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Removal of potassium permanganate from water by modified carbonaceous materials

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ABSTRACT

Potassium permanganate is commonly used in multidiscipline processes as a strong oxidizing agent for oxidative treatment of a great number of organic and inorganic compounds. In this work, a method is proposed for removal of $KMnO_4$ from aqueous solutions and real water samples using treated and activated carbon (AC) sorbents with sulfuric acid. The potential applications of five modified AC sorbents for removal of $KMnO_4$ were explored under different experimental controlling factors including pH, contact time, initial concentration of $KMnO_4$, sorbent dosage, and competing ions by the batch equilibrium technique. The removal values of $KMnO_4$ were found to be ≥99.56% in the examined solutions (pH 1.0–7.0). In pH 1.0–2.0, $KMnO_4$ removal from aqueous solutions was found to proceed by an anion exchange and ion pair interaction mechanisms, while in pH ≥ 3.0–7.0, the uptake of $KMnO_4$ was identified to take place by an initial surface reduction step for the formation of Mn(II) ion and followed by adsorption via a direct complex formation with the AC surface functional groups. The proposed method confirmed an efficient removal of ≥99% of residual $KMnO_4$ from industrial wastewater, seawater, and drinking water in laboratory trials.

Keywords: Potassium permanganate; Carbonaceous materials; Removal

1. Introduction

Potassium permanganate ($KMnO_4$) is well known as a strong oxidizing agent and has been characterized for its efficient reaction with electron-rich organic and inorganic compounds. The redox reaction involving $KMnO_4$ may proceed via several mechanisms and pathways, including direct oxygen transfer, electron exchange, and hydrogen abstraction [1]. Oxidation reactions involving $KMnO_4$ are also dependent on the pH value of contact solution. In strong acidic medium, $KMnO_4$ exhibits high oxidative reactivity with oxidation potential (E^o = +1.51 V) and its reductive product is the Mn^{2+} according to equation Eq. (1). On the other hand, $KMnO_4$ undergoes in acidic–neutral and alkaline pH conditions to produce manganese dioxide with E^o = +0.59 and +1.70 V, respectively, as illustrated by Eqs. (2) and (3) [2].

In strong acidic condition:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad (1)$$

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In acidic-neutral condition:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O \quad (2)$$

In alkaline condition:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^- \quad (3)$$

Due to the strong oxidizing power of permanganate in various solutions, $KMnO_4$ was widely used in chemical oxidation treatment processes of water and soil to remediate organic and inorganic pollutants [3]. In addition, water treatment using $KMnO_4$ was established to replace chlorine treatment in which $KMnO_4$ was used as a pre-oxidation step to react with dissolved organic matters due to its potential capability for elimination of the chlorinated byproducts. Moreover, $KMnO_4$ was also used in drinking water treatment to improve the removal efficiency of contaminants [4].

A number of research papers have been recently reported on the application of $KMnO_4$ as a strong, efficient, and relatively low-cost oxidizing reagent for removal of organic pollutants from aqueous solutions and water samples [1,5–8]. A study was aimed and reported to develop hypersaline MnO_4^- solution (MnO_4^- gel; PG) that was injected into aquifers via wells and found to release MnO_4^- to the flowing water [9]. Batch experiments were carried out to investigate the decomposition of bisphenol A (BPA) by permanganate and the proposed method was found very effective for BPA degradation by producing over 99% remediation of BPA after 15 min at pH 7.0 [10]. Bench-scale experiments were investigated to monitor the potassium permanganate demand and its variation with depth in PAHs contaminated site of a coking plant [11]. The effect of permanganate pre-oxidation on organic matter removal during the coagulation with aluminum chloride using tannic acid as a model compound was investigated and reported [12]. Activated carbon (AC) adsorbent was prepared and treated with $KMnO_4$ for removal of Basic Violet 14 from aqueous solutions [13]. A method was presented to find out the effects of $KMnO_4$ on powdered AC in the treatment and removal of natural organic matter [14].

Oxidative removal of various inorganic species was also reported by a number of research papers. A method was described for oxidation of As(III) by means of four conventional oxidants (chlorine dioxide, sodium hypochlorite, potassium permanganate, and monochloramine) under different test conditions [15]. A three-step method was reported as a treatment process for simultaneous removal of arsenic and iron ions from water involving (i) mild alkaline pH-conditioning by $NaHCO_3$, (ii) oxidation of arsenite and ferrous ions by $KMnO_4$, and (iii) coagulation by $FeCl_3$ [16]. A method was also reported for simultaneous removal of SO_2, NO and Hg^o from flue gas using a complex absorbent containing $KMnO_4$ and under the influence of different types of oxidants, urea concentration, $KMnO_4$ concentration, Hg^o inlet concentration, initial pH, reaction temperature as well as SO_2 and NO concentrations [17].

AC adsorbents have been widely used in combination with $KMnO_4$ in water treatment processes [13,14]. However, in such combined treatment methodology, a direct contact reaction is favored between $KMnO_4$ and AC as well as the removed organic or inorganic adsorbate. If potassium permanganate is present in excess, the surface functional groups will change due to possible redox reaction for the formation of some other surface functional groups such as carboxyl, hydroxyl, ketonic, and ether as previously reported [18–20]. The physical and chemical characteristics of AC adsorbent oxidized by $KMnO_4$ were also studied to evaluate the relationship between oxidant and adsorption process in drinking water treatment as reported in several research papers [13,14,21].

