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Adsorptive removal of Mn(II) from water and wastewater by surfactant-modified alumina

M.U. Khobragade, Anjali Pal*

Civil Engineering Department, Indian Institute of Technology, Kharagpur 721302, India, Tel. +91 0 3222 281920; Fax: +91 0 3222 282254; email: anjalipal@civil.iitkgp.ernet.in (A. Pal)

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ABSTRACT

The adsorptive removal of Mn(II) from aqueous solution on prepared surfactant-modified alumina (SMA) has been studied for the first time. The process of removal is via adsolubilizaion of Mn(II) in the admicelle formed by sodium dodecyl sulfate on the alumina surface. The effects of contact time, initial concentration of Mn(II), adsorbent dose, and pH on removal of Mn(II) have been examined by batch study. Adsorption–desorption equilibrium is reached in 30 min. The optimum range of pH for Mn(II) removal is 6–7. The results obtained are used for the applicability of Freundlich and Langmuir adsorption isotherm. The experimental and theoretical q_e values for both models have been compared. The error analysis and comparison of R^2 values shows that the adsorption follows Freundlich isotherm better. The adsorption kinetics obey pseudo-second-order model. The adsorbent SMA is used for the removal of Mn(II) from the Mn(II)-spiked wastewater and manganese-bearing real industrial wastewater.

Keywords: Mn(II) removal; Surfactant-modified alumina; Adsorption; Adsolubilization; Kinetic studies; Applicability to wastewater treatment

1. Introduction

Rapid industrialization results in the release of wastewater containing large quantities of heavy metals, which may cause harmful effects on both biotic and abiotic components of the environment. The conventional treatment methods used to remove heavy metals from aquatic environment include adsorption, chemical precipitation, ion exchange, membrane filtration, and solvent extraction. However, among these methods some involve high operational and initial cost and some are not efficient for complete removal of heavy metals, especially when they are present at low concentrations. Adsorption process, among all, is found to be highly effective, easy to operate, economical, and is often recommended when the metal ions are present at low concentrations [1–7].

Manganese is a widely used heavy metal and it finds its application in steel alloy, glass and ceramics, paint and varnishes, ink and dye, dry cell batteries, match and fireworks, electroplating, metallurgical process, and mining. Although it is recognized as an essential element for human health, but prolonged inhalation of manganese dust and fume may cause harmful impact on human respiratory tract and brain which may lead to the symptoms like permanent disability, weakness, and even paralysis [8]. While the United States Environmental Protection Agency

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*Corresponding author.

(USEPA) [9] and World Health Organization (WHO) [10] recommend a concentration <0.05 mg/L for manganese in drinking water, in Indian standard the allowable level of Mn(II) in drinking water has been set as 0.1 mg/L [11]. Thus, treating manganese-bearing wastewater by a suitable means is a challenge. Earlier, many adsorbent materials, such as chemically treated modified plant waste [1], natural zeolite [2], clay mineral [3], fruit shell [12], *Albizia procera* legumes [13], activated Chilean zeolites [14], carbon aerogel [15], manganese oxide coated zeolite [16], hematite [17], modified clay [18], activated carbon from coconut shell [19], granular activated carbon [20], chemically treated granular activated carbon [21], kaolinite [22], and tannic acid immobilized activated carbon [23], were used for Mn(II) removal from aqueous solution. The adsorption capacities of the materials and the conditions applied for manganese removal are compiled in Table 1.

Solid surfaces on modification with surfactants show increased efficiency toward pollutant removal [24]. Sodium dodecyl sulfate (SDS), an anionic surfactant (AS), can be used to modify the surface of alumina. Under properly controlled conditions, higher loading of SDS on alumina can form bilayer called admicelle, which has the capability to solubilize organic molecules within it by hydrophobic or ionic interaction. This process is known as “adsolubilization” [25–29]. In our earlier studies, it was shown that surfactant-modified alumina (SMA) can be used to remove cationic dyes (such as crystal violet (CV) [29] and malachite green (MG) [30]) and phenol [31] from aquatic environment through adsolubilization. Among other applications of SDS-coated alumina, the recovery of benzalkonium homologue surfactants from environmental samples (such as raw sewage, treated sewage, and river sample) [32], and the removal of pesticides from contaminated natural water [33], are worth mentioning. Although application of SMA to remove organic contaminants in an efficient manner has been established, however, the potentiality of SMA toward the adsorption of metal ions has not been explored so far. The main objective of the present work is to examine the suitability of SMA as an adsorbent for the effective and efficient removal of Mn(II) from Mn(II)-spiked distilled water (MSDW) and Mn(II)-spiked wastewater (MSWW). Besides this, the material has been evaluated for real manganese-bearing industrial wastewater (RIWW) treatment also. The “surfactant modification of alumina” and plausible “adsolubilization” of Mn(II) on SMA has been

Table 1
Comparison of experimental conditions and adsorption capacities of various adsorbents used for Mn(II) removal

