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Comparative Study of Adsorption Dynamics of Fe(II) Using Bentonite Clay and Activated Carbon

ANIMA S. DADHICH* and Mrs SHAIK KHASIM BEEBI
Department of Environmental Science, College of Engineering, Gandhi Institute of Technology & Management, Visakhapatnam-530 045, India

Demands for a better quality of treated effluent have led to an intensive use of adsorption process as a polishing technology. The present study was aimed at removing iron using a non-conventional adsorbent, bentonite clay and a comparison of the same with activated carbon which happens to be a conventional adsorbent. The effect of contact time, adsorbent dosage, pH and initial concentration on the kinetics of adsorption was studied. It was shown that iron removal increases with increasing contact time and becomes constant after 1 h. In case of both bentonite clay and activated carbon percentage of adsorption was found to increase with increasing adsorbent dosage. The effect of pH on removal of Fe(II) showed that % adsorption increases with inceasing pH up to a certain level; thereafter it decreases. The rate constants for removal of Fe(II) with bentonite clay and activated carbon for varying initial metal concentration showed it to be a first order kinetics. The adsorption data fitted well into Freundlich adsorption isotherm. The comparison of K, the adsorption capacity, and 1/n, the adsorption intensity, values showed that bentonite clay, a non-conventional adsorbent, is on par with activated carbon in effectively removing Fe(II) from an aqueous solution.

Key Words: Adsorption, Dynamics, Fe(II), Bentonite clay, Activated carbon.

INTRODUCTION

Incidences of air and water pollution from metallic industries is increasing at an alarming rate. Several mishaps in the past like Itai-Itai and Minamata cases have caused awareness in the public about toxicity of heavy metals. Metals, depending upon the requirement by human beings, can be divided into two groups—essential and non-essential metals. Non-essential metals like Cr, Pb, Cd, As, adversely affect human beings. Essential metals like Zn, Cu, Fe, Ca, etc. play an important role in the metabolism of human beings.[1–3] But even the essential metals at higher concentration, when they cross permissible limits prove to be harmful. Fe, one of the essential metals, required by human beings for formation of haem can affect detrimentally man and its environment beyond the permissible limits. The various industries contributing iron to the environment include electroplating, iron and steel, ferroalloy etc.[4–6]

The permissible limit of Fe for discharge of industrial effluents as prescribed by Central Pollution Control Board (CPCB) is 3 mg/L[7]. Iron is reported to have high bioaccumulation factor. To meet the stringent limits prescribed by CPCB for safe disposal of industrial effluents various chemical and physical methods are adopted for removal of metals. Adsorption, a physical treatment method, is the promising technique to remove metals from industrial effluents[8]. Activated carbon, in powdered or granular form, is the most frequently used commercial adsorption medium in developed countries. But in developing countries due to its high cost and losses during regeneration, its use on large scale is not feasible. Hence in recent years the research is on to look for low cost and ecofriendly non-conventional adsorbent materials for removal of pollutants from industrial effluents[9,10]. In the present study a comparison of the adsorption dynamics of Fe(II) using bentonite clay, a non-conventional adsorbent and activated carbon was made.

EXPERIMENTAL

The procedures and methods followed to investigate the adsorption using non-conventional adsorbent are given below in detail. All chemicals used were of analytical grade and double distilled water was used for all experimental work.

Batch experiments for adsorption kinetics

Batch studies were conducted to evaluate the effect of the following parameters on adsorption kinetics:

(i) contact time
(ii) Adsorbent dosage
(iii) pH
(iv) Concentration

A generallized procedure was devised to evaluate the effects of above parameters on adsorption process.