Removal of manganese species from water is mainly focused on only manganese (II) ion [22–33]. However, limited data are available concerning $KMnO_4$ toxicity to untargeted species in water systems. In addition, no standard pattern for applications of $KMnO_4$, and therefore it can be used without restriction. Therefore, implementation of $KMnO_4$ as a strong oxidizing agent in water treatment plants will require additional studies [34]. To the best of our knowledge, the potential application of AC for removal of trace amounts of $KMnO_4$ from water and aqueous solutions was not previously reported. Therefore, the aim of this study is mainly focused on the removal processes of $KMnO_4$ from aqueous solutions and real water samples using chemically treated AC adsorbents with 0.1–1.0 mol L^{-1} sulfuric acid. The influence of different experimental controlling factors was also studied, optimized, and evaluated in this study.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical or laboratory grade reagents. Potassium permanganate ($KMnO_4$, 99% purity) was purchased from Biochem for laboratory chemicals and used to freshly prepare a 1,000 mg L^{-1} stock solution. Sulfuric acid (97%) and other metal salts were purchased from Sigma-Aldrich, Germany. Powdered commercial AC was purchased from Adwic Chemicals, Egypt, and used as received.

2.2. *Preparation of modified AC sorbents*

Powdered AC was treated with distilled water by heating and stirring at 110℃ for 1 h in order to remove surface-adsorbed contaminants. The washed AC sorbent was filtered and left to dry in an oven at 60–70℃ for complete dryness. A sample of 10.0 g of dry AC was weighed and transferred to a 250.0 mL beaker containing 100.0 mL of 0.1 M-H_2SO_4 and the reaction mixture was slowly stirred for 3 h, then filtered, washed with distilled water, and dried at 70℃ to produce the AC-1.0 M sorbent. The same procedure was also repeated using different molar concentrations of sulfuric acid such as 0.3, 0.5, 0.7, and 1.0 M to produce AC-0.3 M, AC-0.5 M, AC-0.7 M, and AC-1.0 M sorbents, respectively.

2.3. *Stability of modified AC sorbents*

The stability of modified AC sorbents in aqueous solutions was performed according to the following procedure. A 50 ± 1.0 mg sample of AC-0.1 M, AC-0.3 M, AC-0.5 M, AC-0.7 M, or AC-0.1 M sorbent was added to 50.0 mL of distilled water. This mixture was shaken by automatic shaker for 30 min and filtered, and the filtrate was titrated against standard 0.1 M-sodium hydroxide. The percentage value of leached sulfuric acid from each modified sorbent was determined based on triplicate analysis.

2.4. *Sorption studies*

2.4.1. *Reduction of $KMnO_4$ by modified AC sorbents*

A 50.0 ± 1.0 mg sample of modified AC sorbent was added to a mixture of 10.0 mL of 0.01 M-$KMnO_4$ solution into a 50.0-mL measuring flask. This mixture was shaken for 30 min by an automatic shaker (125 rpm). The mixture was filtered and washed with 50.0 mL of distilled water. 100 ± 1.0 mg of oxalic acid was added to the filtrate, boiled for few minutes and hydroxylamine HCl was then added. The pH value of this solution was adjusted to pH 10.0 and the unextracted Mn(II) in the filtrate was determined by complexometric titration against 0.01 M-EDTA using Erio-T indicator.

2.4.2. *UV–vis spectrophotometric analysis of $KMnO_4$*

According to the operational manual of the UV–vis spectrophotometric determination, adjustments of the instrument parameters gave optimized conditions for the work done. The absorbance full curve of $KMnO_4$ was acquired and found to produce three peaks at 480, 525, and 580 nm and the maximum absorbance was identified at $\lambda = 525$ nm [35]. This wavelength was then used to establish the calibration curve as represented in Fig. 1 by fitting the absorbance against concentration at this specified wavelength of maximum absorption. In addition, $\lambda = 525$ nm was also used to determine the concentration of $KMnO_4$ as described below.

2.4.3. *Effect of pH*

All batch sorption experiments were carried out at room temperature (25 ± 1℃). Each experiment was performed in a 50 mL volumetric flask by mixing a 10.0 mL of 100.0 mg L^{-1} freshly prepared $KMnO_4$ solution with 50.0 ± 1.0 mg of the dry AC sorbent and the pH was adjusted in the range of 1.0–7.0 by the addition of either H_2SO_4 or NaOH. This mixture was shaken by an automatic shaker (125 rpm) for 30.0 min and finally filtered. Residual $KMnO_4$ in the filtrate was detected using UV–vis spectrophotometric determination at $\lambda = 525$ nm. The percentage removal of $KMnO_4$ was calculated according to Eq. (4).

$$\text{Removal efficiency } (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (4)$$

where C_o and C_e are the initial and final concentrations of $KMnO_4$ expressed in mg L^{-1}, respectively.