Adsorbent	AD[a] (g/L)	pH	CT[b] (min)	IC[c] (mg/L)	AC[d] (mg/g)	Reference
Natural zeolite	20	6.0	330	100–400	6.45	[2]
Clay mineral	2.5	NM[e]	2,880	55–550	28.6	[3]
Fruit Shell	4	NM[e]	NM[e]	NM[e]	122	[12]
Albizia procera legume	NM[e]	4.0	30	NM[e]	35.28	[13]
Activated Chilean zeolite	2.5	6–6.8	120	5–600	21.29	[14]
Carbon aerogel	10	6.0	2,880	1–5	1.27	[15]
Manganese oxide coated zeolite	2.5	6.0	120	25–600	30.5	[16]
Hematite	20	8.0	210	1–5	0.18	[17]
Modified clay (K-10, NT-25)	5.0	6.0	60	10–1,000	4.8, 6	[18]
Activated carbon from coconut shell	NM[e]	5.8	NM[e]	NM[e]	51.23	[19]
Granular activated carbon	NM[e]	NM[e]	360	NM[e]	2.54	[20]
Chemically treated granular activated carbon	10	4	2,880	1–5	1.27	[21]
Kaolinite	10	NM[e]	120	NM[e]	0.45	[22]
Tannic acid immobilized activated carbon	2	7	60	1–10	1.13	[23]
SMA	20	6.0	30	10–70	1.31	Present study

[a] AD: Adsorbent dose.

[b] CT: Contact time.

[c] IC: Initial concentration.

[d] AC: Adsorption capacity.

[e] NM: Not mentioned.

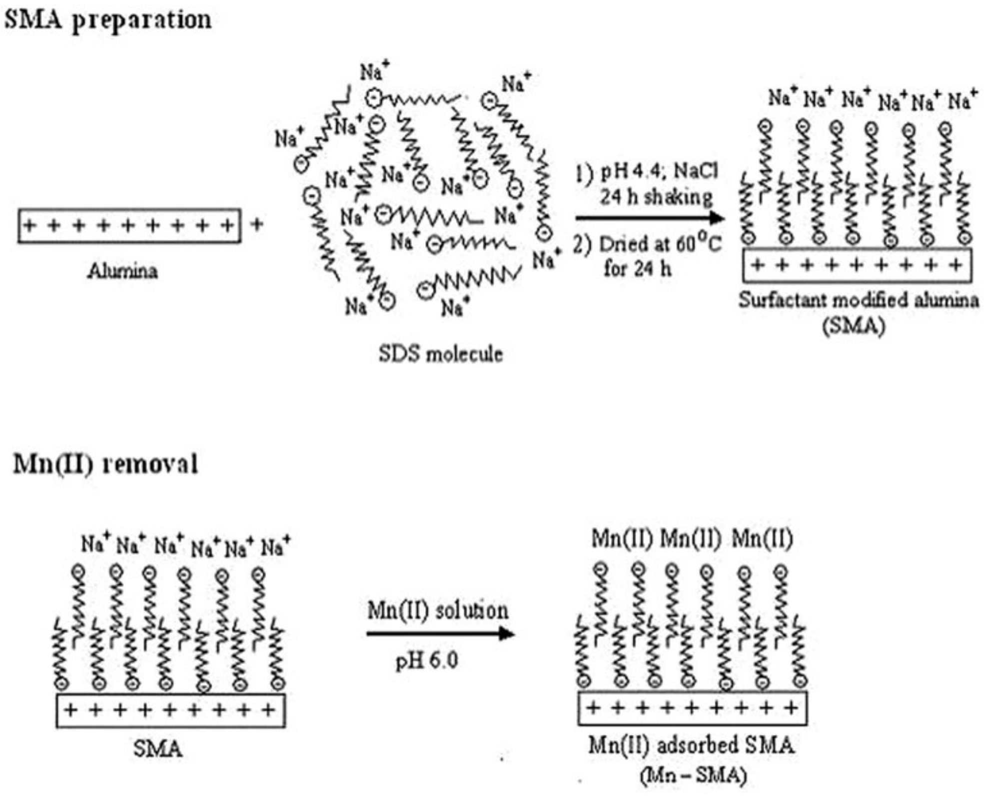

Fig. 1. Schematic of SMA preparation and adsolubilization of Mn(II).

schematically depicted in Fig. 1. To the best of our knowledge this is the first report where SMA has been used as an adsorbent to suppress the level of Mn(II) ions in wastewater.

2. Materials and methods

2.1. Reagents

All chemicals were of high purity and these were used without further purification. The chemicals viz. SDS, acridine orange (ACO) (chemically known as 3,6-bis(dimethyamino acridine), glacial acetic acid, toluene were from BDH (AR grade). The neutral form of alumina used for preparing SMA was from SRL, and it was used without further grinding or sieving. The granulation of neutral alumina used for our studies was 70–290 mesh ASTM and the molecular weight was 101.9. Purified Mn(II) chloride ($MnCl_2 \cdot 4H_2O$) was used as received. The stock solution (500 mg/L) of Mn(II) was prepared by dissolving 1.802 g $MnCl_2 \cdot 4H_2O$ per liter of distilled water. The same stock was used for the preparation of diluted solutions (10–100 mg/L). Double distilled water was used throughout the study.