Iron stock solution was prepared by taking 0.7022 g of ferrous ammonium sulfate in 1000 mL flask. From the stock solution known concentration of iron was taken in 1000 mL flask and made up to the mark with distilled water. The entire solution was poured into 1 L beakers. pH was adjusted using hydrochloric acid. The known quantity of adsorbent, bentonite clay, was added to the beakers. The metal ion aqueous solution was kept in contact with adsorbent for a period of 10 min to 300 min. Samples were withdrawn at different time intervals such as 10, 20, 30, 60, 120, 180, 240 and 300 min. The sample was filtered in a conical flask using Whatman filter paper. The filtrate was taken in a conical flask and iron(II) was estimated using standard method[11,12]. All these experiments were carried out at room temperature. Under the optimum conditons of contact time, pH and adsorbent dosage the initial metal concentration was varied from 10, 20, 30, 40 to 50 mg/L.

The procedure was repeated by taking charcoal as an adsorbent. The equilibrium data was fitted into Freundlich adsorption isotherm.

RESULTS AND DISCUSSION

Effect of contact time: It was shown that the contact time has a great effect on iron removal. By increasing the contact time the adsorption also increasers and becomes constant after 1 h of contact time. This indicates that the equilibrium was obtained in 1 h as there was no further significant change in equilibrium concentration up to 4 h. The percentage reduction in metal ion observed was 85% for bentonite clay, whereas for activated carbon which is a conventional adsorbent it was found to be 87.5% (Fig. 1).

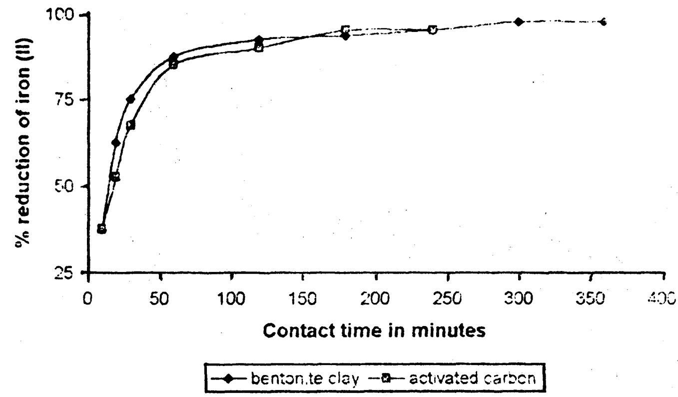

Fig. 1. % Reduction *vs.* contact time

Effect of adsorbent dosage: The effect of various adsorbent dosages of bentonite clay on iron removal was studied. It was observed that as the amount of adsorbent dosage is increased from 2, 4, 6, 8 to 10 g, the percentage reduction of the metal ion increases continuously (Fig. 2). A similar observation was made for activated carbon. The rate of adsorption depends on the driving forces per unit area and in this case since the initial concentration is constantly increasing, the adsorbent dosage increases the surface area available for adsorption; hence percentage reduction increases. The percentage reductions for an initial concentration of 20 mg/L of iron for contact time of 1 h with a dosage of 10 g of bentonite clay and activated carbon were 85 and 87.5% respectively.