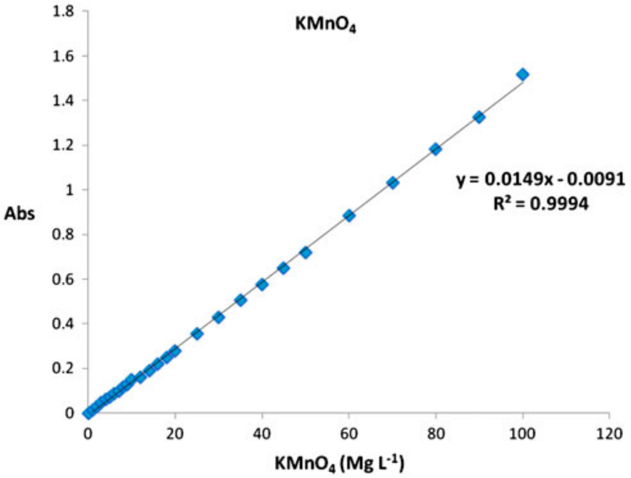

Fig. 1. Calibration curve of $KMnO_4$.

2.4.4. Effect of contact time

The previously mentioned batch experiment procedure was also carried out at different shaking time values, viz. 1.0, 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0 min and the optimum pH 1.0 and 7.0 were adjusted using H_2SO_4 or NaOH solution. The residual $KMnO_4$ in the filtrate was detected using UV–vis spectrophotometric determination at $\lambda = 525$ nm and the percentage removal of $KMnO_4$ at each time value was calculated from Eq. (4).

2.4.5. Effect of sorbent dosage

Similar batch experiments were carried out by mixing a 10.0 mL freshly prepared solution of 100.0 mg L^{-1} $KMnO_4$ using different sorbent masses, 2.0, 5.0, 10.0, 20.0, 40.0, 60.0, 80.0, and 100.0 ± 1.0 mg. The optimum pH 1.0 and 7.0 were adjusted by H_2SO_4 or NaOH solution. The mixture, in each case, was shaken for 30.0 min by an automatic shaker (125 rpm) and the residual $KMnO_4$ in the filtrate was detected using UV–vis spectrophotometric determination at $\lambda = 525$ nm and the removal percentage of $KMnO_4$ was evaluated from Eq. (4).

2.4.6. Effect of initial metal concentration

Freshly prepared solutions (10.0 mL) with 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, and 100.0 mg L^{-1} $KMnO_4$ were used to conduct this study. These solutions were mixed with 20.0 ± 1.0 mg of the dry AC sorbent, adjusted to pH 1.0 and 7.0, and shaken for 30 min (125 rpm). The mixture was filtered and the residual $KMnO_4$ in the filtrate was detected using UV–vis spectrophotometric determination at $\lambda = 525$ nm. The percentage removal of $KMnO_4$ was determined from Eq. (4).

2.4.7. Effect of interfering ion

Several selected metal salts such as Na_2SO_4, $MgSO_4$, $CaSO_4$, $ZnSO_4$, $NiSO_4$, and $(NH_4)_2SO_4$ were used to study the effect of coexisting ions on the percentage removal of $KMnO_4$ using various modified AC sorbents. The solutions were prepared by mixing 10.0 mL of 100.0 mg L^{-1} $KMnO_4$ with 10.0 ± 1.0 mg of the interfering salt and 50 ± 1.0 mg of the dry AC sorbent was then added in a 50 mL volumetric flask. The optimum pH 1.0 was adjusted by adding H_2SO_4 and the sorption mixture was shaken for 30.0 min (125 rpm) and filtered. The residual $KMnO_4$ in the filtrate was detected using UV–vis spectrophotometric determination at $\lambda = 525$ nm. The percentage removal of $KMnO_4$ was evaluated from Eq. (4). For successful comparison, the previous experiment was evaluated in the absence of the interfering ion. The same previous removal procedure was also repeated at pH 7.0.

2.4.8. Application of modified AC sorbents for removal of $KMnO_4$ from various water samples

500 mL of the tested tap water, sea water, and industrial wastewater samples were spiked with 5.0 mg L^{-1} $KMnO_4$ and adjusted to pH 1.0 and 7.0 by the addition of H_2SO_4 or NaOH solution. These were mixed with 100.0 ± 1.0 mg of the dry AC sorbent and shaken for 30 min. The residual $KMnO_4$ in solution was filtered and detected using UV–vis spectrophotometric determination at $\lambda = 525$ nm. The removal value of $KMnO_4$ was calculated from Eq. (4).

3. Results and discussion

3.1. Surface modification and characterization

In this work, AC was treated with various concentrations of sulfuric acid, viz. 0.1, 0.3, 0.5, 0.7, and 1.0 mol L^{-1} to produce AC-0.1 M, AC-0.3 M, AC-0.5 M, AC-0.7 M, and AC-1.0 M sorbents, respectively. The stability of loaded sulfuric acid on the surface of AC sorbents in aqueous solution was determined by direct shaking of these sorbents in distilled water. The leached amount of sulfuric acid was then titrated against standard 0.1 M sodium hydroxide. The identified percentage values of leached sulfuric acid from the surface of modified AC sorbents were determined on the basis of triplicate analysis and found in the range of 7.4–12.5 ± 1.5%.

