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Research Article

Cu^{2+} REMOVAL FROM AQUEOUS SOLUTION USING *SIDA CORDIFOLIA* STEM ACTIVATED CARBON BY BATCH TECHNIQUE

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ABSTRACT

The importance on the removal of Cu^{2+} from the aqueous solution using activated *Sida cordifolia* carbon is narrated elaborately in the present study. The parameters studied included contact time, adsorbent dose, initial pH and other ionic effects. Freundlich and Langmuir isotherm models were applied to the equilibrium experimental data. The maximum adsorption capacity (q_m) obtained from the Langmuir isotherm linear plots were 62.548, at an initial pH of 6.8 at 30°C. Thermodynamic data indicated that the process was endothermic, spontaneous and feasible. The adsorption followed pseudo second order reaction equation and the rate is mainly controlled by intra-particle diffusion. As a result, ASCC could be an important low-cost adsorbent for removal of $Cu^{2+}$from aqueous solution.

Keywords: Activated *Sida cordifolia* Carbon (ASCC), Copper bivalent ions (Cu^{2+}), Batch method, Adsorption isotherm, Kinetics, Thermodynamic parameters.

1. INTRODUCTION

The presence of heavy metals in the aquatic environment is one of the major distresses because of their toxicity and threat to human life and the environment. Wastewater from industries releases into nearby land or rivers without any treatment because the conventional treatment methods are not cost effective in the Indian context [1-3]. On the other hand, low cost technologies never allow a wishful metal ion removal and it has certain disadvantages. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different metal ions, recognizing the economic drawback of commercial activated carbon [4, 5]. Many investigators have studied the feasibility of using inexpensive alternative materials for the removal of metals from water and wastewater [6, 7].

In this present study, the removal of Cu^{2+} using activated carbon prepared from the stem of *Sida cordifolia*. The kinetic and equilibrium adsorption data obtained were utilized to illustrate the sample systematized. The literature survey shows that no work has been done so for lift up the *Sidacordifolia* as an adsorbent on this present carbon.

2. EXPERIMENTAL

2.1. Preparation of adsorbate

All the reagents used in the experiments were of analytical (AR) grade and were obtained from scientific equipment company Trichy. The stock solution was prepared by dissolving required amount of copper sulphate ($(CuSO_4).5H_2O$) in 1000 mL of double distilled water. All experimental solutions were prepared by diluting the stock solution to the essential concentration.

2.2. Preparation of adsorbent

The natural plant material of *Sidacordifolia* used in the present investigations was collected from a nearby Poompuhar area as shown in fig. 1. The stem was washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110°C. Afterward, carbonization of the stem was carried out by adding w/v ratio Conc. H_2SO_4 to get the primary carbon. The primary carbon was activated at >900°C for 6 hrs under optimized conditions to obtain the activated carbon.

2.3. Batch Method

The metal ions solutions were made to a known concentration such as, 50 ml of 10, 20,30, 40 and 50 mg/L and added with the 25 mg of activated carbon adsorbent (ASCC). Then these were agitated by shaker at 30, 40, 50, and 60°C in defined time intervals. The samples were withdrawn and filtered and were then analyzed in UV-Visible spectrophotometer. The effect of initial pH on Cu^{2+}removal was studied over a pH range of 3.0-9.0 and the pH of metal ion solution was adjusted using addition of diluted hydrochloric acid or sodium hydroxide solution. The effect of adsorbent dose on the removal of Cu^{2+} was investigated using the procedures described above with different adsorbent dosage like 10, 25, 50, 100, 200 and 250 mg. All the other parameters kept constant. The amount of adsorption at time t, q_t (mg/g), can be determined using the following formula [8, 9].