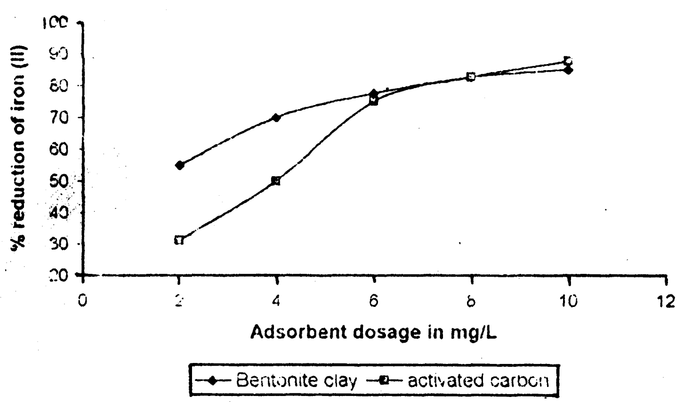

Fig. 2. % Reduction of iron(II) *vs.* adsorbent dosage

Effect of pH: Batch experiments were conducted at different pH values to investigate the effect of pH on adsorption of iron with bentonite clay and activated carbon. The percentage adsorption of metal increased with increase in pH. In the case of bentonite clay the percentage removal increased from 45, 52.5 to 85 per cent as the pH was increased from 2, 4 to 6 respectively. As the pH increases from 6 to 8 the percentage removal decreases to 80% (Fig. 3). The decrease in percentage reduction at high pH value may be owing to the fact that metal ions generally form hydroxides at higher pH. Metal ion adsorption is mostly governed by the free metal ion concentration. At high pH hydroxyl ions compete with the metal ion for the adsorption.

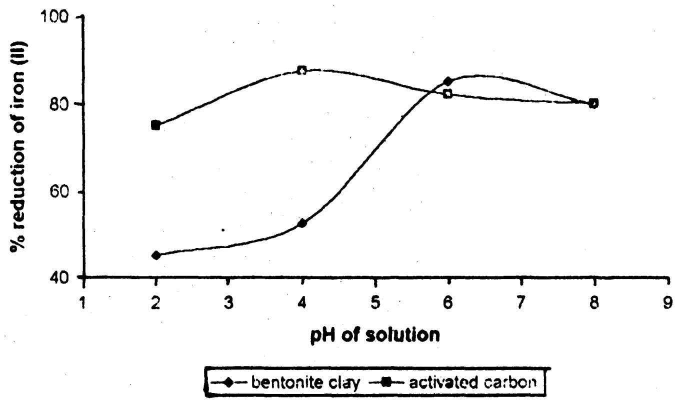

Fig. 3. Reduction of iron(II) *vs.* pH

A similar observation is noted for activated carbon; as pH is increased from 2 to 4, the percentage reduction increases from 75 to 87.5. Thereafter further increase in pH from 4, 6 to 8 causes reduction in adsorption of metal ions. The percentage reduction observed was 87.5%, 82 and 80%, respectively (Fig. 3). The increase in hydrogen ion concentration at low pH of 4 may result in neutralization of negative or positive charges at the surface of the adsorbent thereby reducing hindrance to diffusion and making more of the active surface of the adsorbent.

Effect of concentration: Several investigators have reported reduction in percentage adsorption with increase in metal ion concentration. A similar observation is reported from data obtained for removal of Fe(II) using bentonite

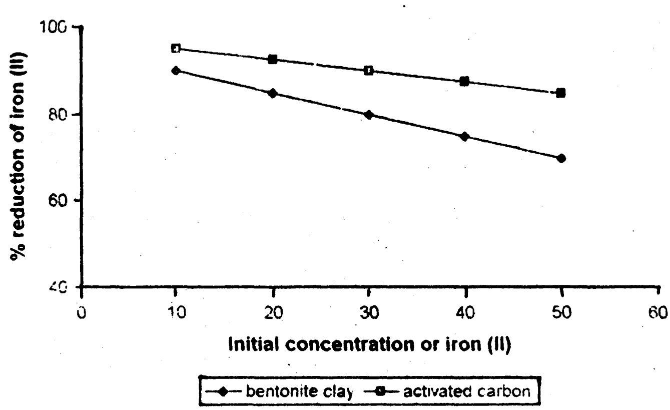

Fig. 4. % Reduction of iron(II) *vs.* initial concentration

clay and activated carbon as adsorbents. The initial Fe(II) concentrations were taken from 10, 20, 30, 40 up to 50 mg/L with adsorbent dosage of 10 g/L at a pH of 6 for a contact time of 1 h. The percentage removal of iron gradually decreases from 90, 85, 80, 75 to 70% as the metal ion concentration increases (Fig. 4). In case of activated carbon, the percentage reduction decreases from 95, 92.5, 90, 87.5 and 85% with increase in metal ion concentration (Table-2).