The modified AC sorbents were characterized using various instrumental methods of analysis such as Fourier transform infrared (FT-IR) and scanning electron microscope (SEM) as effective techniques for structural characterization and evaluation of the surface morphology. Fig. 2(a)–(c) shows the FT-IR spectra of free AC, AC-0.1 M, and AC-1.0 M, respectively. The FT-IR spectra were recorded in the range 400–4,000 cm^{-1}. As shown in Fig. 2(a), the spectrum of AC sorbent is referring to the complex nature of this sorbent and is characterized by the presence of a number of peaks. A broad peak at 3,405 cm^{-1} is mainly related to the O–H stretching bond or adsorbed water molecule as previously reported [36,37]. The observed peak at 2,923 cm^{-1} could be assigned to the aliphatic CH-stretching frequency. The peak at 1,614 cm^{-1} is mainly due to the formation of oxygen functional groups based on highly conjugated C=O stretching in carboxylic or carboxylate as well as carbonyl groups

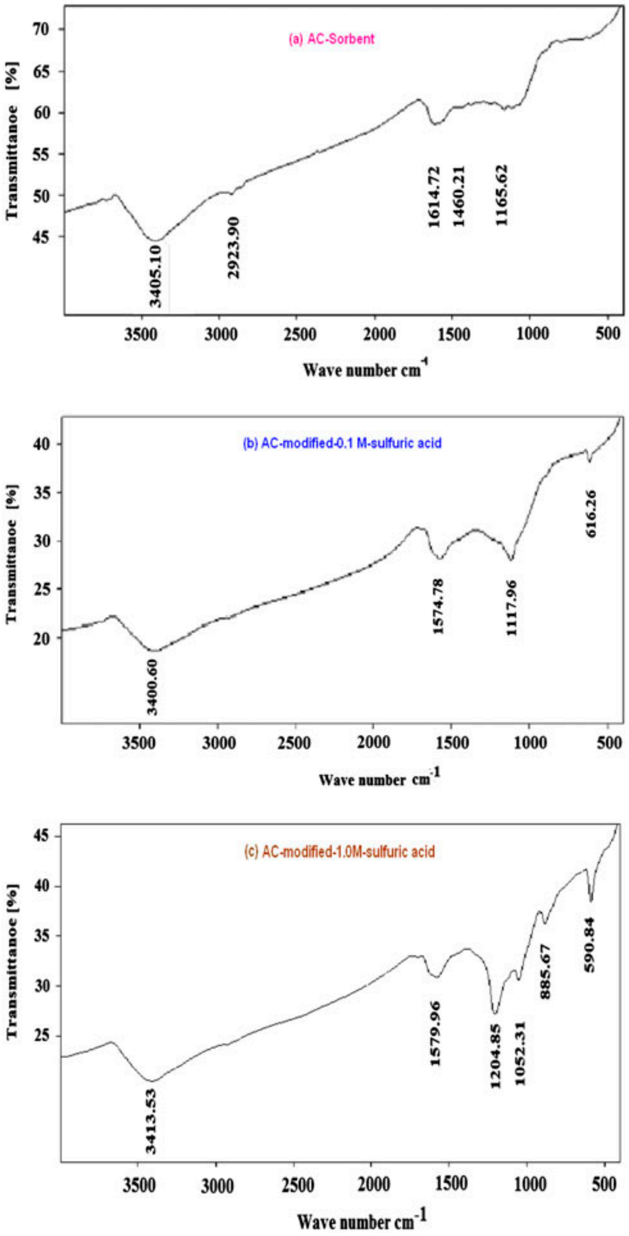

Fig. 2. FT-IR spectrum of various AC sorbents.

[38]. Another peak centered at 1,165 cm^{-1} is assigned to the frequency of C–O bond in methoxyl group. The assigned peak at 1,460 cm^{-1} is ascribed to the presence of δ(C–H) from methyl groups [39]. Some other peaks appear in the range of 590–1,052 cm^{-1} and these could be assigned to the =C–H band similar to alkenes.

The SEM images of free AC, AC-0.1 M, and AC-1.0 M sorbents are represented in Fig. 3(a)–(c), respectively. Fig. 3(a) shows the SEM image of AC sorbent using 2,000 magnification order and the particles are distributed in a homogenous fashion with different shapes and sizes. On the other hand, Fig. 3(b) and (c) represents the image of treated AC sorbent with 0.1 and 1.0 M sulfuric acid using 5,000 magnification order. Some pores were characterized

