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Manganese dioxide nanowhiskers: A potential adsorbent for the removal of Hg(II) from water

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A B S T R A C T

Manganese dioxide nanowhiskers (MDN), prepared by the reduction of potassium permanganate by ethyl alcohol has been investigated as an adsorbent for Hg(II) removal from aqueous medium. Characterization of the as-synthesized material was carried out using transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). SEM and TEM data showed that the as-synthesized MDN looks like agglomerated whiskers of 5–10 nm in diameter and 100–300 nm in length. XRD data revealed the formation of birnessite type layered manganese dioxide. Mn(IV) oxidation state of Mn in MDN was confirmed by XPS. Batch experiments were conducted to evaluate the Hg(II) adsorption capacity of MDN. Hg(II) adsorption on MDN is a fast process and the kinetics followed a pseudo-second-order rate equation. The Hg(II) uptake varied with pH and showed optimum performance at pH 6–9. The experimental evidence revealed that physisorption is the dominating mechanism in Hg(II) removal. Considering the practical difficulty in handling nanomaterials, MDN was supported on Al_2O_3 (MDN@Al_2O_3) and the composite was shown to be an efficient adsorbent for Hg(II) from simulated chlor-alkali industrial effluent. The results suggest that this material can be a practical solution for Hg(II) scavenging in several industrial processes.

1. Introduction

Mercury is a toxic heavy metal widely used in industries related to chlor-alkali, pharmaceuticals, manufacturing of pressure and temperature measurement devices, mining and dental implants. Effluent discharges from these industries exhibit wide distribution in concentration and composition of mercury [1,2]. Once released into the environment, mercury can undergo complex physical, chemical, and biological transformations and can accumulate in the food chain and cause neurological, nephrological, reproductive, and genetic disorders in humans [3]. A recent study on the status of mercury in ground water in various states of India showed an alarming situation. Drinking water sample from Panipat industrial area (Haryana, India) showed the highest level, 268 times the upper safe limit [4]. These higher levels are due to the discharge of mercury bearing effluents having concentrations above the permissible limit of 0.01 mg L^{-1}.

Technologies like ion exchange [5], amalgamation [6] and adsorption [7] are reported for Hg(II) removal from wastewater. Adsorption technology has been widely accepted because of its effectiveness, efficiency and economics. Metal oxides possess higher adsorption capacity, metal ion affinity, and ability to remove metals in trace concentrations with the possibility of recovery and reuse [8]. Oxides of manganese are considered to be one of the most important scavengers of aqueous trace metals and have been extensively studied for the removal of various toxic heavy metal pollutants such as As [9], Pb [10], Cd [11], Cu [12], and Ni [13] from drinking as well as wastewater. Apart from their excellent heavy metal uptake capacity, they are also interesting because of low cost, eco-friendly nature and abundant availability. Surprisingly, very limited studies have been carried out to explore the ability of manganese oxide to remove Hg(II) from aqueous medium. The reported studies on Hg(II) removal by manganese oxides showed a wide variation in adsorption capacity (0.13–113 mg g^{-1}) [14–16]. Though these data are obtained at various experimental conditions and they are not necessarily comparable, the data clearly show the importance of synthetic route and the crystal structure of the manganese oxide in Hg(II) uptake. Besides, to the best of our knowledge, no mechanistic and surface binding details of Hg(II) on MnO_2 are available in the literature.

Recent findings show that nanomaterials are highly promising in water purification process due to their unique properties like higher surface area per unit volume, ease with which they can be anchored onto solid matrices and the ability to functionalize with different functional groups to enhance their affinity towards target molecules [17]. A recent study by Subramanian et al. [18]

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has proposed a simple, low cost, fast, and eco-friendly method for the preparation of nanostructured manganese oxide. This approach requires only one starting manganese precursor, $KMnO_4$, simplifying the post-synthesis treatment and thereby increasing the viability in commercial applications. In one such approach, where manganese oxide nanospheres were synthesized by the reaction between potassium permanganate and oleic acid and was tested for its Hg(II) removal capacity [19]. The uptake was found to be less (0.84 mg g^{-1}) and may be due to the hausmannite structure, which clearly indicates the importance of reducing agent and post-synthesis treatment of the product.

In the present study, manganese dioxide nanowhiskers (MDN), prepared by the reaction of potassium permanganate and ethyl alcohol, was tested for its Hg(II) uptake in detail. Various spectroscopic and microscopic examinations were done to characterize the material and evaluate its performance for Hg(II) uptake. The surface binding details of Hg(II) on MDN was established through spectroscopy, coupled with adsorption experiments. Considering the practical difficulties in handling free standing nanomaterials, studies were extended to immobilize the MDN on micron size alumina particles (MDN@Al_2O_3). The utility of the as-prepared composite material were demonstrated by cleaning-up Hg(II) from a synthetically prepared industrial effluent of practical significance (chlor-alkali industrial effluent). Regeneration and reusability of the supported adsorbent was also studied to evaluate the economics of the adsorbent as the Hg(II) removal medium.