$$q_t = V \times \frac{(C_0 - C_t)}{w} \tag{1}$$

Where, $q_{(t)}$ is the mass of adsorbedCu^{2+} per unit mass of adsorbent (mg g^{-1}), C_0 and C_t are the initial and actual concentration (g dm^{-3}) of Cu^{2+} at time, respectively V is the volume of the treated solution (L),'w' is the mass of ASCC (g). The removal percentage of Cu^{2+} can be calculated as following relationship,

$$\% \text{ Removal} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{2}$$

Fig. 1: ***Sida cordifolia***

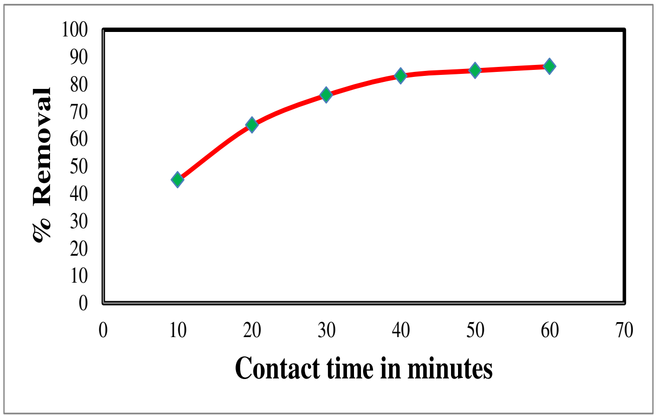
3. RESULTS AND DISCUSSION

3.1. The effective parameters study

The effect of contact time [10] on the adsorption capacity of ASCC for Cu^{2+} was evaluated. The equilibrium data given in table 1 and fig. 2 clearly shows that the removal of Cu (II) increases at the initial period of contact time with maximum of the adsorption was complete within 40 minutes. Equilibrium was achieved within 50 minutes, for that reason an equilibration period of 60 minutes was selected for all forthcoming experiments.

Table 1: Equilibrium parameters for the adsorption of Cu^{2+}onto ASCC

C_0	Ce (Mg / L)				q_e (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
10	2.58	2.09	1.40	1.33	14.83	15.81	17.20	17.35	74.17	79.06	86.02	86.73
20	5.49	4.99	4.51	3.49	29.03	30.02	30.98	33.02	72.57	75.06	77.46	82.54
30	11.40	10.87	9.47	8.78	37.19	38.25	41.05	42.44	61.99	63.76	68.42	70.74
40	17.49	16.00	15.18	14.24	45.01	48.00	49.65	51.53	56.26	60.00	62.06	64.41
50	25.93	25.03	24.48	23.02	48.14	49.94	51.04	53.95	48.14	49.94	51.04	53.95



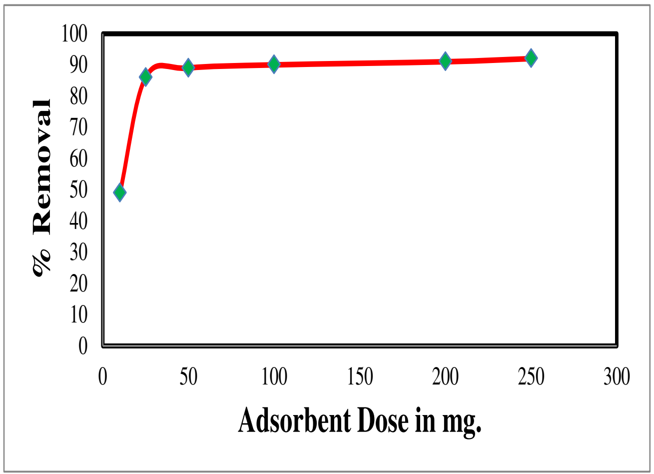
[Cu^{2+}]=25mg/L; Temperature 30°C; Adsor-bent dose= 0.025g/ 50mL.

Fig. 2: Effect of contact time on the removal of Cu^{2+}

The adsorption of the Cu^{2+} on ASCC was studied by varying the adsorbent dose [11] for 50 mg/L of Cu^{2+} concentration. The percentage of removal increased with increases in the ASCC dose, which is attributed to increased carbon surface area and the availability of more adsorption sites. The results obtained from this study are shown in fig. 3. The maximum of the removal percentage was attained in 25 mg, hereafter slightly increase for adsorption for that effective reason lake of adsorbate. Therefore in this study, 25 mg of ASCC was chosen due its highest adsorption capacity.