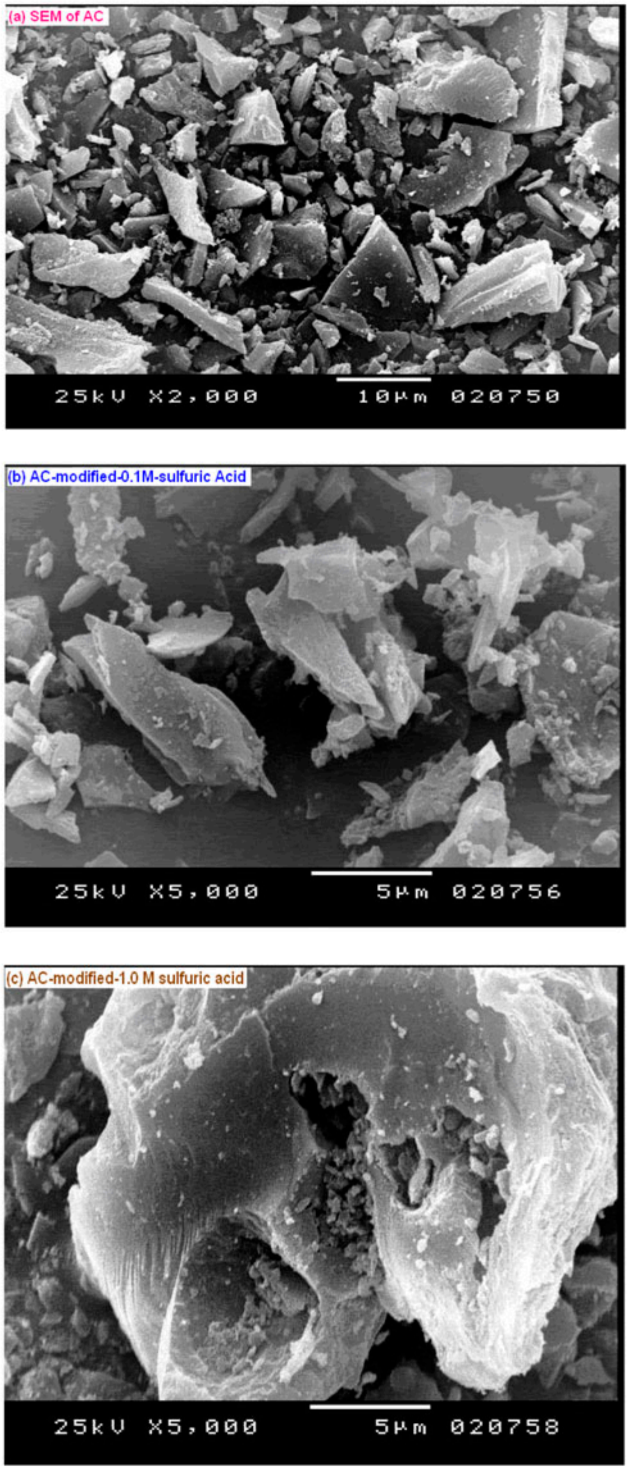

Fig. 3. SEM images of various AC sorbents.

especially in Fig. 2(c) which indicate a good possibility for the adsorption and trapping of the interacting adsorbate.

3.2. *Uptake of $KMnO_4$ and adsorptive removal of Mn(II) by various AC sorbents*

A study was made to confirm the possible removal of Mn(II) as the reduction product of $KMnO_4$ from aqueous solutions by various treated AC sorbents. The direct contact of $KMnO_4$ with modified AC sorbent was examined for the formation of Mn(II) as the reduction product of $KMnO_4$. The produced Mn(II) was evaluated for its adsorptive removal by AC sorbents and the results of this study are compiled in Table 1. It is important to report that the color of solution upon reaction of $KMnO_4$ with modified AC sorbents was turned to colorless and this behavior refers to the complete removal of $KMnO_4$ via three different mechanisms. The first one is related to an anion exchange mechanism in which a direct adsorptive exchange of MnO_4^- by the loaded SO_4^{2-} on the surface of AC sorbents in the presence of low pH values of contact solution (pH 1.0–2.0) [28]. In addition, the second possible mechanism may be related to the formation of ion pairing between MnO_4^- and surface protonated groups. The percentage removal values of $KMnO_4$ by these two mechanisms are characterized as 36.0, 43.0, 44.6, 46.2, and 50.0% by AC-0.1 M, AC-0.3 M, AC-0.5 M, AC-0.7 M, and AC-1.0 M sorbents, respectively. The third mechanism is mainly due to the reduction reaction of $KMnO_4$ to produce Mn(II) in solution which is then adsorbed by the surface functional groups of AC sorbents via a complex formation reaction in the contact solutions with pH ≥ 3.0. Thus, it is evident from the listed data that a reduction process of $KMnO_4$ was taken place and the modified AC sorbents were found to produce 97.30–100.0% reduction and adsorptive removal of Mn(II) from aqueous solution in pH 7.0. In addition, a gradual increase in the percentage extraction values of Mn(II) by all AC sorbents was also evident by the increase in the pH value of contact solution. This behavior is mainly due to the strong capability of Mn(II) to bind and form complexes with the active surface functional groups such as OH, COOH, and C=O [38].

3.3. *Adsorptive removal of $KMnO_4$–Mn(II) by modified AC sorbents in the presence of various controlling parameters*

3.3.1. *Effect of pH on the adsorptive removal of $KMnO_4$–Mn(II)*

The effect of pH value of contact solution on the removal process of $KMnO_4$–Mn(II) was studied in various acidic and neutral solutions with (pH 1.0–7.0) and the results of this study are listed in Table 2. The percentage extraction values of $KMnO_4$ were found to be ≥99.55% in all aqueous solutions by the examined AC sorbents. In pH 1.0 solution, removal of $KMnO_4$ was found to proceed via anion exchange mechanism by producing percentage extraction values ≥99.66–99.95%. At higher pH value (pH 7.0), the percentage extraction of Mn(II) as the reduction product of $KMnO_4$ was found in the range of 99.65–99.93% due to the possibility of complex formation as described in Section 3.2. Therefore, the listed data in Table 2 refer to the excellent recovery values of $KMnO_4$ from aqueous solutions in the pH range 1.0–7.0.