Adsorption generally follows first order rate kinetics. The rate constants for removal of Fe(II) with bentonite clay and activated carbon for varying metal ion concentration were calculated using the equation given below:

$$K = 1/t \ln C_i/C_e,$$

where t = contact time

C_i = initial concentration of the metal ion

C_e = remaining concentration of the metal ion after adsorption.

The results have been given in Tables 1 and 2. It is highlighted from the data that the percentage decreases with increase in metal concentration of the adsorbate solution even though the amount absorbed increases.

TABLE-1
% REMOVAL OF Fe(II) USING BENTONITE CLAY FOR VARIOUS INITIAL CONCENTRATIONS.

Initial conc. of Fe(II)	Final conc. of Fe(II)	Amount of iron adsorbed	q_e	log C_e	log q_e	K (min^{-1})	% removal of Fe(II)
10	1	9	0.9	1.1760	0.5440	0.03837	90.0
20	3	17	1.7	1.0000	0.4771	0.03161	85.0
30	6	24	2.4	0.7781	0.3880	0.02682	80.0
40	10	30	3.0	0.4771	0.2304	0.02310	75.0
50	15	35	3.5	0.0000	0.0451	0.20060	70.0

TABLE-2
% REMOVAL OF Fe(II) USING ACTIVATED CARBON FOR VARIOUS INITIAL CONCENTRATIONS

Initial conc. of Fe(II)	Final conc. of Fe(II)	Amount of iron adsorbed	q_e	log C_e	log q_e	K (min^{-1})	% removal of Fe(II)
5	0.25	4.75	0.475	–0.6020	–0.3279	0.4992	95.00
10	0.75	9.75	0.975	–0.1249	–0.0132	0.04317	92.50
15	1.50	13.75	1.375	0.1760	0.1367	0.0383	90.00
20	2.50	17.50	1.750	0.3979	0.2430	0.0346	87.50
25	3.75	21.25	2.125	0.5740	0.3263	0.0316	85.00

A graph plotted between ln C_i / C_e *vs* k straight curve passes through origin suggesting the first order rate kinetics (Fig. 7 and 8).

The equilibrium data fitted into Freundlich adsorption isotherm and were found to be linear over a wide range of concentrations (Figures 5 and 6). The Freundlich constants k and 1/n have been calculated and are given in Table-3. The values

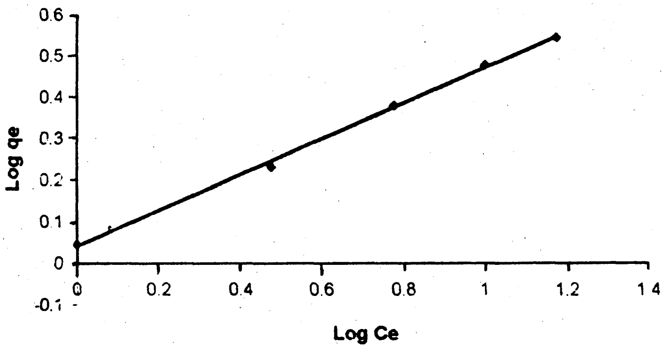

Fig. 5. Plot of log Ce vs. log qe for various concentrations of Fe(II) using bentonite clay

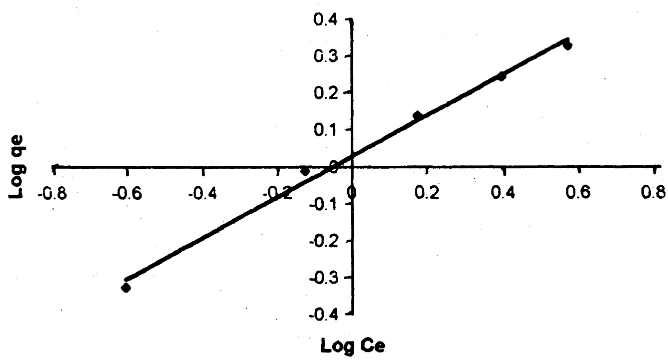

Fig. 6. Plot of log Ce vs. log qe for various concentrations of Fe(II) using activated carbon