The effect of pH [12] plays important role in adsorption therefore the effects of initial pH were studied in the pH range of 3-9 for removal of $Cu^{2+}$from aqueous solution. The percentage of removal increased around 53.95 % to

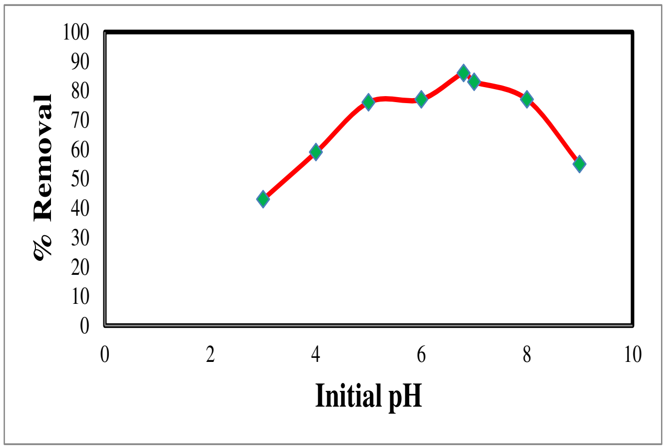
86.73 % whereas it decreased slowly after pH 6.8 that is pH_{zpc} (Zero point charge) as shown in fig. 4. The pH_{zpc} of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. It is well-known that for cationic Cu^{2+} adsorption, negatively charged groups on the adsorbent are necessary. At lower pH values ($pH < pH_{zpc}$) the surface charge of the surface of ASCC may get positively charged as a result of being surrounded by H^+ ions and thus the competitive effects of H^+ ions as well as the electrostatic repulsion between the Cu^{2+} and the positively charged active adsorption sites on the surface of the ASCC lead to a decrease in the uptake of Cu (II) ion. In contrast, at higher pH values ($pH > pH_{zpc}$) the surface of ASCC may acquire a negative charge leading to an increase in Cu^{2+} uptake due to the electrostatic force of attraction in addition the precipitation reaction is likely to take place. On the other hand, neutral surface of adsorbent to support the maximum Cu^{2+} removal from aqueous solution, as the result initial pH value was optimized as pH 6.8.



[Cu^{2+}]=25mg/L; Temperature 30°C; Contact Time 60 min.

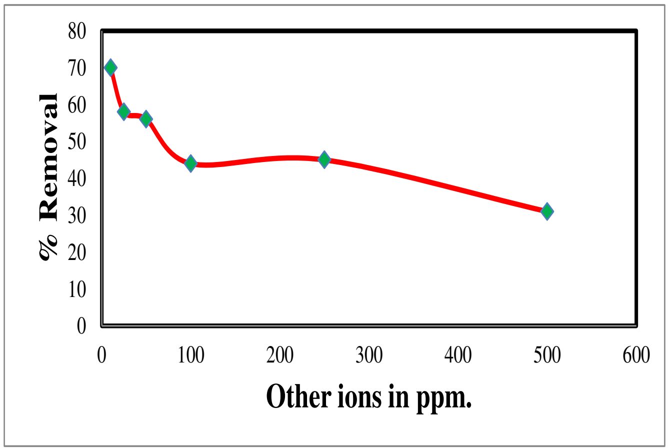
Fig. 3: Effect of adsorbent dose on the removal of Cu^{2+}

The effect of other ion [13] was studied at different concentrations of chloride ion like 10, 25, 50, 100, 250, and 500 mg/L. Chloride ion were added to 50ml of Cu^{2+} solutions and additional parameters were constant. The result shown in the fig. 5 reveals that low concentration of chloride ion does not affect the percentage of Cu^{2+} removal, because the interaction of chloride ion at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases for that reason the percentage of Cu^{2+} removal decreases.



[Cu^{2+}]=25mg/L; Temperature 30°C; Adsorbent dose=0.025g/ 50mL.

Fig. 4: Effect of initial pH on the removal of Cu^{2+}



[Cu^{2+}]=25mg/L; Contact time=60 min.; Adsorbent dose= 0.025g /50mL.

Fig. 5: Effect of other ionic strength on the removal of Cu^{2+}

3.2. Adsorption Models

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

3.2.1. Freundlich model

The Freundlich model [14] which is an indicative of surface heterogeneity of the adsorbent is described by the following equation.

$$\log q_e = \log K_f + \frac{1}{n_f}\log C_e \qquad (3)$$

Where, q_e (mgg^{-1}) is the amount of Cu^{2+} adsorbed at equilibrium, C_e (mol L^{-1}) is the equilibrium concentration, K_f and $1/n_f$ are Freundlich constants related with adsorption capacity and adsorption intensity respectively. The Freundlich plots drawn between log q_e and log C_e for the adsorption of Cu^{2+} were shown fig. 6 and it makes that correlation co-efficient (R^2) values within 0.94 to 0.98, as a result temperature studied indicating that Freundlich model was applicable to the present study these values listed in table 2.

