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Research Article

ADSORPTION DYNAMICS OF MANGANESE (II) ION ONTO ACTIVATED CARBON PREPARED FROM THE WOOD OF *ADINA CORDIFOLIA HOOK*

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Abstract

The use of cheap and ecofriendly adsorbents have been studied as an alternative substitution of commercial activated carbon for the removal of Manganese (II) ion from aqueous solution. Adsorbent prepared from *Adina cordifolia hook* was experimented under batch mode. The influence of initial concentrations of metal ion solution, adsorption dose and contact time on the removal process was investigated. Adsorbent dosage of 0.050 g/L showed maximum dye uptake capacity (qe) of 31.09 mg/g for an initial dye concentration of 50 mg/L. Experimental data were fitted into linearised form of Lagergren and Ho kinetic equations for pseudo first order and pseudo second order models respectively. The kinetic parameters have been calculated and discussed in detail. The results revealed that the adsorption of Manganese (II) ion onto chosen adsorbent followed the pseudo second order kinetics. Intra particle diffusion was confirmed as one of the rate determining steps using Webber Morris plot parameters.

Keywords: adsorption; kinetics; Manganese (II) ion; activated carbon; *Adina cordifolia hook*

1. Introduction

Nowadays, pollution becomes increasingly prevalent in our daily life. In some areas, it has a fairly negative impact on our health. Among all the pollutions, heavy metal is an important part which should never be neglected. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, manganese and arsenic [1]. Removing toxic heavy metals from industrial wastewater is an urgent environmental issue. Heavy metals are non-degradable and can accumulate in animals and plants, so they must be removed from wastewater [2]. The most important technologies include chemical precipitation, electroflotation, ion exchange, reverse osmosis and adsorption onto activated carbon [3]. These methods are not cost effective in the Indian context. Low-cost and nonconventional adsorbents include agricultural wastes, such as natural compost, Irish peat, planer shell, walnut shell, and biomass, such as Aspergillus tureens and Macular remanniamus [4], chitoson [5] and peat moss [6].

Many reports have appeared on the development of activated carbon from cheaper and readily available materials [7]. The objective of this work was to evaluate the potential of activated carbon prepared from *wood* of *Adina cordifolia hook* for the removal of manganese (II) ions from water.

2.Materials and Methods

2.1.Preparation of adsorbent

The activated carbon was prepared from the wood of *Adina cordifolia Hook.* The wood were cut into smaller pieces and soaked in concentrated H_2SO_4 at 1:1 ratio (weight of raw material/volume of acid) for 24 h and activated at 160°C for 5 h. The activated carbon was repeatedly washed with distilled water until the pH of the wash water became the pH of the distilled water (nearly 7). The carbon obtained was dried at 110 ± 1°C for

nearly 2 h to remove the moisture. The above prepared carbon was named ACHC.

2.2.Adsorption studies

Adsorption of Manganese (II) ions onto ACHC was carried by a batch method. The effect of contact time and initial concentration of Manganese (II) ions were investigated at three temperatures were 305, 315 and 325 K. The adsorption process was carried out with three different initial concentrations at 25 mg/L, 50 mg/L and 75 mg/L of Manganese (II) ion. 50 mg of adsorbent was taken in 100 mL iodine flask. 50 mL of

the adsorbate solution was added to the flask. This aliquot was shaken in rotary shaker at 150 rpm for predetermined time [8, 9]. Then the solution was centrifuged and the adsorbate concentration of the centrifugate was measured using AAS to determine the percentage removal of the adsorbate from the solution. The kinetic experiments were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120 and 140 minutes.
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Nomenclature	
C_i , C_t and C_e	Initial Concentration, at the time 't' and at equilibrium respectively
q_e and q_t	Quantity adsorbed at the time 't' and at equilibrium respectively
V	Volume of the adsorbate solution in liter (L)
W	Mass of the adsorbent in gram (g)
Q_e	Amount of solute adsorbed per unit weight of adsorbent (mg/g)
C_e	Equilibrium concentration of solute in the bulk solution (mg/L)
T	Temperature (K)
k_1	Rate constant of adsorption (l/min)
k_2	Second-order constants
t	Time in minutes
h	Initial adsorption rate (mg/g min)
k_p	Intra-particle diffusion rate constant
C	Thickness of the boundary film
N	Number of data points
C	Concentration in ppm

