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# Adsorption, kinetic and thermodynamic studies for manganese extraction from aqueous medium using mesoporous silica

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## ARTICLE INFO

## ABSTRACT

This paper describes studies of functionalized mesoporous silica employed as adsorbent for Mn(II) from aqueous solutions. The surface area of MCM-41 and diethylenetriamine functionalized-MCM-41 used in this study were 760 and 318 $m^2 \, g^{-1}$ ($N_2$ adsorption). A strong dependence on pH in the Mn(II) adsorption capacity and best results were obtained at pH 6.5–7. The adsorption onto the diethylenetriamine functionalized-MCM-41 followed the pseudo-second-order kinetic model and the highest reaction rate 0.324 $min^{-1}$ was observed at low initial concentration 10 ppm. The equilibrium data showed excellent correlation with the Langmuir isotherm model and the maximum adsorption capacity of Mn(II) reached 88.9 mg/g for DETA-MCM-41 indicating that the adsorption occurs on a homogeneous surface by monolayer sorption without interaction between the adsorbed ions. These data contribute to the understanding of mechanisms involved in mesoporous silica and provide some practical clues to improve the adsorption efficiency (uptake capacity and kinetics) of Mn(II) ions.

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## 1. Introduction

Manganese (Mn) is an element that is present in the environment. It is commonly found in drinking water and is essential for human health at low concentrations [1]. However, excessive concentrations of Mn(II) could result in metallic tasting water and many health problems. Manganese is present in ground water as a divalent ion $Mn^{++}$ and is considered a pollutant mainly because it may causes nervous system damage, leading to Parkinson's disease, and injures arterial breastwork and the myocardium. The World Health Organization has set a guideline of 0.4 mg/L for Mn(II) intake control from drinking water [2]; and the limit value in the Chinese Standard for Drinking Water Quality is 0.1 mg/L [3]. In neutral and alkaline environments, Mn(II) is difficult to be oxidized [4]. Conventional treatment for Mn(II) removal generally requires the use of strong oxidizing agents such as potassium permanganate, chlorine, hypochlorite, chlorine dioxide or ozone [5]. The generation of other pollutants or toxins is the major disadvantage of these oxidizers. Although chlorine or $KMnO_4$ oxidation combined with sand filtration is usually applied for Mn(II) removal, its concentration in the treated water is still difficult to meet the accepted levels requirements for drinking water [6]. In fact, as the effects of pollutants accumulation and sedimentation, the concentration of Mn(II)

is variable, and the variation of water quality such as solution pH may cause a sudden release of Mn(II) [7].

To develop extraction method for removal of Mn(II) from solution, in the presence of other heavy metals, functionalized mesoporous silica nanoparticles have been explored due to their high metal uptake capacities, good physical and chemical stabilities, uniform structures made of mesopore channels regularly organized in space [8–10]. Summaries of some reported studies of Mn(II) ions adsorption for different materials are presented in Table 1. Although these adsorption capacities correspond to different experimental conditions, they are representative of the tendency to uptake Mn(II) ions.

Silica based adsorbents are of particular interest as they exhibit enhanced accessibility to active centers [13,14], and fast mass transfer rates in the regular porous environment [15,16]. These combination of factors have led to high capacity adsorbents [16]. To this end no papers reported the results of kinetic studies and thermodynamic results on Mn(II) adsorption onto mesoporous silica.

The aim of this work was to study the adsorption of Mn(II) ions onto amino-functionalized mesoporous silica. The linearized Langmuir and Freundlich equations were used to fit the equilibrium isotherms. Kinetic data were analyzed by pseudo-first, pseudo-second and intra-particle diffusion models to obtain the kinetic constants and thermodynamic study of Mn(II) removal and postulate the mechanism of Mn(II) removal by porous materials. This

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work is part of a series of adsorption studies in well characterized mesoporous silica (MCM-41) [17,18].

## 2. Experimental

### 2.1. Materials and reagent

Cetyltrimethylammonium bromide (CTAB), 98%, was supplied by BDH. Aqueous ammonia (30% $NH_3$), tetraethoxysilane (TEOS) 98%, hydrogen peroxide solution (30 wt.%), N-(3-trimethoxysilylpropyl) diethylenetriamine (DETA-TMS), ethanol absolute, 1000 µg mL$^{-1}$ of Mn(II) standard solution and toluene (+99%) were purchased from Sigma Aldrich. Nitric acid (65 wt.%) was provided by Fisher Scientific. Glassware was soaked in 5% $HNO_3$ overnight and cleaned with deionised water before use. All products were used as supplied and deionised water was used throughout this work.

### 2.2. Mesoporous silica preparations and functionalization

The synthesis method and functionalization MCM-41 was prepared according to the method reported in Ref. [17]. Approximately 9.0 g of CTAB was dissolved under slight warming (35 °C) in a mixture of 210 mL of distilled $H_2O$ and 100 mL of aqueous $NH_3$. To this clear solution, 50 mL of TEOS was slowly added under stirring. After further stirring for 4 h, the gel was aged at room temperature for 48 h in a closed container. The product was obtained by filtration, washed with 800 mL of distilled $H_2O$, and dried in air at room temperature. To remove the surfactant microwave digestion (MWD) was performed by using a MARS 5 microwave digestion system (CEM Corporation, Buckingham, UK) was used at an operating power of approximately 1600 W. The pressure and temperature inside the microwave were controlled to be lower than 1.3 MPa and 200 °C, respectively. Samples (approx. 0.1 g) were added to multiple Teflon vessels to which 1.5 mL of $HNO_3$ and 0.70 mL of $H_2O_2$ were added. Microwave digestion was operated at a working frequency of 2450 MHz and 220 V for 15 min. The product (MCM-41) was filtered, washed with copious amounts of distilled $H_2O$ and dried at 100 °C for 2 h.