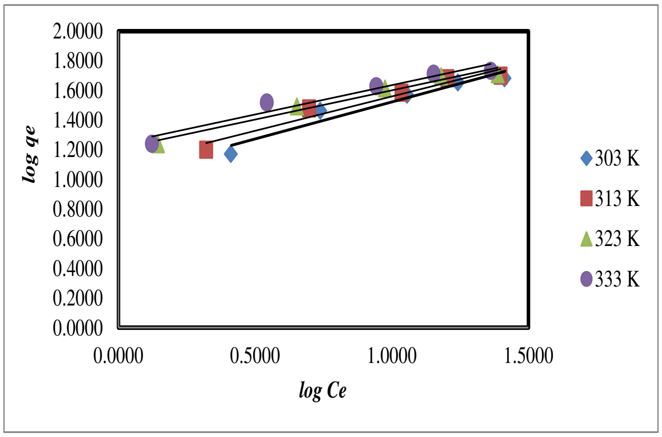


Fig. 6: Freundlich adsorption isotherm plot for the removal of Cu^{2+}

3.2.2. *Langmuir model*

The Langmuir adsorption isotherm [15, 16] equation which is valid for monolayer adsorption on to a surface is given below.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (4)$$

Where, q_e (mgg^{-1}) is the amount of Cu^{2+} adsorbed at the equilibrium concentration C_e (mol L^{-1}), q_m (mgg^{-1}) is the maximum monolayer adsorption capacity of Langmuir isotherm and K_L (L mol^{-1}) is the Langmuir constant related to energy of adsorption. The plots drawn between C_e/q_e and C_e for the adsorption of Cu^{2+} was found linear as shown in fig.7. The correlation co-efficient (R^2) values confirm good agreement with experimental results. The values of the monolayer capacity (q_m) and equilibrium constant (K_L) has been evaluated from the intercept and slope of the plots and given in table 2. These facts suggest that Cu^{2+} is adsorbed in the form of monolayer coverage on the surface of the prepared adsorbent.

In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L by the equation.

$$R_L = \frac{1}{1 + K_L C_0} \qquad (5)$$

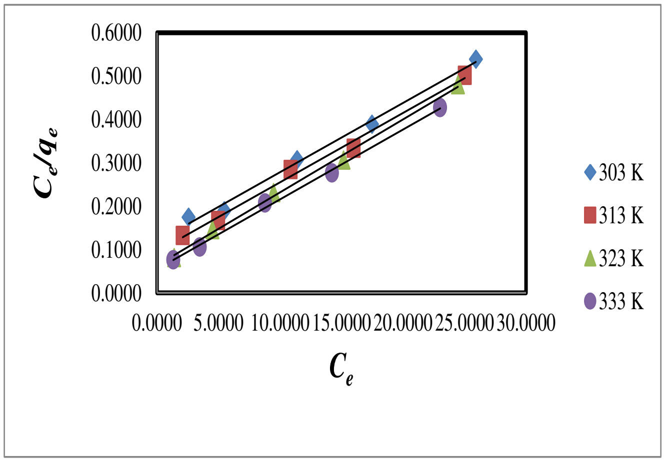


Fig. 7: Langmuir adsorption isotherm for the removal of Cu^{2+}

Table 2: Freundlich and Langmuir isotherm parameters for the adsorption of Cu^{2+} onto ASCC

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	**K_f(mg/g) (L/mg)$^{1/n}$**	10.542	12.430	16.057	17.418
	n_f	2.006	2.150	2.533	2.539
	R^2	0.936	0.950	0.969	0.943
Langmuir	**q_m(mg/g)**	62.548	62.406	59.382	62.081
	K_L (L/mg)	0.135	0.170	0.266	0.295
	R^2	0.993	0.992	0.997	0.997

Where, C_o (mg/L) is the highest initial concentration of Cu^{2+} and K_L (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly. $R_L > 1$, $0 < R_L < 1$, $R_L = 0$ and $R_L = 1$ are unfavorable adsorption, favorable adsorption, irreversible adsorption and linear adsorption respectively.