2.3.Data Processing Tools

Table - 1 Data Processing Tools

S. No.	Parameters		Formulae
1.	**Mass balance relationships**	% of Removal	$(C_i - C_t) \times V/C_i$
		Quantity adsorbed at equilibrium, q_e	$(C_i - C_e) \times V/W$
		Quantity adsorbed at the time t, q_t	$(C_i - C_t) \times V/W$
2.	**Kinetic Models & SSE %**	Pseudo First order kinetics (Legergren equation)	$\log (q_e-q_t)=\log q_e - k_1/2.303 \times t$
		Pseudo Second order kinetics (Ho equation)	$t/q_t=1/k_2.q_e^2 +1/q_e t$
		The initial adsorption rate h	$h = k_2q_e^2$
		Intra particle diffusion (Weber–Morris equation)	$q_t = k_pt^{1/2} + C$
		Sum of error squares	SSE (%) = $[(q_e)_{exp}-(q_e)_{cal}]^2/ N$

3.Results and Discussion

3.1 Effect of dose

The adsorption of Manganese (II) ion onto ACHC were studied by varying the dose of the adsorbent from 10 mg/ 50 mL to 70 mg/ 50 mL by taking 50 mg/ L of the adsorbate concentration which were shown in

the Figure 1. The percentage of removal of Manganese (II) ion from aqueous solution increased with increase of carbon dose. This is due to the increased carbon surface area and availability of more adsorption sites [1]. 50 mg of adsorbent per 50 mL of adsorbate solution was chosen for further studies.
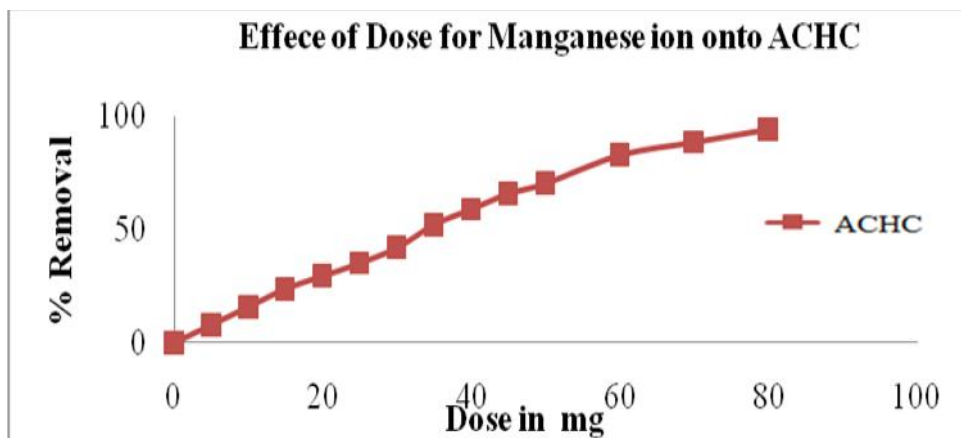

Figure 1

3.2 Effect of contact time for different initial concentrations

The experimental results for adsorption of Manganese (II) ion onto activated carbon at various concentrations and contact times at 305 K temperature are shown in Figure 2 as representative graph. The equilibrium data reveal that percentage of adsorption decreased with increase in initial Manganese (II) ion concentration but .