2.2. Instrumentation

Fast sequential flame atomic absorption spectrometer (AA240FS) was used for manganese determination. Five standard solutions of known concentrations (1–5 mg/L) of Mn(II) were used for the calibration curve. The samples having Mn(II) concentration beyond the range of calibrated concentration were diluted. A shaker–incubator was used to agitate the samples for a defined contact time. Metrohm 761 compact IC was used for the measurement of cations (except Mn and Fe) and anions present in the wastewater. Digital pH meter (GENEI India) was used for measurement of pH. The calibration of pH meter was done using known buffer solutions of pH 4 and 7. A spectrophotometer (Thermo Spectronic UV1, UK) was used for absorbance measurement. Electronic balance (Mettler Toledo) was used for weighing purpose. Digital conductivity meter/TDS meter (Eutech CON 510) was used for the measurement of electrical conductivity/total dissolved solids, respectively. A scanning electron microscope (SEM) (JEOL/JSM 5800, Japan) with energy dispersive X-ray (EDX) attachment was used for SEM and EDX analysis of the powdered samples. During the sample preparation, a pinch of powder was mixed in 10 mL alcohol. This sample was then dispersed using an ultrasonicator. Few drops of samples were then adhered on the surface of the carbon tape and mounted on small square aluminum piece and then dried. This dried sample was used for SEM imaging.

2.3. Preparation of adsorbent (SMA)

The schematic for the preparation of SMA and the removal of Mn(II) using SMA are shown in Fig. 1. Firstly, the alumina was treated with SDS (molecular formula: $CH_3(CH_2)_{11}OSO_3Na$; molecular weight: 288.38; water solubility: 250 g/L at 20°C; critical micelle concentration (CMC): 8.1×10^{-3} mol/L), which is a representative member of AS, to form admicelle structures on their surfaces. Secondly, this SMA was used as an adsorbent for the removal of manganese from water. The SMA was prepared following the procedure reported earlier [29]. Typically, alumina (100 g) was shaken for 24 h with SDS solution having concentration 20,000 mg/L along with NaCl (at concentration 2,500 mg/L). The zero point charge (pH_{ZPC}) of the alumina was 9.15. Therefore, the pH was adjusted to 4.4. After shaking, the supernatant was collected and the alumina was washed thoroughly, initially with tap water and finally with distilled water. Then, the material was dried at 60°C for 24 h. The alumina thus obtained is called SMA, which was used as the adsorbent material in our study. The SDS coverage on alumina surface was determined following the method reported earlier [34] and the loading was found to be 78.23 mg/g of alumina.

2.4. Characterization of adsorbent by SEM and EDX

The size, shape, morphology, and the elemental composition of the adsorbent particles before and after the Mn(II) removal was observed through SEM and EDX analyses. No significant changes were observed in the SEM images (Fig. 2(a) and (b)) of SMA after Mn(II) adsorption. The EDX analyses of the SMA before and after Mn(II) removal confirm the incorporation of manganese (~0.21%) on the adsorbent surface (Table 2).

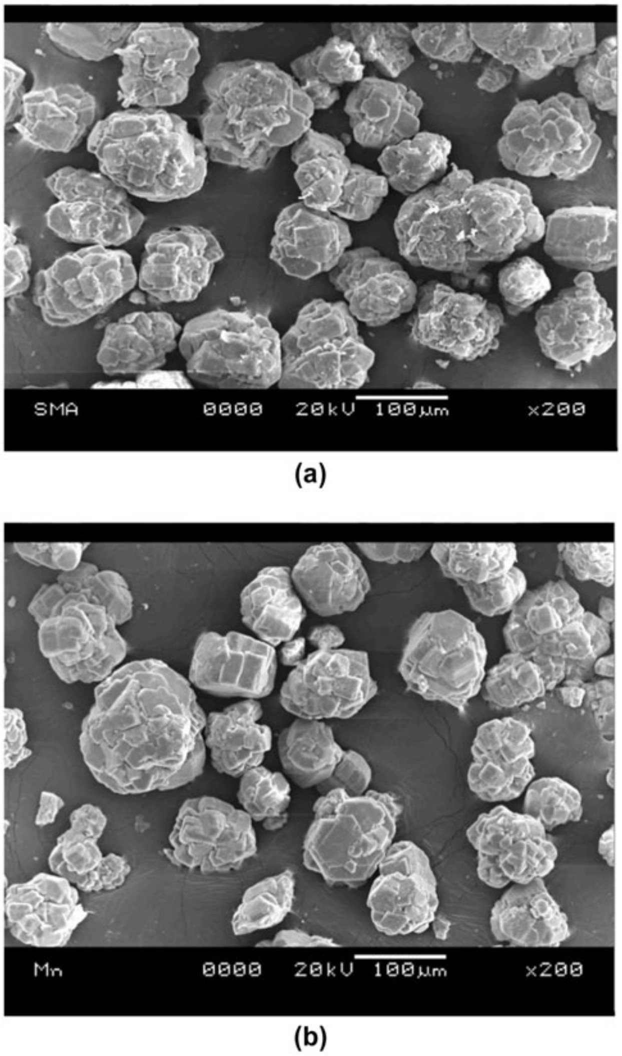

Fig. 2. (a) SEM image of SMA; (b) SEM image of manganese-adsorbed SMA.

Table 2
Atomic % of elements in SMA and Mn(II)-adsorbed SMA

	Atomic %	
Element	SMA[a]	Mn(II)-adsorbed SMA
O	60.73	60.13
Al	38.12	39.26
Na	0.32	0.31
Cl	0.83	0.09
Mn	–	0.21

[a] SMA: Surfactant-modified alumina.

