Fly ash for the removal of Mn(II) from aqueous solutions and wastewaters

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Abstract

Application of fly ash, a waste material of thermal power plants has been investigated for the removal of manganese from aqueous solutions and wastewaters. The removal was found to be highly concentration dependent and higher removal (%) was obtained at low concentrations of Mn(II) in the solutions. The removal decreased from 74.2 to 47.2% by increasing the Mn(II) concentration from 1.5 to 5.0 mg l^{-1} at 298 K, pH 8.0, and 1.0×10^{-2} M NaClO$_4$ ionic strength. Removal, however, decreased from 51.3 to 7.2% by increasing the adsorbent particle size from 100 to 250 μm. The process of Mn(II) is exothermic in nature. Thermodynamic parameters namely free energy, ΔG°, enthalpy, ΔH°, and entropy, ΔS° were calculated and were found to be -0.72, 7.34 and 28.28 kcal mol^{-1} at 298 K. Heat of adsorption as a function of surface coverage was also calculated and was 8.20 kcal mol^{-1} at 298 K. The data can be used for designing treatment plants for the treatment of Mn(II) rich waters and wastewaters.

1. Introduction

Fly ash is a by-product of coal burning in different industrial applications. It is regarded as an irritant responsible for air pollution as well as posing disposal problems. This problem becomes more severe where coal available is of poor quality with 35–40% of ash content and this is responsible for producing greater quantities of fly ash. Application of coal as a fuel in most industries results in generation of greater amount of fly ash presenting many problems and these factors compel application and utilization of fly ash. Applications of fly ash are reported [1] in cement manufacture. Alkaline fly ash is also reported to act as binding agent for fixation of heavy metals and nutrients in waste and organic matter [2–5]. Some scientific workers have used modified fly ash for removal of pollutants from water and wastewater [6–12] leading to application of fly ash as adsorbent for water and wastewater reclamation. Manganese is the second most abundant metal in nature. Its most common mineral is pyrolusite (MnO$_2$). It is an essential metal for human system

and many enzymes are activated by manganese. Manganese has variety of applications in ceramics, dry battery cells, and electrical coils and manganese is an alloying element of many alloys. In addition to the disposal of untreated discharge from above applications into water, another major source of pollution of Mn is burning of coal and oil [13,14]. Intake of higher concentrations manganese causes *mangenese psychosis*, an irreversible neurological disorder. It is characterized by uncontrollable laughter, sexual excitement and impotence [13]. It is also reported to cause '*manganese pneumonia*'. Like most of the metallic species excessive supply of Mn to plants has detrimental effects [15].

Because of toxicity and non-degradable nature of metallic species, scientific workers world over have carried out significant work on their removal from aqueous solutions and industrial effluents. Solvent extraction, ion exchange, precipitation, adsorption on activated carbon, etc., have been commonly used methodologies in removal of metallic species from aqueous solutions and wastewaters [16–20]. But expensive nature of these methods limits their application to developed nations only. In order to bring down the cost of treatment of the wastewaters rich in metallic species, the scientific workers have tried different materials [21–25].

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Present work has been addressed to the use of fly ash procured from a nearby thermal power plant for removal of Mn(II) from aqueous solutions and wastewater samples. Effect of various important parameters on removal has also been discussed.

2. Experimental

2.1. Materials

All the chemicals used in the experiments were procured from B.D.H., Mumbai, India and were of A.R. grade. The adsorbent, fly ash was obtained from a nearby thermal power plant, Patratu Thermal Power Station (PTPS). Fly ash is a well-known waste material of thermal power plants. Fly ash is basically a mixture of a number of metallic oxides with silica (44.28% by weight), alumina (28.24% by weight) as its major constituents. Other constituents of fly ash are iron oxide, magnesia and titanium dioxide. Composition of fly ash varies and depends on the quality of coal used for combustion. Indian coal is mainly lignite and contains ash up to 30–40% [26]. Combustion of this coal produces more amount of fly ash. In order to remove earthen impurities the fly ash was washed several times with normal water and then with de-ionized water.