the actual amount of Manganese (II) ion adsorbed per unit mass of carbon increased with increase in metal ion concentration. This means that the adsorption is highly dependent on the initial concentration of Manganese ion. This is because the ratio between the surface available on the adsorbent and concentration of adsorbate in the solution phase, decrease with the increase of initial concentration of the solute [5 & 10]
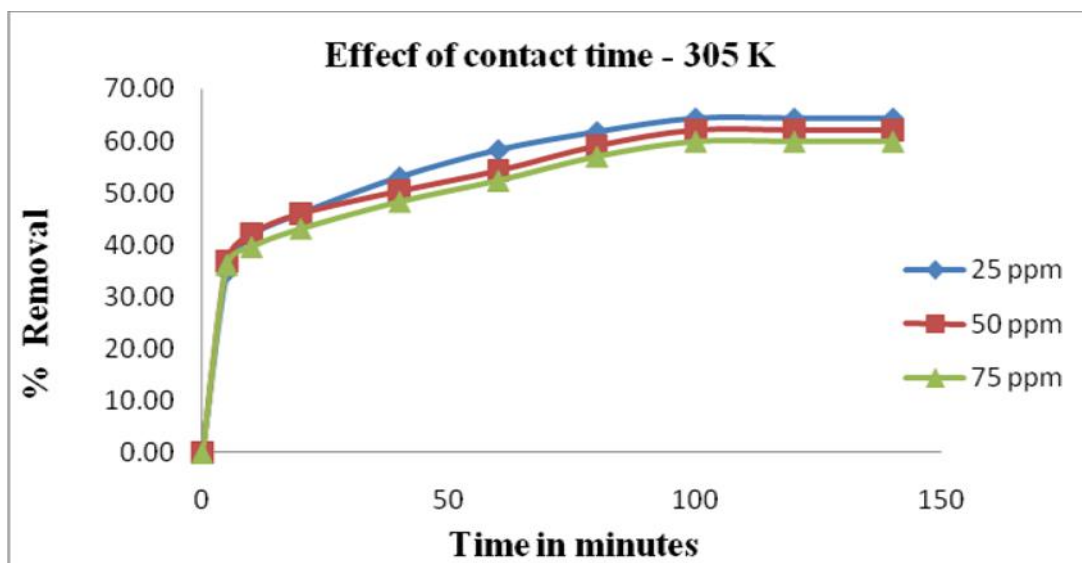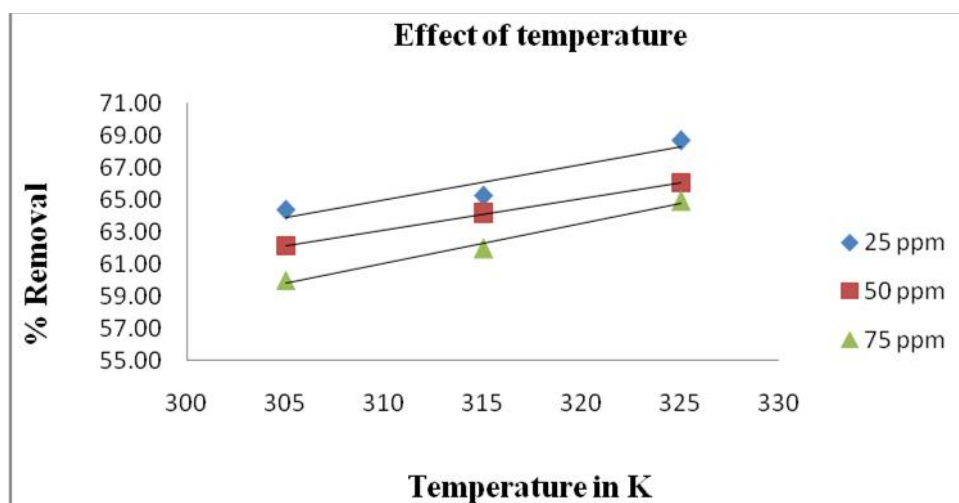

Figure 2

3.3 Effect of temperature

The percentage of removal increased with an increase of temperature of the solution for all studied initial concentrations of the metal ion. The results are given in Table 2. Plots of percentage removal versus temperature were given in Figures 3. The reason may be as follows, At higher temperature, pores may widen up due to increased vibration. So that more number of solute may enter into the pore and get adsorbed in the inner part of the pore surfaces.

Table – 2 Effect of temperature on Mn ion adsorption
[pH = 7; Dose = 50 mg/ 50 mL; Contact time = 140 min]

Initial Concentration (mg/L)	Temperature (K)	% Removal
25	305	64.35
	315	65.22
	325	68.70
50	305	62.17
	315	64.13
	325	66.09
75	305	60.00
	315	61.96
	325	64.93

Figure 3

3.3 Kinetic models

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. The results obtained from pseudo first order and second order kinetic models for manganese ions were presented in Table 3. Representative graphs at 305 K were shown in Figures 4, 5 and 6. The first order rate constant k_1 (min^{-1}) ranged from 1.38×10^{-2} to 2.76×10^{-2} and second order rate constant k_2 (g/mg.min) ranged from 3.00×10^{-3} to 12.00×10^{-3}.