2.5. Experimental methods for batch studies

The effect of pH, initial concentration of Mn(II) ions, contact time, and adsorbent dose were examined through batch experiments. In a typical procedure, the required quantity of dry SMA was weighed and placed in wide mouth bottle having capacity 30 mL, and to it 20 mL of synthetic sample of Mn(II) was added. The mouth of the bottle was sealed with plastic cap and then the bottle was shaken in an incubator–shaker at

150 rpm for defined period at 30°C. After that the sample was filtered through normal filter paper and the filtrate was collected. The absorbance of the filtrate was measured at 279.5 nm using AAS and the concentration of manganese was found out from the pre-established calibration curve. The removal efficiency (%) of Mn(II) was calculated using Eq. (1), where C_0 is the initial concentration (mg/L) and C is the final concentration (mg/L) in solution.

$$\text{Removal efficiency} = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

2.6. Adsorption isotherm

The adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solutions at constant temperature. In literature, several types of isothermal adsorption relation exist. The adsorption isotherm can be explained by using the most common relationship between the amount of adsorbate (mg) adsorbed per unit mass of adsorbent (g) and the equilibrium concentration in the solution (mg/L). In our work, Langmuir and Freundlich isotherm models were studied.

2.6.1. Langmuir isotherm

The Langmuir isotherm is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of surface. Eq. (2) represents the Langmuir isotherm and Eq. (3) represents its linearized form. The value of q_e is calculated using Eq. (4), where q_e = amount of adsorbate (mg) adsorbed (at equilibrium) per unit mass (g) of adsorbent, C_e = equilibrium concentration (mg/L), a = Langmuir constant related to adsorption energy (L/mg), b = maximum adsorption capacity (mg/g), M is the dose (g/L) of adsorbent applied to the sample, and C_0 is the initial adsorbate concentration (mg/L).

$$q_e = \frac{a\,b\,C_e}{1 + a\,C_e} \tag{2}$$

$$\frac{1}{q_e} = \frac{1}{a\,b}\left(\frac{1}{C_e}\right) + \frac{1}{b} \tag{3}$$

$$q_e = \frac{C_0 - C_e}{M} \tag{4}$$

The essential characteristics of Langmuir isotherm can be described by a dimensionless equilibrium parameter R_L and is determined by Eq. (5) where C_0 is the initial concentration of

$$R_L = \frac{1}{(1 + a\,C_0)} \tag{5}$$

Mn(II) and a is the Langmuir constant. R_L is also called as separation factor and is useful to know the applicability of adsorption process. When $R_L < 1$ it signifies favorable adsorption, R_L = zero implies that the adsorption process is irreversible, $R_L > 1$ indicates unfavorable adsorption, and $R_L = 1$ reveals linear adsorption [19].

2.6.2. Freundlich isotherm

The Freundlich adsorption isotherm is mathematically expressed by Eq. (6) and the linearized form of the model is given by Eq. (7), where K and n are constants. K is related to the adsorption capacity (mg of contaminant removed per unit mass (g) of adsorbent), and n indicates the adsorption intensity.

$$q_e = KC^{1/n} \tag{6}$$

$$\log q_e = \frac{1}{n}\log C_e + \log K \tag{7}$$

2.6.3. Error analysis in adsorption isotherm

Linear regression analysis has been the most workable tool [35] to analyze the adsorption isotherm data for the evaluation of fitness of the model equation [36]. In addition to this, the best fit of isotherm can also be estimated using non-linear error function such as residual root mean square error (RMSE) [37]. The standard equation of this error function is presented in Eq. (8), where n is the number of data points.

$$\text{RMSE} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(q_e\,(\text{expt}) - q_e\,(\text{theo})\right)^2} \tag{8}$$

3. Results and discussion

3.1. Effect of contact time

The effect of contact time up to 70 min on the uptake of Mn(II) ion at different initial concentrations (20, 30, 50, 70, and 100 mg/L) were investigated. This

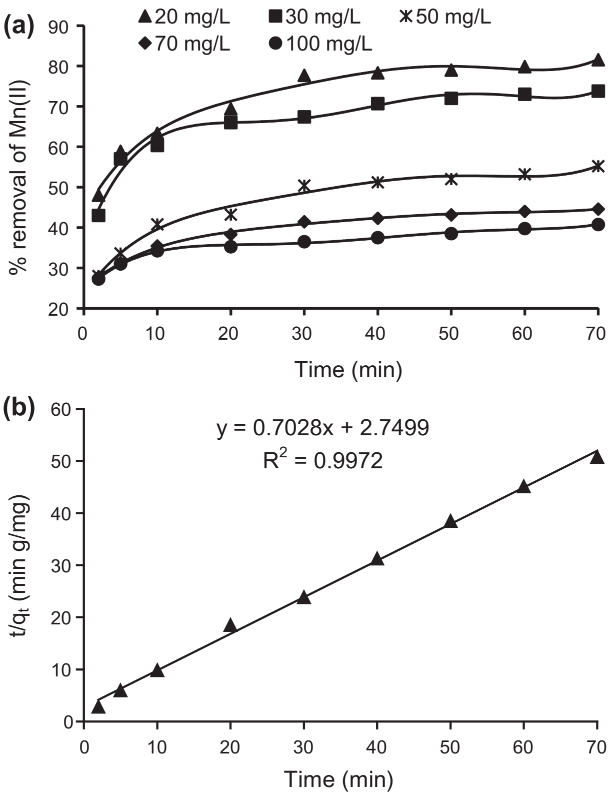

Fig. 3. (a) Effect of contact time on removal of Mn(II); (b) Pseudo-second-order kinetic model for 50 mg/L Mn(II).

was performed on 20 mL of synthetic Mn(II) sample using 20 g/L adsorbent dose. The percentage of Mn (II) removal with time is shown in Fig. 3(a). It is clear from the figure that the removal is very fast, and maximum removal takes place within the first 30 min of contact time. After 30 min the removal rate becomes almost constant, indicating that adsorption–desorption equilibrium is reached. For this reason, 30 min contact time was used for further studies. This equilibrium time is much less as compared to other reported adsorbents for Mn(II) removal [2,15]. This quick removal is an indication of adsolubilization, and it is advantageous for continuous mode of operations.