3.3.2. *Effect of contact time on the adsorptive removal of $KMnO_4$–Mn(II)*

The effect of contact time on the percentage extraction of $KMnO_4$–Mn(II) was also studied and evaluated in this section in order to find out the

Table 1
Percentage extraction values of $KMnO_4$–Mn(II) by modified AC sorbents

	% Removal of $KMnO_4$–Mn(II) by modified AC-H_2SO_4 sorbents[a]				
pH	AC-0.1 M	AC-0.3 M	AC-0.5 M	AC-0.7 M	AC-1.0 M
1	12.90	34.40	36.60	38.70	43.00
2	36.00	43.00	44.60	46.20	50.50
3	80.10	80.60	81.20	84.40	84.90
4	82.30	83.90	90.90	92.50	95.20
5	94.60	95.20	96.20	97.30	97.30
6	96.20	97.30	97.30	98.40	99.50
7	97.30	97.80	98.40	98.90	100.0

[a] Values are based on triplicate analysis with ±1.0%.

Table 2
Percentage extraction values of $KMnO_4$–Mn(II) in different pH solutions

	% Extraction of $KMnO_4$–Mn(II) in different pH values[a]				
pH	AC-0.1 M	AC-0.3 M	AC-0.5 M	AC-0.7 M	AC-1.0 M
1	99.66	99.76	99.87	99.93	99.95
2	99.55	99.66	99.75	99.82	99.89
3	99.56	99.61	99.74	99.81	99.89
4	99.56	99.61	99.74	99.81	99.90
5	99.56	99.61	99.74	99.81	99.90
6	99.61	99.65	99.76	99.85	99.90
7	99.65	99.73	99.85	99.88	99.93

[a] Values are based on triplicate analysis with ±1.0%.

removal rapidness of both species, $KMnO_4$ and Mn (II). This factor was accomplished using two different pH values, 1.0 and 7.0, to monitor the adsorption progress of $KMnO_4$ and Mn(II), respectively. The time interval values were selected as 1.0, 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0 min for both cases. The results of this study are represented in Fig. 4(a) and (b) at pH 7.0 and 1.0, respectively. The uptake process of $KMnO_4$ in pH 1.0 was found very fast due to almost complete removal after only one minute of contact time. The identified percentage values of $KMnO_4$ by all modified AC sorbents were found to be ≥99.45% and this confirms the efficient application of modified AC sorbents for removal of $KMnO_4$ from aqueous solutions. In pH 7.0, the AC sorbents were also found to exhibit excellent recovery values of Mn(II) as the reduced ion of $KMnO_4$. After one min of contact time, the identified values for removal of Mn(II) from aqueous solution by AC-0.1 M, AC-0.3 M, AC-0.5 M, AC-0.7 M, and AC-1.0 M were found as 99.32, 99.45, 99.50, 88.58, and 99.67%, respectively.

The results of this study confirm that the evaluated AC sorbents are highly efficient in removal of $KMnO_4$ and Mn(II) from adjusted aqueous solutions at pH 1.0 and 7.0, respectively.

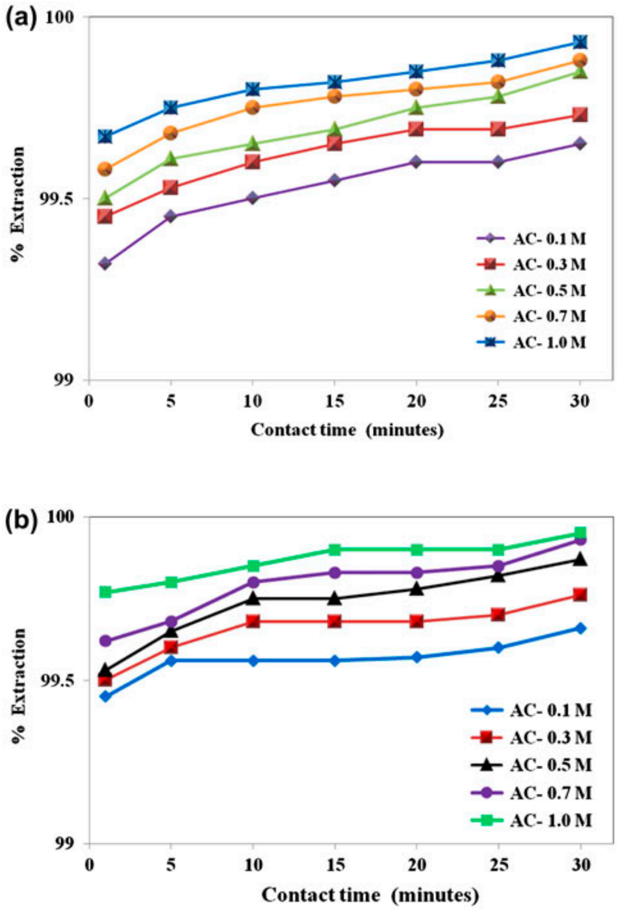

Fig. 4. Effect of contact time on the removal process of Mn (II) from different pH values. (a) Effect of contact time (pH 7.0), and (b) effect of contact time (pH 1.0).