2. Materials and methods

2.1. Materials

Chemicals used in this study were of analytical grade. Potassium permanganate and ethyl alcohol were procured from Merck Ltd., India and Jiangsu Huaxi International Trade Co.-Ltd., China, respectively. Rhodamine 6G was purchased from Fluka Chemicals, Switzerland. A stock solution of 1000 mg L^{-1} Hg(II) was prepared from mercuric chloride (Glaxo Laboratories Ltd., India) using distilled water. Required concentrations of the samples were prepared by serial dilutions of the stock solution. Neutral activated aluminium oxide was purchased from Maharashtra Chemical Products, India and particles below 100 μm in size were collected by screening.

2.2. Preparation of MDN and MDN@Al_2O_3

MDN was synthesized by the reaction between potassium permanganate and ethyl alcohol, similar to a procedure reported by Subramanian et al. [18]. In this method, 0.5 g of potassium permanganate was dissolved in 300 mL of distilled water. 10 mL of ethyl alcohol was added drop-wise to the above solution while stirring. A brownish-black precipitate, which formed was filtered and washed thoroughly to remove any byproducts. The product obtained was dried at 60 °C overnight, ground well and stored in an airtight container for further use. For the synthesis of MDN@Al_2O_3, 20 g of Al_2O_3 was soaked in 30 mL of 0.01 M potassium permanganate for 2 h and 10 mL of ethyl alcohol was added drop-wise while stirring. The product was separated from the solution by appropriate screening, washed thoroughly and dried at 60 °C overnight.

2.3. Characterization of the adsorbents

TEM was carried out using a JEM 3010, 300 kV instrument with an ultra high resolution (UHR) polepiece (JEOL, Japan). The samples for TEM were prepared by dropping the sample dispersion on amorphous carbon films supported on a copper grid and dried in ambience. Surface morphology and elemental analysis of the as-prepared samples were done using a SEM equipped with EDAX (FEI QUANTA-200 SEM, Czechoslovakia). For this, the samples were drop-casted on an indium tin oxide (ITO) conducting glass and dried. XRD data were collected with an X-ray diffractometer (Bruker AXS, D8 Discover, USA) using Cu-Kα radiation (λ = 1.54 Å). The samples were scanned in the 2θ range of 10–90°. The XPS measurements were conducted using an Omicron ESCAProbe spectrometer (Omicron Nanotechnology, Taunusstein, Germany), with monochromatized Mg Kα X-rays ($h\nu$ = 1253.6 eV). The specimens were prepared as drop cast films on a sample stub and a constant analyzer energy of 20 eV was used for the measurements. The amount of manganese coated on MDN@Al_2O_3 was quantified by acid digestion method suggested by national environment protection council [20]. The concentration of manganese was measured using atomic absorption spectrophotometer (PerkinElmer, AA analyst 700, USA) and a hollow cathode lamp (HCL).

Table 1
Composition of simulated chlor-alkali industrial effluent.

Parameters (mg L^{-1})	Quantity
pH@25 °C	8.6
Hg(II)	20.0
Pb(II)	2.2
Cd(II)	1.1
Mg(II)	33.2
Ca(II)	51.1
Na(I)	241.6
Cl^-	379.2
NO_3^-	343.5
PO_4^{3-}	19.0
NH_4^+	31.5
BOD_5	79.0
Conductivity (mS cm^{-1})	19.6

2.4. Hg(II) uptake studies

Hg(II) batch adsorption experiments were carried out in 250 mL glass conical flasks. The working volume of the solution was taken as 100 mL at pH 5.5 (±0.2) and dose of MDN was maintained as 10 mg. The flasks were kept for shaking at 160 ± 5 rpm in an orbital shaker (Riviera, India) at 30 ± 2 °C. Samples were withdrawn at predetermined time intervals and residual concentration of Hg(II) was detected using a PerkinElmer Lambda 25 UV–vis absorption spectrometer, USA [7]. For detection, the sample, KI buffer and Rhodamine 6G solutions were added in 2:1:1 ratio. For detecting residual concentrations of Hg(II) below 0.2 mg L^{-1}, all samples were concentrated 20 times. Effect of contact time on Hg(II) uptake was studied for 10, 20, 30 and 40 mg L^{-1} Hg(II). The samples were collected at specific time intervals for residual Hg(II) analysis. Equilibrium studies were performed as a function of temperature (20, 30 and 40 °C). The Hg(II) concentrations were varied over a range of 10–40 mg L^{-1}. The samples were collected after the equilibrium contact time of 1 h and analyzed for residual Hg(II) concentrations. Effect of adsorbent dose (2.5–100 mg) was investigated for 10 mg L^{-1} Hg(II). Hg(II) uptake was also investigated as a function of pH by varying it from around 2–10 and at an initial Hg(II) concentration of 20 mg L^{-1}. The initial pHs of the samples were adjusted using dilute NaOH or HCl solution.

2.5. Application for the treatment of simulated chlor-alkali industrial effluent

Chlor-alkali industrial effluent was simulated (Table 1) and the effect of adsorbent dose on Hg(II) removal was studied using MDN and MDN@Al_2O_3. A control experiment was carried out using Al_2O_3. The economic viability of any adsorbent depends upon