saturation capacity of other adsorbents used for iron (II) ions adsorption. Adsorption kinetics was modelled using the pseudo first order, pseudo second order kinetic equations, and intra-particle diffusion models. Sorption kinetics showed a good agreement of the experimental data. The pseudo second order kinetic reaction is the rate controlling step with some intra particle diffusion. The high adsorption intensity of *Glossocardia linearifolia* Stem activated carbon and its affinity for Iron(II) ions can help to solve many adsorption challenges in the industry and in water purification processes.

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