The initial sorption rate 'h' increases directly with an increase of initial Manganese (II) ion concentration at each temperature.

Experimental q_e, calculated q_e and SSE % for the pseudo first order and pseudo second order kinetics were given in Table 3. It shows that q_e (exp) is close to

q_e (cal) for second order kinetics. It can be seen that SSE (%) value is lower for the second order kinetic model than that of pseudo first order kinetic model. This confirms the applicability of the pseudo second order kinetic model. The determination coefficient (R^2) for pseudo first order model ranged between 0.794 and 0.985 whereas these values for the second order model were close to 1. It indicates that the experimental data best fitted into pseudo second order.

Intra particle diffusion rate constant K_p values were found to increase with an increase of Manganese (II) ion concentration that reveals the rate of adsorption is governed by the diffusion of adsorbed Manganese ions within the pores of the adsorbent. Present results show the pore diffusion limits the overall rate of the Manganese (II) ion adsorption [9, 13 & 14].

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Table - 3 Kinetic parameters for the removal of Manganese (II) ion by ACHC

| C (ppm)	T (K)	First Order Kinetics					Second Order Kinetics					Intra Particle Diffusion	
		k_1 (min^{-1})	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	R^2	SSE %	$k_2 \times 10^{-3}$ (g/mg.min)	$q_{e(cal)}$ (mg/g)	h	R^2	SSE %	k_p (mg/g.min)	R^2
25	305	0.0253	7.62	16.09	0.815	1.82	10.00	16.95	2.85	0.996	0.29	0.83	0.998