2.2. Methods

To maintain a uniform particle size, fly ash was sieved through sieves mechanically. Chemical characterization of the adsorbent was carried out by Indian Standard Methods [27]. The average particle size of the adsorbent was measured by Particle Size Analyzer, Model HIAC-320 (Royco Institute Division, USA) and the surface charge by Lazer Zee Meter, Model QS/7 (Quanta Chrome Corporation, USA) and the porosity by mercury porosimeter.

2.3. Batch adsorption experiments

Batch adsorption experiments were carried out by agitating 1.0 g of fly ash sample with 50 ml aqueous solution of Mn(II) of desired concentration, temperature and pH in different properly cleaned polythene bottles on a shaking thermostat with a constant speed of 100 rpm. At the end of predetermined time intervals, fly ash was removed from the aqueous solutions by centrifugation at 10,000 rpm for 10 min. The progress of adsorption was assessed by determining the residual concentration of Mn(II) in supernatant by an atomic absorption spectrophotometer (Model GBC 302, Australia) [28].

3. Results

3.1. Chemical characterization of the adsorbent

Chemical characterization of fly ash, the adsorbent used in the present studies shows (Table 1) that its main constituents are silica (44.28%) and alumina (28.24%). Oxides of other metals are present in traces. Its surface area was found to be 61.82 $m^2 g^{-1}$,

Table 1
Physiochemical analysis of PTPS fly ash

Components	wt.%
Silica	44.28
Alumina	28.24
Iron oxide	2.21
Magnesia	1.47
Loss on ignition	3.02
Specific gravity	0.41
Surface area (m^2/g)	61.82
Porosity	0.29

which is quite significant. Porosity of fly ash was also determined and found to be 0.29.

3.2. Effect of contact time and initial concentration

Effect of contact time and concentration on the removal of Mn(II) has been shown in Fig. 1. It is clear from this figure that by varying concentration of Mn(II) in solution from 1.5 to 5.0 mg l^{-1}, the removal (%) decreased from 74.2 to 47.2% at 298 K, pH 8.0, 1.0×10^{-2} M NaClO$_4$ ionic strength at 100 rpm. This figure shows sharp rise in removal of Mn(II) in initial stages. Then gradually it attains equilibrium in 100 min and becomes constant. It shows that the process of Mn(II) removal on fly ash is highly concentration dependent. Higher percentage removal in lower concentration ranges has lot of industrial significance as in most cases the waste waters and industrial effluents have been reported to have lower concentrations of metallic species including that of Mn(II) [29].

3.3. Determination of rate constant for the process of removal

The rate constant for the process of removal of Mn(II) was determined by Lagergren's equation [17]:

$$\log(q_e - q) = \log q_e - \left(\frac{2.303}{k_{ad}}\right) t \qquad (1)$$
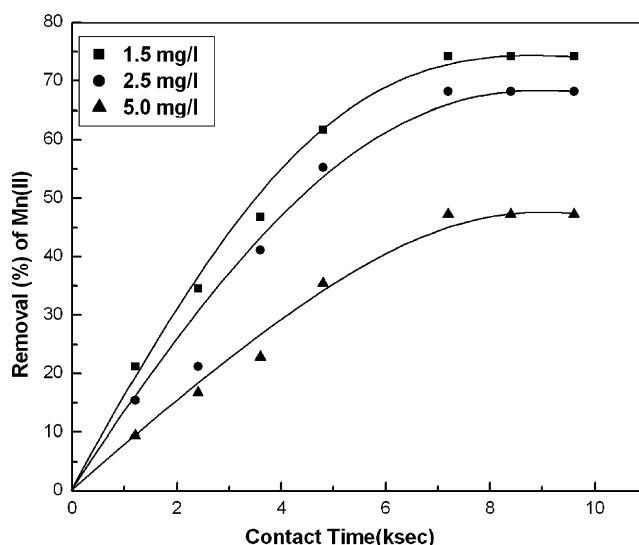