The removal of Mn(II) ion (initial conc.: 50 mg/L) under the experimental conditions (SMA dose: 20 g/L) followed pseudo-second-order kinetics (Fig. 3(b)). This indicates that the interaction of Mn(II) with the adsorbent surface is chemical/ionic in nature [38,39]. This speaks in favor of adsolubilization of Mn(II) on the admicelle with negative charge on its outer surface.

3.2. Effect of initial concentration

The effect of initial Mn(II) concentration with constant adsorbent dose was studied. For this study, Mn(II) concentrations were varied in the range 10–100 mg/L keeping the SMA dose fixed at 20 g/L. After shaking for 30 min (at 150 rpm) followed by filtration, the remaining Mn(II) concentration in the filtrate was determined. Fig. 4 shows the percentage of Mn(II) removal at its various initial concentrations (at a constant SMA dose). The removal efficiency decreased as the initial concentration was increased. It was observed that in the range of initial Mn(II) concentration 10–100 mg/L, the removal efficiency varied within 88.2–34.2%. In this context, it is important to mention that only alumina showed much less removal of Mn(II) under similar conditions. For example at a dose of 20 g/L, alumina could remove only ~46% when initial concentration of Mn(II) was 20 mg/L. However, under identical condition the observed removal of Mn(II) was ~74% in case of SMA. This clearly indicates that the surface modification of alumina plays a significant role in Mn(II) removal.

Fig. 4 shows the plot of q_e (mg of adsorbate removed per gram of SMA) versus C_0 (initial concentration). It is clear from the figure that q_e increases with the increase in the initial Mn(II) concentration. This is due to the increase in the driving force of the concentration gradient with the higher initial Mn(II) concentration [40].

3.3. Effect of adsorbent dose

The percent removal of solute from aqueous solution depends on the adsorbent dose. The study was conducted at 30˚C to examine the effect of SMA dose on the removal of Mn(II) ion (20 mL; conc. 20 mg/L). The adsorbent doses were varied in the range 3–30 g/L. After allowing the optimum contact time, the adsorbent material was separated and the remaining Mn(II) concentration was measured. The plot of Mn(II) removal (%) versus adsorbent dose is

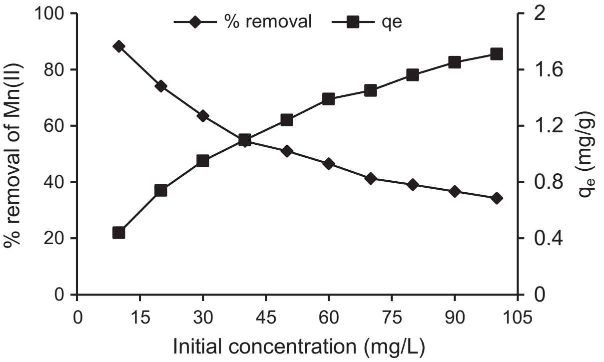

Fig. 4. Effect of initial concentration on removal of Mn(II) using SMA as adsorbent (dose: 20 g /L).

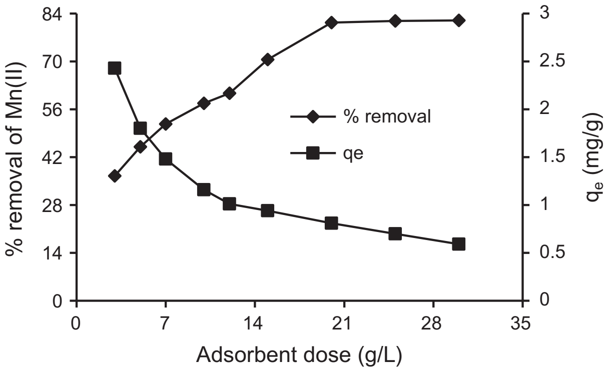

Fig. 5. Effect of adsorbent dose on removal of Mn(II) (conc.: 20 mg/L) using SMA as adsorbent.

shown in Fig. 5. The curve shows that the removal increases as the dose increases. This is due to the fact that with a higher adsorbent dose more active sites are available while the solute concentration remains fixed [41]. On the other hand, as plotted in the same figure, the adsorption capacity (q_e) decreases with the increase in adsorbent dose. This is because on increasing the adsorbent dose lower utilization of adsorption capacity takes place [42,43].