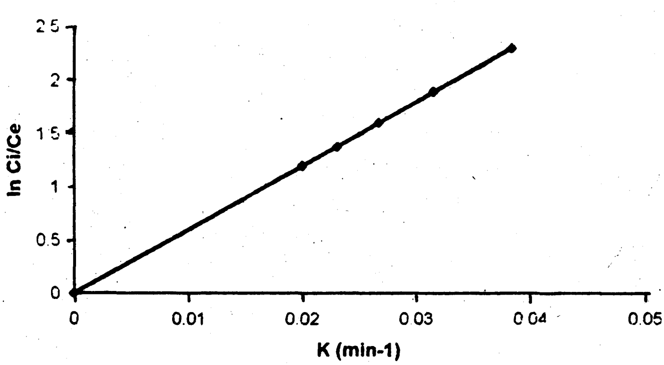

Fig. 7. Plot of rate constant K *vs.* ln Ci/Ce for bentonite clay

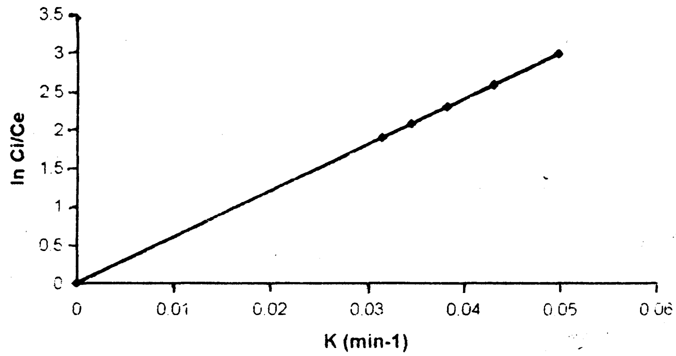

Fig. 8. Plot of rate constant K *vs.* ln Ci/Ce for activated carbon

indicate that the adsorption capacity of bentonite clay and activated carbon, for the metal ion under study, is in the order:

bentonite clay > activated carbon.

As the value of 1/n is ≅ 1, it indicates favourable adsorption (Table-3)

TABLE-3
FREUNDLICH ISOTHERM CONSTANTS FOR ADROPTION OF Fe(II) AT ROOM TEMP

Type of adsorbent	Particle size (micron)	K	l/n	Concentration range of Fe(II) in mg/ L
Bentonite clay	425	4.50	1.18	10–50
Activated carbon	300	3.57	1.16	5–25

Despite the fact that activated carbon has smaller particle size than bentonite clay, its unique montmorillanite octahedral structure makes bentonite clay an adsorbent with efficiency on par with the activated carbon.

Conclusion

The optimum contact time for removal of Fe(II) using both bentonite clay and activated carbon was 1 h. The optimum pH for adsorptin of Fe(II) from aqueous solution using bentonite clay was found to 6. And for activated carbon it was 4. The optimum dosage of adsorbent for removal of Fe(II) was found out to be 10 g/L. The percentage removal for an initial concentration of 10 mg/L for a dosage of 10 g/L of bentonite clay at pH 6 and for contact time 1 h was 90% whereas for a concentration of 50 mg/L under the same optimum conditions was shown to be 70% indicating that higher concentration of metal ions the efficiency of the adsorbents decreases.The effectiveness of non-conventional adsorbents may be acknowledged from the fact that from 50 to 100% removal is obtained under optimum conditions to the cost of adsorbent involved.

Thus the prospects of using this nonconventional adsorbent effectively for removal of Fe(II) even at small adsorbent dosage are quite feasible. This may prove to be a low-cost and helpful non-conventional adsorbent for management of waste containing Fe(II) coming from small scale industries for which economic waste management measures are a boon.

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