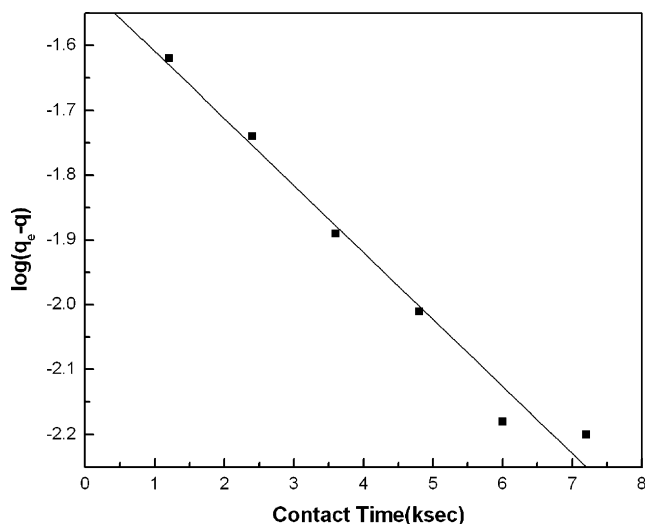Fig. 1. Effect of contact time and concentration on the removal of Mn(II).

Fig. 2. Lagergren's plot for kinetic modeling for removal of Mn(II).

Fig. 4. Maximum removal (%) of Mn(II) on fly ash at different values of pH.

where q_e and q (both mg g^{-1}) are the amounts of Mn(II) adsorbed at equilibrium and at any time 't', respectively. k_{ad} (ks^{-1}) is the rate constant of adsorption. The value of k_{ad} was determined by the graph 'log($q_e - q$) versus t' (Fig. 2) and was found to be 1.84×10^{-2} ks^{-1} at 1.5 mg l^{-1} Mn(II) concentration, 298 K and 1.0×10^{-2} NaClO$_4$ ionic strength.

3.4. Effect of pH on removal of Mn(II)

Effect of pH on removal of Mn(II) by adsorption on fly ash was studied and it was found that removal was higher in alkaline range of pH. The removal increased from 41.7 to 92.2% by varying the pH of the solution from 3.0 to 8.5 (Fig. 3) at 1.5 mg l^{-1} concentration, 298 K temperature and 1.0×10^{-2} M NaClO$_4$ ionic strength. Fig. 4 shows maximum removal (%) of Mn(II) at different values of pH.

The removal of Mn(II) at different values of pH can also be explained on the basis of pH$_{zpc}$. At a pH below pH$_{zpc}$ of
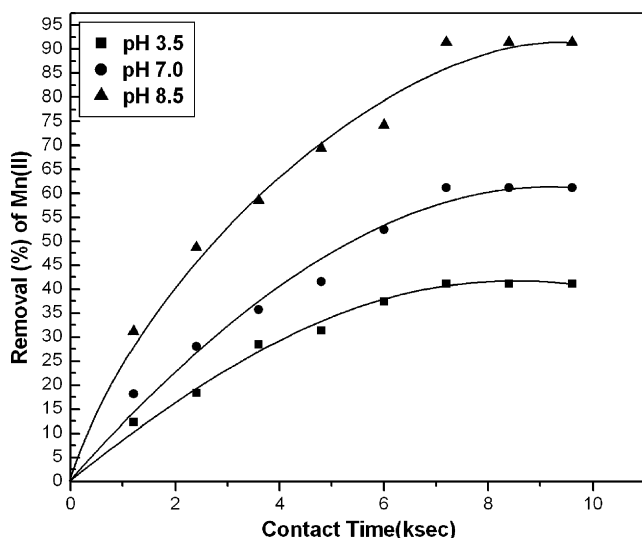

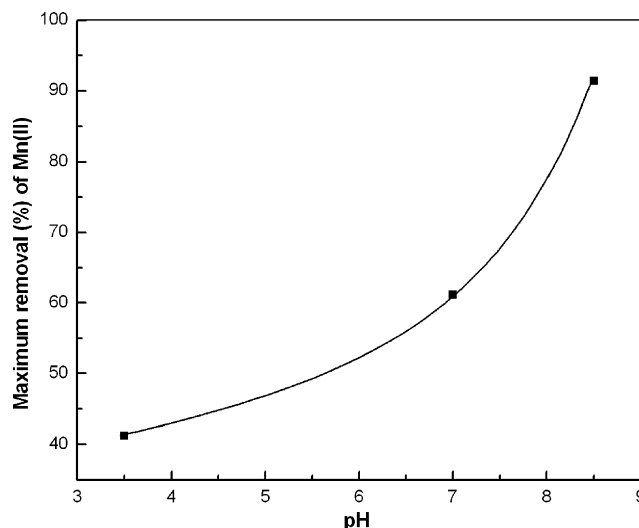Fig. 3. Effect of pH on removal of Mn(II).