3.4. Effect of pH

The pH is an important factor in wastewater treatment, and it decides the type of treatment required for the removal of various contaminants present in the effluents. In our study, the effect of pH on the removal of Mn(II) was investigated with Mn(II) solution having concentration 30 mg/L. The pH of distilled water was adjusted to 4.08, 5.03 6.07, 8.05, and 10.03 using 0.1 N HCl and 0.1 N NaOH. At pH 10.03, the solution containing Mn(II) turned yellow and the pH of the solution dropped to 8.34. This is due to the formation of hydrated MnO_2. Hence, the study was performed in the range of pH 4.0–8.1. The SMA at a dose of 20 g/L was placed in different plastic bottles and to each of them 20 mL sample of Mn(II) at pre-maintained pH was poured. The bottles were shaken at 150 rpm for 30 min at 30˚C. The obtained data were analyzed and plotted as the percentage of Mn(II) removal versus pH (Fig. 6). The figure shows that at pH 4.04, 5.03, 6.07, and 8.05 the removal efficiencies were 43.48, 57.88, 61.08, and 62.02%, respectively. Hence, the entire study was conducted at pH 6–7.

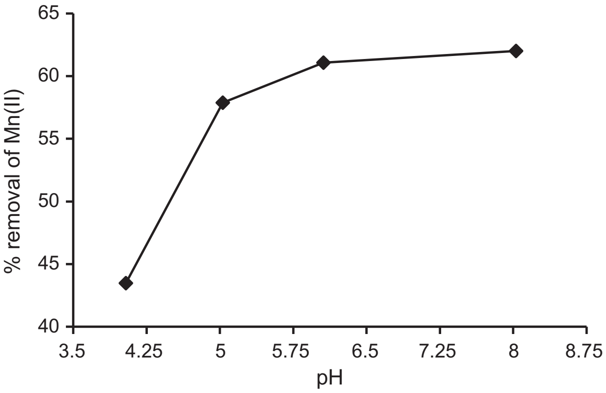

Fig. 6. Effect of pH on removal of Mn(II) (conc.: 30 mg/L) using SMA as adsorbent (dose: 20 g/ L).

3.5. Adsorption isotherm

The applicability of Langmuir and Freundlich adsorption isotherm was tested for the removal of Mn(II) at constant adsorbent dose (20 g/L) with varying initial Mn(II) concentrations in the range 10–70 mg/L. The contact time applied was 30 min and the temperature 30˚C. The constants for both the isotherms were calculated from the slope and intercept of the Eqs. (3) and (7). Fig. 7(a) and (b) show the Langmuir ($1/q_e$ versus $1/C_e$) and Freundlich isotherm plots (log q_e versus log C_e), respectively. It is clear

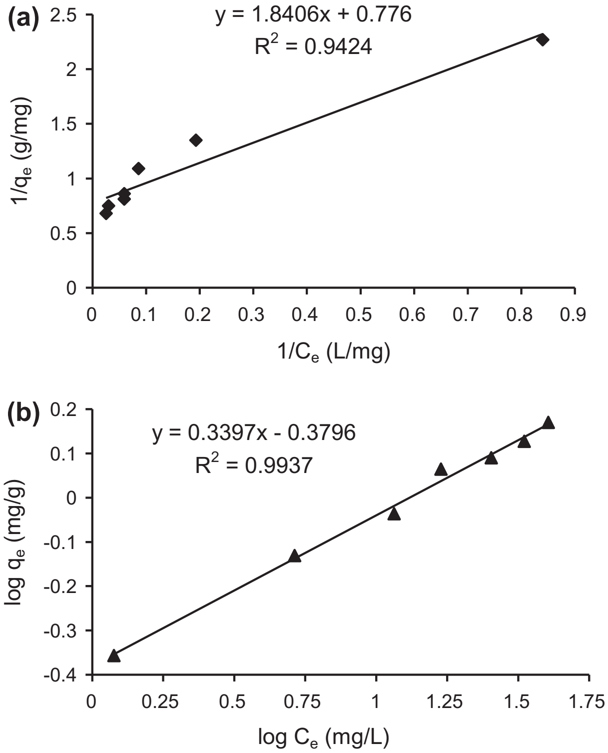

Fig. 7. (a) Langmuir and (b) Freundlich adsorption isotherm on removal of Mn(II) using SMA as adsorbent.

Table 3
Langmuir adsorption isotherm constants for Mn(II) removal by SMA

		Langmuir adsorption isotherm constants				
T (K)	q_e (expt) (mg/g)	q_e (theo) (mg/g)	% of deviation	a (L/mg)	b (mg/g)	R^2
303	1.47	1.22	−20.49	0.42	1.29	0.9424

Table 4
Freundlich adsorption isotherm constants for Mn(II) removal by SMA

		Freundlich adsorption isotherm constants				
T (K)	q_e (expt) (mg/g)	q_e (theo) (mg/g)	% of deviation	n	K (mg/g)	R^2
303	1.47	1.48	0.68	2.94	0.42	0.9937

from the coefficient of determination (R^2) and from the q_e(theo) and q_e(expt) values (Tables 3 and 4) (calculated/obtained against 70 mg/L Mn(II) concentration) that Freundlich model is better followed. Values of "K" and "n" have been calculated from the intercept and slope of the Freundlich plot, respectively, and are shown in Table 4. Adsorption is favorable for values $0.1 < 1/n < 1.0$ [19]. In our case, the obtained value of n speaks about the favorable adsorption on the surfactant-modified surface. Further, the non-linear error functions (RMSE) have been calculated for both Langmuir and Freundlich isotherm models. The RMSE value for Langmuir is found to be 0.102, while that for Freundlich it is 0.0041. This also indicates that the adsorption follows Freundlich model better.