	315	0.0276	8.05	16.30	0.985	2.89	11.00	16.95	3.03	0.996	0.21	0.90	0.999
	325	0.0368	10.64	17.17	0.932	3.04	12.00	17.86	3.73	0.997	0.23	0.96	0.991
50	305	0.0184	11.02	31.09	0.794	4.52	5.00	32.26	5.65	0.995	0.39	1.09	0.995
	315	0.0253	15.07	33.04	0.981	5.99	6.00	34.48	6.94	0.997	0.46	1.30	0.990
	325	0.0253	17.54	35.65	0.979	8.21	7.00	37.04	9.09	0.997	0.48	1.90	0.980
75	305	0.0138	14.16	45.00	0.810	6.35	3.00	47.62	7.87	0.995	0.87	1.36	0.999
	315	0.0253	21.04	48.70	0.977	9.22	4.00	52.63	9.71	0.996	1.13	2.07	0.990
	325	0.0230	25.94	52.17	0.985	12.67	4.00	55.56	13.5	0.996	1.31	2.58	0.983
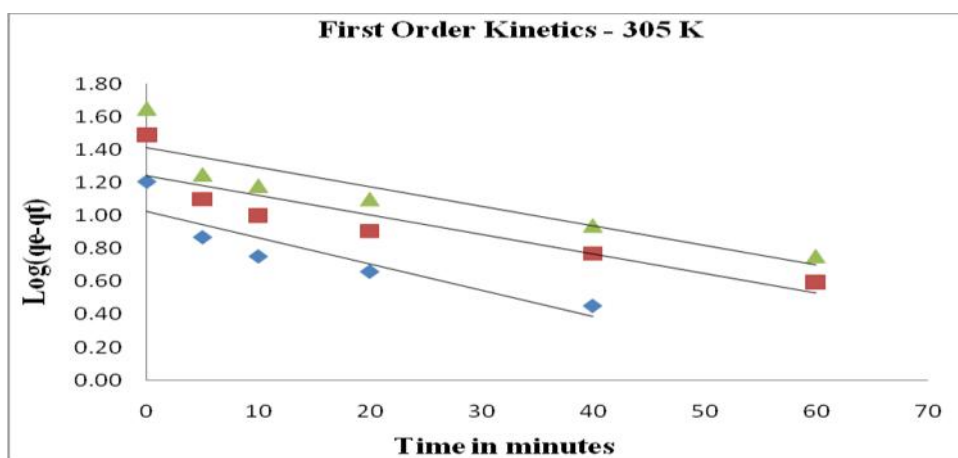
Figure 4
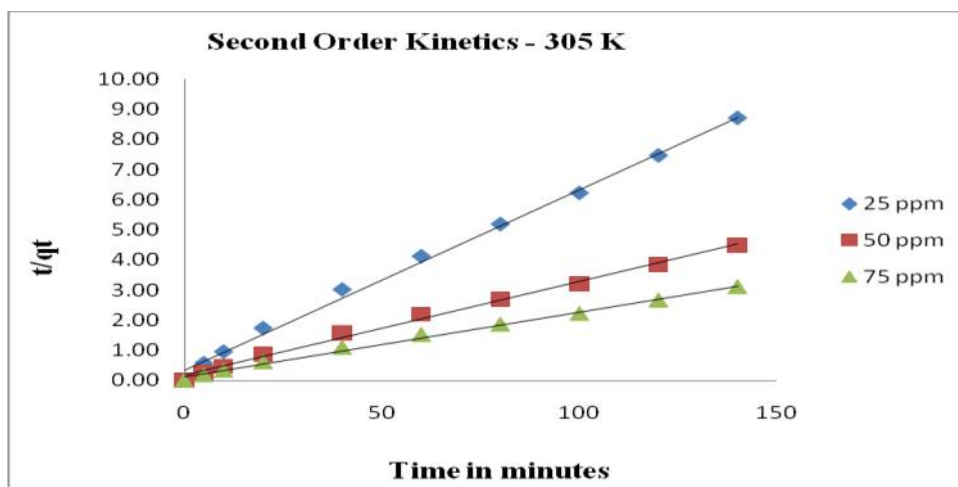
Figure 5
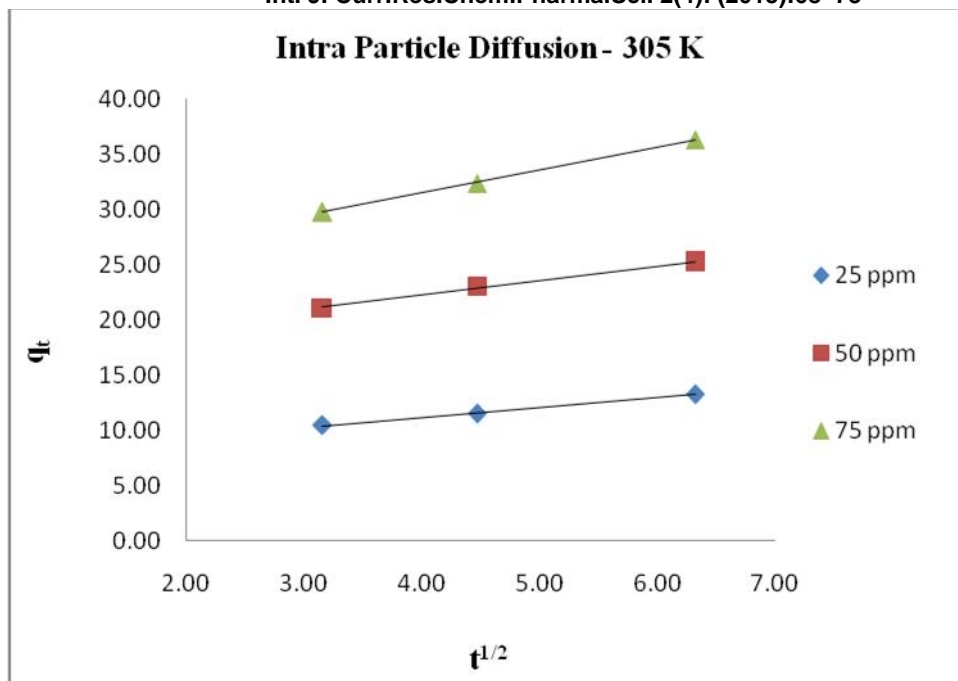
Figure 6

4. Conclusion

Activated carbon (ACHC) was prepared from *Adina cordifolia* Hook. Adsorption experiments were carried out as a function of contact time, initial concentration in a batch mode process. Experimental data indicated that ACHC was effective in removing Manganese from aqueous solution. The percentage of removal increased with an increase in contact time and achieved equilibrium around 100 minutes when 50 mg ACHC was used as adsorbents for 50 mL solution. Adsorption capacity of ACHC was found to be higher at higher initial concentrations. In the kinetics studies, R^2 value and SSE (%) revealed that the process of adsorption followed pseudo first order kinetics. Percentage found to increase with the increase of temperature.

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