the adsorbent, its surface is negatively charged whereas above pH$_{zpc}$, the surface is positively charged. pH$_{zpc}$ of the selected fly ash is 2.4. The surface of the adsorbent was positively charged beyond pH 2.4 and it is expected that the surface becomes more positively charged and thus the enhanced favorable electrostatic forces resulted in increasing removal of Mn(II).

Maximum removal of Mn(II) by the adsorption at pH 8.5 can be understood on the basis of presence of Mn^{2+} as Mn(H$_2$O)$_6$$^{2+}$, a hexaaqua ion at this pH range where its oxidation is resisted and thus removal at this pH value is because of adsorption only. Further, at higher pH, Mn(OH)$_2$ is formed and this is also observed during the experiments. This is further supported by earlier reports [11].

3.5. Effect of particle size

To study the effect of adsorbent particle size on removal of Mn(II), experiments were conducted at 100,150 and 250 μm diameter of fly ash particles. The removal decrease from 74.2 to 51.3% by increasing the diameter of the adsorbent particles from 100 to 250 μm at 1.5 mg l^{-1} Mn(II) concentration, pH 8.0 and 298 K (Fig. 5). Higher external surface area in smaller particle sizes at a constant amount of the adsorbent is the reason for higher removal of manganese at low particle sizes [29,30]. Further, the increase in removal with particle size does not have a 'directly proportional' relationship. Possible reason for this finding may be the lower free concentration of Mn(II) for smaller fly ash particles is significantly less than that for the larger adsorbent particles. This leads to comparatively lower value of adsorbed species.

3.6. Effect of temperature on removal of Mn(II)

Temperature has a pronounced effect on removal of pollutant species from aqueous solutions and industrial effluents with most adsorption process being exothermic in nature [31–33]. Investigation for present process also revealed its exothermic nature. The removal decreased from 74.2 to 51.2% by increas-
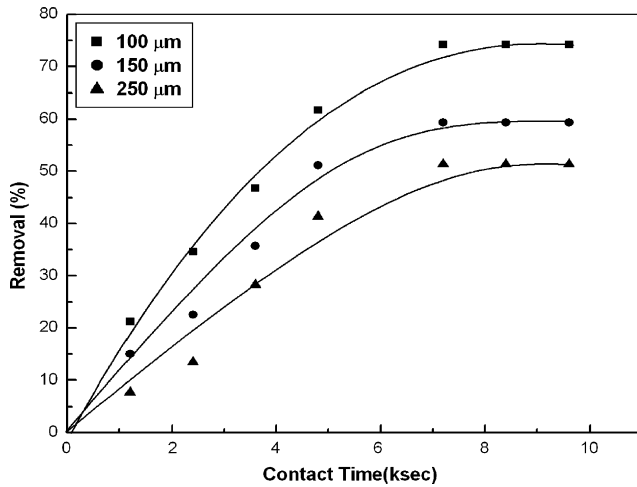
Fig. 5. Effect of particle size of the adsorbent on removal of fly ash.

ing the temperature from 298 to 308 K (Fig. 6) at $1.5\,mg\,l^{-1}$ Mn(II) concentration, 298 K, 8.0 pH, 100 rpm and 1.0×10^{-2} M NaClO$_4$ ionic strength. The variation in the removal may be a result of enhanced escaping tendency of pollutant species at increasing temperatures. The possibility of increased solubility at higher temperatures and hence a lower adsorption can also not be ruled out.