The dimensionless parameter R_L indicates the type of isotherm (irreversible $R_L = 0$, favorable $0 < R_L < 1$, linear $R_L = 1$, or unfavorable $R_L > 1$). The value of R_L has been calculated using the Langmuir adsorption isotherm constant "a" (Eq. 5) and found to be 0.19 at 30°C for Mn(II) solution having concentration 10 mg/L. This value indicates that the adsorption process is favorable [19].

3.6. Applicability of SMA to treat MSWW

The applicability of SMA as an adsorbent was examined with a real wastewater collected from a canal situated at Bhilai, Chhattisgarh. The wastewater sample was comprised of domestic sewage (as a major portion) from the township area and treated water from a steel manufacturing industry. The well mixed wastewater sample was collected at a depth of 0.3−0.5 m below the water surface of the canal. The collected sample was then transported to the laboratory and was preserved at 4°C in a refrigerator for

Table 5
Characteristics of Mn(II)-spiked wastewater (MSWW) before and after treatment with SMA

Characteristics	Concentration before treatment	Concentration after treatment
pH	6.0	7.97
Mangansese (mg/L)	10	4.30
Chloride (mg/L)	252.51	93.94
Sulfate (mg/L)	7.80	6.59
Sodium (mg/L)	154.65	89.97
Calcium (mg/L)	77.70	4.95
Magnesium (mg/L)	26.73	23.33
Potassium (mg/L)	4.05	2.85
Turbidity (NTU)	9.0	0.4
Electrical conductivity (μmhos/cm)	841	535
Total dissolved solid (mg/L)	540	349
Iron (mg/L)	0.91	0.49
Chemical oxygen demand (mg/L)	173.42	95.68

further use. Preliminary studies reveal that the effluent does not contain any manganese. Thus, Mn(II) at a known concentration of 10 mg/L was spiked into the sample water. This manganese-spiked wastewater was designated as MSWW. Before the treatment, the characteristics of effluent were determined. The water quality parameters are presented in Table 5. The effluent was treated in two steps. In the first step, the pH of the solution was adjusted to ~6.0 using 0.5 N HNO_3; in the second step, the wastewater was treated with SMA. The idea was to minimize the effect of pH on the removal of Mn(II). It is well known that Mn(II) can be removed significantly by adjusting the pH to the alkaline range. Moreover, upon treatment with SMA, the pH of the water increases slightly. In the treatment procedure, the adsorbent dose used was 20 g/L, shaking speed 150 rpm, contact time 30 min, and temperature 30˚C. The measured characteristics of the sample after the treatment are reported in Table 5. It is obvious from the compiled data that SMA has the potential to improve the quality of water by reducing the level of other contaminants. The removal of Mn(II) was ~57%, which was less compared to that obtained for the MSDW. This was due to the presence of various cations, anions, and other substances in the effluent. One interesting observation, however, is that iron and other ions present in the MSWW are also removed by SMA along with Mn(II) leading to better quality water.

A comparative study on the effect of adsorbent dose (1, 5, 10, and 20 g/L) on Mn(II) removal from MSWW and MSDW has been made. In both cases, the initial spiked Mn(II) concentration was 10 mg/L. It is found that the removal of Mn(II) increases with the increase in adsorbent dose for both MSWW and MSDW (Fig. 8(a)).

The effect of contact time on the removal of Mn(II) from MSWW and MSDW using SMA was investigated. The experiments were conducted with solutions (each 20 mL) having Mn(II) concentration 10 mg/L using SMA dose of 20 g/L. It was noted that at 30 min of contact time, the adsorption–desorption equilibrium was attained, and at this point the removal efficiency was 57.7% for MSWW and 88.04% for MSDW (Fig. 8(b)). After 30 min the adsorption was not very significant.

Pseudo-second-order kinetic models were applied to both MSWW and MSDW (Fig. 8(c)). The R^2 values for MSWW and MSDW are 0.999 and 0.999 indicating that pseudo-second-order model is followed. The q_e(theo) and q_e(expt) are compared for MSWW and MSDW, and the percentage deviations are calculated. It is found to be within ±1.23%.

3.7. Applicability of SMA to treat Mn(II)-bearing real industrial wastewater

The efficacy of SMA for manganese removal from real industrial wastewater (RIWW) was examined on a sample collected from a metal tube manufacturing industry situated in Maharashtra. The concentration of manganese originally present in the wastewater was 10.27 mg/L. The experimental procedure was the same as applied for MSWW sample having 10 mg/L concentration. The SMA dose used was 20 g/L and