The R_L values in the middle of 0 to 1 indicate favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L values are given in table 3. The values of K_L increased with increasing dose of adsorbent for ASCC. The high K_L values indicate more adsorption affinity (q_m) around 62.548 mg/L for ASCC.

Table 3: Dimensionless separation factor (r_l) for the adsorption of Cu^{2+} onto ASCC

(C_0)	**Dimensionless separation factor (R_L)**			
	30°C	**40°C**	**50°C**	**60°C**
10	0.4253	0.3708	0.2729	0.2531
20	0.2701	0.2276	0.1580	0.1449
30	0.1978	0.1642	0.1112	0.1015
40	0.1561	0.1284	0.0858	0.0781
50	0.1289	0.1054	0.0698	0.0635

3.3. Thermodynamic treatment of the adsorption process

Thermodynamic [17] parameters associated with the adsorption, via standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were calculated. The free energy of adsorption process considering the adsorption equilibrium constant K_0 is given by the equation,

$$\Delta G^0 = -RT\ln K_0 \tag{6}$$

Where, ΔG^0 is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin, R is the universal gas constant (8.314 J mol/K) and K_0depicts the adsorption mechanism and it'sexpressed in following equation,

$$\ln K_o = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{7}$$

Where, ΔH° is the standard heat change of sorption (kJ/mol) and ΔS° is standard entropy change (kJ/mol). The value of ΔH° and ΔS° can be obtained from the slope and intercept of plot of $\ln K_0$ against 1/T. The value of thermodynamic parameter calculated from equation 6 and 7 are shown in table 4. The thermodynamic treatment of the sorption data indicates that ΔG° values were negative at all temperatures and the positive values of ΔS° depicted the spontaneous nature of adsorption of Cu^{2+}onto ASCC. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. The low ΔH° value depicts adsorption of Cu^{2+} is physisorbed onto ASCC.

Table 4: Thermodynamic parameter for the adsorption of Cu^{2+} onto ASCC

(C_0)	**ΔG°**				**ΔH°**	**ΔS°**
	30°C	**40°C**	**50°C**	**60°C**		
10	-2657.177	-3456.671	-4879.458	-5198.431	24.902	91.039
20	-2451.382	-2866.616	-3314.398	-4300.773	15.608	59.250
30	-1231.695	-1469.862	-2075.951	-2443.827	11.630	42.251
40	-634.386	-1055.328	-1321.400	-1642.465	9.341	33.032
50	-187.568	-6.392	-112.070	-438.392	6.203	19.786

3.4. Kinetic models

3.4.1. Pseudo-second-order

In order to investigate the mechanism of adsorption, kinetic models [18] are generally used to test experimental data. Pseudo-second-order equations can be used assuming that the measured concentrations are equal to surface concentrations. The linearized form of pseudo second order equation becomes.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{8}$$

Where, q_t (mgg^{-1}) is the amount of adsorbed Cu^{2+}on the adsorbent at time t, q_e the equilibrium sorption uptake and k_2, (min^{-1}) is the rate constant of pseudo-second-order adsorption. The plot t/q_t versus t gives a straight line indicates second order kinetic model is applicable then q_e and k_2 were determined from the slope and intercept of the plot, respectively. The high regression value indicate the adsorption reaction exist a pseudo-second-order and the values shown in table 5 reaction obeys pseudo-secound order kinetics. The obtained values are shown in the table 5.

3.4.2. The Elovich equation

The Elovich model [19] equation is generally expressed as

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{9}$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is desorption constant (g/mg) during any one experiment. If Cu^{2+} adsorption fits with the Elovich model, a plots drawn between of q_t and ln(t) yields 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 co-efficient (R^2) are summarized in table 5. This model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase the pore or active site on the ASCC adsorbent.