3.3.3. *Effect of sorbent dose on the adsorptive removal of $KMnO_4$–Mn(II)*

The effect of sorbent dosage on the removal of $KMnO_4$ and Mn(II) by modified AC in the range of 2.0–100.0 mg and using 100 mg L^{-1} as the initial concentration sorbents was also studied as an important factor by varying the selected sorbent dosages of $KMnO_4$. The selected contact time was adjusted to 30.0 min and the results of sorbent dosage on the removal efficiency of modified AC sorbent for Mn(II) in pH 7.0 and $KMnO_4$ in pH 1.0 are graphed in Fig. 5(a) and (b), respectively. The AC sorbent dosage was found to exhibit a slight increase in the percentage extraction values of $KMnO_4$ from pH 1.0 and Mn (II) from pH 7.0 solution upon increasing the sorbent dosage. A 2.0 mg of sorbent dosage was found to produce 97.20–97.85% for $KMnO_4$ removal from pH 1.0. Moreover, the percentage recovery of Mn(II) from pH 7.0 solution using a 2.0-mg dosage of all evaluated AC sorbents was characterized in the range of 97.18–97.85%. The collected data refer to the high efficiency of modified AC sorbents to afford complete uptake (99.32–99.88%) and (99.25–99.75%) of $KMnO_4$ and Mn(II), respectively, using only 10.0 mg of the examined AC sorbents.

3.3.4. Effect of initial concentration of $KMnO_4$ on the adsorptive removal of $KMnO_4$–Mn(II)

The effect of different initial concentrations of $KMnO_4$ on the removal efficiency of $KMnO_4$ and Mn (II) using modified AC sorbents was evaluated by varying the concentration of $KMnO_4$ in the range of 10.0–100.0 mg L^{-1}. The sorbent dosage was selected as 2.0 mg and shaking time was adjusted to 30 min. The results of this study are represented in Fig. 6 and clearly show excellent and complete percentage extraction and uptake values of $KMnO_4$ from pH 1.0 by all studied and evaluated AC sorbents. The same behavior was also characterized for removal of Mn(II) from pH 7.0 as the reducing product by all AC sorbents. A slight decrease in the extraction values was evident upon increasing the concentration of $KMnO_4$ from 10.0 to 100.0 mg L^{-1} and the minimum identified percentage range of $KMnO_4$ was 97.18–97.89% (pH 1.0) and that of Mn(II) was 97.10–97.81% (pH 7.0).

3.3.5. Effect of interfering ions on the adsorptive removal of $KMnO_4$–Mn(II)

The effect of interfering cations such as Na(I), Mg (II), Ca(II), Ni(II), Zn(II), and NH_4^+ as well as anion such as SO_4^{2-} in the form of Na_2SO_4, $MgSO_4$, $CaSO_4$, $ZnSO_4$, $NiSO_4$, and $(NH_4)_2SO_4$ were used to evaluate the removal processes of $KMnO_4$ from pH 1.0 and Mn (II) from pH 7.0 by all modified AC sorbents. In this study, a 10.0 mg sample of the interfering salt was

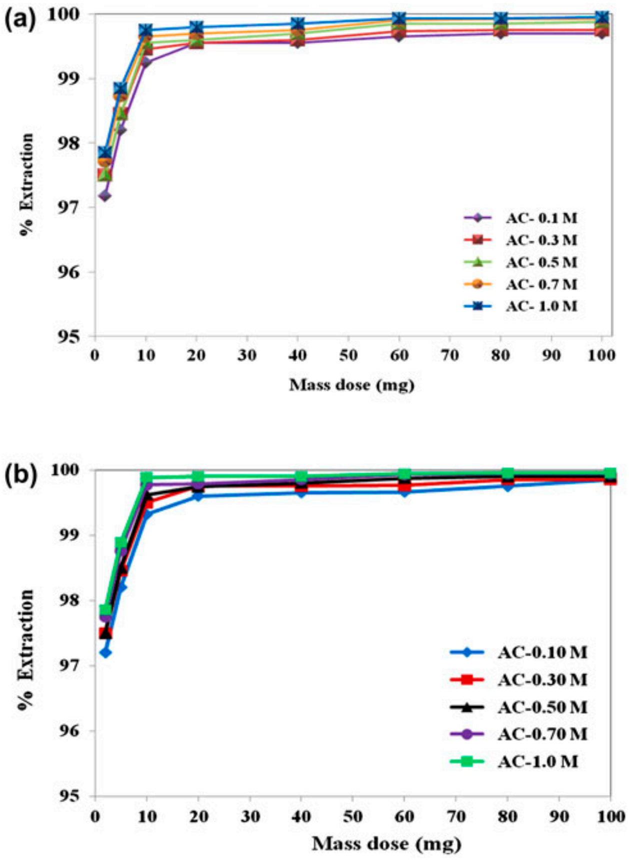

Fig. 5. Effect of AC sorbent dosage on the removal process of Mn(II) from different pH values. (a) Effect of AC sorbent dosage (pH 7.0) and (b) effect of AC sorbent dosage (pH 1.0).