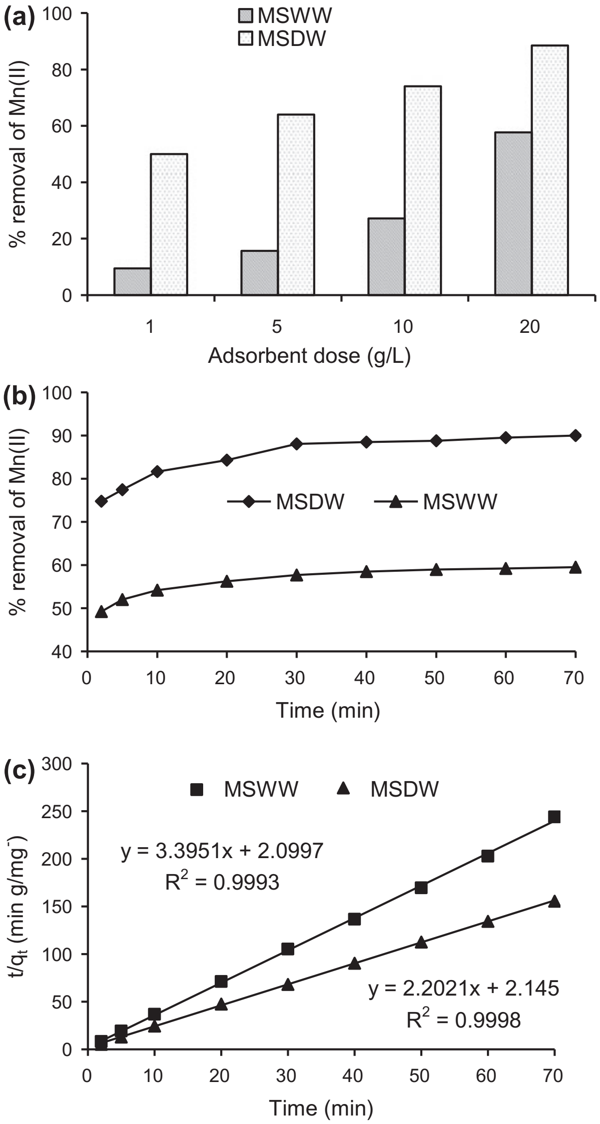

Fig. 8. (a) Effect of adsorbent dose, (b) Effect of contact time, (c) Comparison of pseudo-second-order kinetic models for Mn(II)-spiked wastewater (MSWW) and Mn (II)-spiked distilled water (MSDW).

Table 6
Characteristics of real industrial wastewater (RIWW) before and after treatment with SMA

Characteristics	Concentration before treatment	Concentration after treatment
pH	6.0	7.46
Turbidity (NTU)	8	1.6
Electrical conductivity (μmhos/cm)	686	476
Total dissolved solids (mg/L)	548	345
Total alkalinity (mg/L)	154	78
Total hardness (mg/L)	260	112
Biochemical oxygen demand (mg/L)	38	22
Chemical oxygen demand (mg/L)	168.3	88.3
Calcium (mg/L)	67.2	33.2
Magnesium (mg/L)	22.08	13.2
Sodium (mg/L)	36.75	22.67
Potassium (mg/L)	0.91	0.54
Fluoride (mg/L)	0.952	0.52
Chloride (mg/L)	66.53	23.65
Sulfate (mg/L)	47.26	30.21
Phosphate (mg/L)	2.57	1.43
Nitrate (mg/L)	4.6	2.1
Manganese (mg/L)	10.27	3.67

the contact time was 30 min. Before the treatment with SMA, the pH of the water sample was ~7.4. Thus, the pH was adjusted to 6.0 using 1 N HCl. The water quality parameters before and after treatment are compiled in Table 6, which indicates that ~64% removal of manganese takes place. It is encouraging to observe that the treatment improved the water quality in terms of other contaminants.

3.8. Desorption study and reuse of material

In every treatment process, sludge management is an important step. Therefore, it is pertinent to examine the extent of desorption of Mn(II) from the exhausted SMA. In our study, first the SMA was loaded with Mn (II) to form manganese-loaded SMA (Mn-SMA). For this study, 20 mL solution having the initial Mn(II) concentration of 50 mg/L was used and 0.4 g SMA (at a dose of 20 g/L) was applied. The remaining concentration of Mn(II) in solution after 30 min of contact was 25.75 mg/L. In the second step, the recovery of the adsorbed amount of manganese from SMA was carried out using two different extracting solutions viz. (i) aqueous 1 N HCl, and (ii) aqueous 0.2 M Na_2-EDTA. For this study, exhausted SMA (0.4 g) was shaken at an agitation speed of 150 rpm with 20 mL of extracting solution for 30 min at 30˚C. It was interesting to observe that ~35% desorption took place in case of aqueous HCl and ~92% desorption occurred in aqueous Na_2-EDTA. The regenerated SMA from Na_2-EDTA treatment was reused for Mn(II) adsorption but the removal efficiency was poor (~20%). This prompted us to prepare SMA out of the exhausted material after treating the material with 0.25 M NaOH followed by thorough washing with water, drying, and treatment with SDS under controlled conditions. It was surprising that the newly prepared SMA out of the exhausted material showed similar efficiency for Mn(II) removal when compared with freshly prepared SMA.

In our earlier report, it was demonstrated that aqueous NaOH (0.25 N) could desorb SDS from SMA. Therefore, aqueous NaOH might not be a good choice to desorb Mn(II) from the exhausted Mn-SMA. However, no Mn(II) was desorbed from Mn-SMA upon treatment with 1 N NaOH.

4. Conclusions

SMA, as an adsorbent, has shown the promise in removing manganese from MSDW, MSWW, and from RIWW. The plausible mechanism of removal is through adsolubilization. The effects of various parameters (such as contact time, initial Mn(II) concentration, adsorbent dose, pH) have been studied. The optimum pH range for the removal of Mn(II) is 6–7. The entire studies have been carried out at 30˚C. The removal of Mn(II) is fast and the equilibrium reaches in 30 min following pseudo-second-order model. The adsorption obeys Freundlich isotherm. The adsorbed Mn(II) could be desorbed efficiently (~ 92%) from the exhausted SMA by 0.2 M Na_2-EDTA, and the adsorbent can be reused to prepare fresh SMA.

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