Surface modification of MCM-41 was carried out by condensation using the N-(3-trimethoxysilylpropyl) diethylenetriamine with MCM-41 (Scheme 1). Briefly, approximately 5 g of MCM-41 was pre-treated at 140 °C for 2 h before being immersed in 50 cm$^3$ of toluene and 10 cm$^3$ of DETA-TMS, in a 250 cm$^3$ flask. The mixture was refluxed for 4 h and the solid produced was filtered, washed with 100 cm$^3$ ethanol, and oven-dried at 80 °C for 2 h to produce a DETA-MCM-41 sorbent.

**Table 1**
Manganese ions adsorption capacity for different materials.

| Material | Mn(II) uptake (mg g$^{-1}$) | References |
|---|---|---|
| Clinoptilolite–Fe system | 27.12 | [11] |
| Clinoptilolite from Turkey | 4.22 | [12] |
| Na–montmorillonite | 3.22 | [2] |
| Granular activated carbon | 2.54 | [4] |
| Nigerian kaolinite clay | 111.11 | [6] |
| Manganese oxide coated zeolite | 27.5 | [7] |
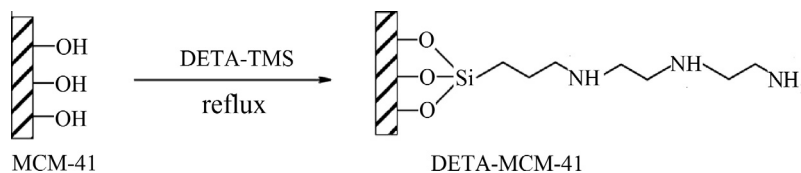
### 2.3. Characterization and Analysis

The surface areas of the MCM-41 were measured using nitrogen physisorption isotherms. The Brumauer–Emmett–Teller (BET) surface areas were calculated using experimental points at a relative pressure ($P/P_0$) of 0.05–0.25. The total pore volume was calculated from the $N_2$ amount adsorbed at the $P/P_0$ of 0.99 for each sample. Both samples exhibited a Type IV adsorption isotherm typical of mesoporous solids. Desorption isotherms were used to calculate the pore diameters. Elemental analysis (EA) was carried out using an Exeter Analytical CE440 elemental function. Total concentration of Mn(II) in water samples was determined using a PerkinElmer AAnalyst200 flame atomic absorption spectrometry (FAAS) instrument. Calibration standards (0.0, 0.1, 0.5, 1, 1.5 and 2 µg cm$^{-3}$) were prepared in 5% $HNO_3$. Method parameters used are shown in Table 2. The method detection limit (MDL) for Mn(II) was 0.015 µg cm$^{-3}$.

### 2.4. Adsorption process and effect of pH

Approximately 10 mg of functionalized MCM-41 was suspended in 20 mL of solution containing 20 µg mL$^{-1}$ Mn(II) ions in 50 mL beaker and the solution was stirred (250 rpm) using MyLab (Magnetic Stirrer with Hot Plate-SLMSH300) for approximately 2 h. After this time the solution was removed and analyzed for Mn(II) by flame atomic absorption spectrometry (FAAS). This process was repeated until saturation of the sorbent as indicated by a measurement of Mn(II) in the solution aliquot. The extraction was examined at various pH values (between 1 and 9) with solution modification achieved via the addition of small amounts of 1 M ammonium hydroxide.

### 2.5. Adsorption isotherms

The Langmuir [19] or Freundlich [20] models were applied to measured data to study adsorption isotherms. Solutions containing initial concentrations of Mn(II) at 10, 50, 100 or 200 µg cm$^{-3}$ were prepared. To each solution 0.05 g of sorbent was added and the solution was stirred at 250 rpm for 120 min at room temperature, solutions were adjusted to provide a pH of 7. The amounts of Mn(II) extracted at equilibrium, $q_e$ (mg/g) were calculated according to Eq. (1):

$$q_e = \frac{C_0 - C_e}{W} V \tag{1}$$

where $C_0$ and $C_e$ (mg/g) were the liquid phase initial and equilibrium concentrations of the Mn(II) respectively. $V$ was the volume of the solution (cm$^3$), and $W$ was the mass of sorbent (g) used [21]. The sorption equilibrium data were analyzed according to Langmuir Eq. (2) and Freundlich Eq. (3) isotherm models [22].

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m b}\right) + \left(\frac{1}{q_m}\right) C_e \tag{2}$$

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \tag{3}$$

where $q_e$ and $C_e$ were the equilibrium concentrations of the Mn(II) ions in the adsorbed and liquid phases in mg/g and mg/L, respec-



**Scheme 1.** Modification of MCM-41 using N-(3-trimethoxysilylpropyl) diethylenetriamine.