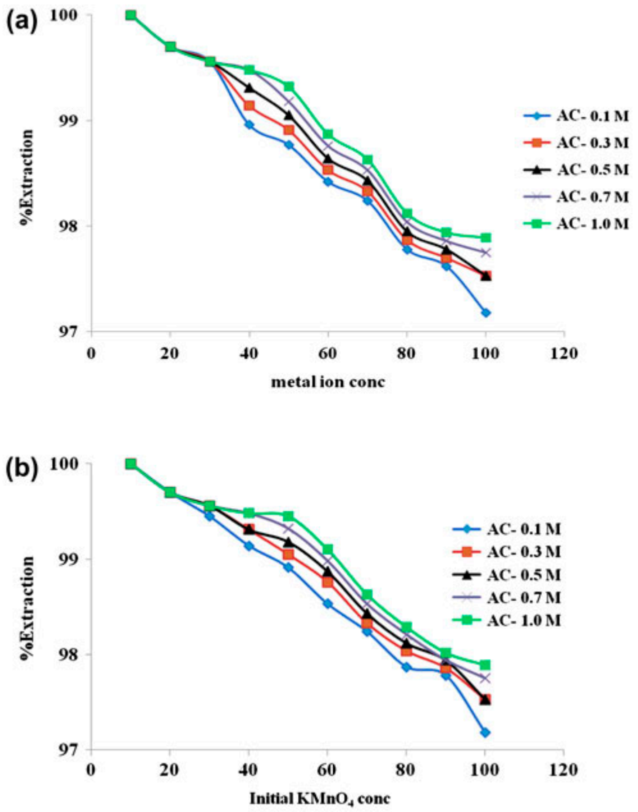

Fig. 6. Effect of initial concentration of $KMnO_4$ on the percentage extraction values of Mn(II) in different pH values. (a) Effect of initial concentration of $KMnO_4$ (pH 7.0) and (b) effect of initial concentration of $KMnO_4$ (pH 1.0).

Table 3
Effect of interfering species on the percentage extraction values of $KMnO_4$ at pH 1.0

	% Extraction of $KMnO_4$ in the presence of interfering compound[a]				
Interfering species	AC-0.1 M	AC-0.3 M	AC-0.5 M	AC-0.7 M	AC-1.0 M
Na_2SO_4	99.65	99.63	99.81	99.84	99.73
$MgSO_4$	99.65	99.63	99.74	99.84	99.20
$CaSO_4$	99.60	99.63	99.87	99.93	99.80
$ZnSO_4$	99.65	99.56	99.74	99.93	99.73
$NiSO_4$	99.60	99.47	99.87	99.84	99.80
$(NH_4)_2SO_4$	99.60	99.56	99.81	99.64	99.53
Absence of interference	99.65	99.76	99.87	99.93	99.94

[a]Values are based on triplicate analysis with ±1.0%.

Table 4
Effect of interfering species on the percentage extraction values of Mn(II) at pH 7.0

	% Extraction of Mn(II) in the presence of interfering species[a]				
Interfering species	AC-0.1 M	AC-0.3 M	AC-0.5 M	AC-0.7 M	AC-1.0 M
Na_2SO_4	99.65	99.73	99.85	99.88	99.84
$MgSO_4$	99.65	99.67	99.64	99.81	99.92
$CaSO_4$	99.57	99.73	99.75	99.81	99.92
$ZnSO_4$	99.65	99.57	99.85	99.88	99.92
$NiSO_4$	99.57	99.67	99.75	99.81	99.84
$(NH_4)_2SO_4$	99.62	99.73	99.64	99.88	99.84
Absence of interference	99.65	99.73	99.85	99.90	99.93

[a]Values are based on triplicate analysis with ±1.0%.

added to $KMnO_4$ solution and the experimental procedure was completed under the optimum conditions of contact time and sorbent dosage. The presence of interfering ions in aqueous solutions with pH 1.0 and 7.0 was found to maintain the effectiveness of all AC sorbents to react and bind with $KMnO_4$ and Mn(II), respectively. It is also evident that no direct interaction or contribution of the interfering ions in the adsorption process as listed in Tables 3 and 4.

3.4. Applications of modified AC sorbents for removal of $KMnO_4$ from real water samples

The capability and efficiency of modified AC sorbents to remove $KMnO_4$ from real water samples such as industrial wastewater, sea water, and drinking tap water were further studied and evaluated by the batch equilibrium technique as the final and most important step to examine their potential applications in water treatment. In this study, a 100.0 ± 1.0 mg sample of AC sorbent was added to the selected water sample and spiked with trace concentration of 5.0 mg L^{-1} of $KMnO_4$. The pH value of these water samples was adjusted to pH 1.0 and 7.0. The selected contact time was 30.0 min. The percentage extraction values of the spiked 5.0 mg L^{-1} of $KMnO_4$ in the examined industrial wastewater, sea water, and drinking tap water samples by all modified AC sorbents were found to correspond to 99.4–100.0 ± 1.0% and these results give additional evidences for the suitable implementation of modified AC sorbents for removal of existing $KMnO_4$ from any water sample or matrix.

4. Conclusion

The modified AC sorbents were found to be highly efficient for removal of $KMnO_4$ from aqueous solutions and real water samples in the presence of pH 1.0–7.0. Adsorptive removal of $KMnO_4$ from pH 1.0–2.0 was suggested to take place by ion pair interaction and anion exchange mechanisms. Removal of $KMnO_4$ in the presence of pH 3.0–7.0 was found to proceed via reduction of Mn(II) and complex formation of this ion with the surface functional groups. Adsorptive removal of $KMnO_4$ was found very fast and nearly complete after one minute of contact time in both pH

1.0 and 7.0. The percentage extraction values for removal of $KMnO_4$ from industrial wastewater, sea water, and drinking tap water were found to be 100.0 ± 0.5%.

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