3.7. Thermodynamic studies

Thermodynamic studies are used to elucidate the mechanistic aspects of the process of removal. For the present investigations the thermodynamic parameters namely variation of free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were determined [34] using following well-known relations:

$$\Delta G^{\circ} = -RT \ln K_L \tag{2}$$

$$\Delta H^{\circ} = R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \left(\frac{K_2}{K_1} \right) \tag{3}$$
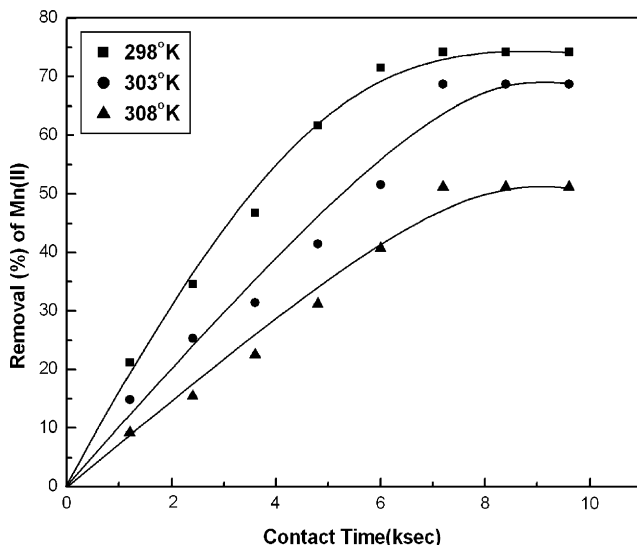

Fig. 6. Effect of temperature on removal of Mn(II).

Table 2
Thermodynamic parameters for the removal of Mn(II) by fly ash

Temperature (K)	$-\Delta G^{\circ}$ (kcal mol^{-1})	$-\Delta H^{\circ}$ (kcal mol^{-1})	$-\Delta S^{\circ}$ (kcal mol^{-1})
298	0.72	7.34	28.28
303	0.43	4.28	13.49
308	0.31		

Table 3
Heat of adsorption as a function of surface coverage (ΔH_x) at different values of surface coverage

Surface coverage (m^2 g^{-1} of Mn(II))	Heat of adsorption $-\Delta H_x$ (kcal mol^{-1})
0.15	8.20
0.20	8.03
0.25	7.82
0.30	7.55
0.35	7.18

$$\Delta S^{\circ} = \left(\frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \right) \tag{4}$$

where R is the gas constant, K_1 and K_2 the equilibrium constants at temperatures T_1 and T_2 (K), and K_L is Langmuir's constant ($1\,g^{-1}$). The values of the above parameters were calculated and are given in Table 2. The negative values of ΔG° (Table 2) indicate feasibility and spontaneity of the process of removal of Mn(II) by adsorption on the chosen fly ash. Reduction in values of ΔG° shows that at higher temperatures its values are low as compared with lower temperatures. This further confirms exothermic nature of the process of removal. The negative values of enthalpy also support that the process is exothermic in nature. Negative values of enthalpy change in present case also indicate that it's a favorable adsorption [35].

According to Clausius–Clapeyron equation [36], the heat of adsorption is a function of surface coverage. During the process of removal of Mn(II) by adsorption on fly ash, it was observed (Table 3) that the values of heat of adsorption, ΔH_x, decreased with surface coverage of the adsorbent. This variation in the values of ΔH_x may be attributed to two factors namely heterogeneity of the adsorbent surface and incident of interactions between different groups and adsorbed Mn(II) species [37].

4. Conclusions

An application of the PTPS fly ash has been investigated for removal of Mn(II) from aqueous solutions. The following conclusions can be drawn:

1. Fly ash can be successfully used for Mn(II) removal.
2. The removal is highly dependent on initial concentration of Mn(II) in solution and higher removal (%) has been observed in lower concentration ranges.
3. Rate constant of adsorption was found to be $2.12 \times 10^{-2}\,ks^{-1}$.

4. Effect of different important parameters on the removal of Mn(II) has been discussed.
5. Thermodynamic parameters have been calculated and the process of Mn(II) is spontaneous and exothermic.

The data obtained can serve as background data for designing treatment plants for treatment of Mn(II) wastewater economically. Though a detailed cost analysis is yet to be carried out, process of removal seems to be economically viable suitable for developing nations like India.

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