3.4.3. Intra-particle diffusion model

Kinetic data was further analyzed using the intra-particle diffusion model [20] based on the following equation:

$$\log R = \log K_{id} + \alpha \log t \tag{10}$$

Where, k_{id} is the intra-particle diffusion rate constant, reveals to the thickness of the boundary layer. According to above equation, a plot was drawn between log R and log t gives a straight line that indicates the adsorption mechanism follows the intra-particle diffusion process and the evidence of correlation co-efficient values are close to unity.

Table 5: The kinetic parameters for adsorption of Cu^{2+} onto ASCC

C_0	Temp °C	Pseudo second order				Elovich model			Intra-particle diffusion		
		q_e	k_2	R^2	h	α	β	R^2	α	K_{id}	R^2
10	30	64.8486	7.40E-05	0.8967	0.3113	8.3E-01	1.38E-01	0.9603	2.1616	0.8598	0.9993
	40	25.3928	9.82E-04	0.9510	0.6332	1.3E+00	1.71E-01	0.9592	8.5540	0.5357	0.9920
	50	20.4950	3.62E-03	0.9859	1.5199	4.7E+00	2.57E-01	0.9592	27.0198	0.2767	0.9795
	60	20.3323	4.03E-03	0.9877	1.6672	5.9E+00	2.71E-01	0.9592	4.3538	0.2569	0.9783
20	30	32.7849	2.66E-04	0.4082	0.2859	1.5E+00	5.72E-02	0.9865	0.2595	1.4167	0.9221
	40	41.9765	8.45E-04	0.9409	1.4882	3.1E+00	1.05E-01	0.9288	12.0682	0.4342	0.9702
	50	41.0277	1.13E-03	0.9757	1.8977	4.1E+00	1.10E-01	0.9601	15.8765	0.3817	0.9829
	60	40.4631	1.51E-03	0.9748	2.4660	6.4E+00	1.22E-01	0.9431	3.8263	0.3143	0.9715
30	30	49.5008	7.70E-04	0.8811	1.8869	4.3E+00	9.39E-02	0.8280	11.7321	0.3846	0.8839
	40	49.9727	1.06E-03	0.9747	2.6502	6.0E+00	9.21E-02	0.9402	14.8054	0.3571	0.9561
	50	55.6058	8.31E-04	0.9822	2.5686	5.3E+00	7.90E-02	0.9677	13.4617	0.3992	0.9808
	60	51.5960	1.54E-03	0.9996	4.0973	1.0E+01	9.31E-02	0.9889	3.7075	0.3104	0.9774
40	30	60.9633	8.38E-04	0.9916	3.1143	5.9E+00	6.83E-02	0.9734	10.5070	0.4239	0.9586
	40	63.6371	8.30E-04	0.9988	3.3598	6.6E+00	6.70E-02	0.9905	11.8374	0.4058	0.9739
	50	63.7043	9.68E-04	0.9980	3.9274	8.0E+00	6.86E-02	0.9820	13.9545	0.3747	0.9642
	60	65.1047	1.02E-03	0.9985	4.3141	9.1E+00	6.87E-02	0.9835	3.2966	0.3561	0.9682
50	30	75.9747	2.99E-04	0.7965	1.7275	3.6E+00	5.83E-02	0.8589	4.9184	0.5339	0.9333
	40	76.9176	3.17E-04	0.8205	1.8764	3.9E+00	5.74E-02	0.8635	5.5399	0.5146	0.9350
	50	72.6211	4.18E-04	0.8545	2.2056	4.6E+00	6.08E-02	0.8563	7.1709	0.4575	0.9230
	60	77.2872	3.77E-04	0.8287	2.2530	4.7E+00	5.68E-02	0.8425	2.3561	0.4685	0.9133

4. CONCLUSION

The ASCC prepared from *Sidacordifolia* was found effective in removing Cu^{2+} from aqueous solution. The adsorption is faster and the rate is mainly controlled by intra-particle diffusion. Using the sorption equation obtained from the Langmuir and Freundlich isotherms, it was found that ASCC is an effective one for the removal of Cu^{2+}. The equilibrium data conformed well to the Langmuir and Freundlich isotherm models. The temperature variation study showed that the Cu^{2+} adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the Cu^{2+}solution. pH dependent results and desorption of metal ion in mineral acid suggest that the adsorption of metal ion on ASCC involves chemisorptions as well as physisorption mechanism.

Conflict of Interest

None declared

5. REFERENCES

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