

Magnetic manganese dioxide as an amphoteric adsorbent for removal of harmful inorganic contaminants from water

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ABSTRACT

Manganese dioxide (δ -MnO₂) with magnetic properties has been synthesized by precipitation of MnO₂ in the presence of magnetite. The resulting material has a particle size distribution between 0.5 and 5 μ m. Magnetization of the material is in the order of magnitude of that of magnetite. Therefore a solid–liquid separation by means of moderate magnetic fields is possible. Due to the properties of δ -MnO₂ the point of zero charge of the surface is about 2.5. Therefore, the adsorbent is almost exclusively a cation exchanger although sorption of oxoanions is also possible. Sorption experiment with Cd²⁺, Ni²⁺, and Pb²⁺ ions revealed a preferred sorption. Alkaline earth ions such as Ca²⁺ affect the uptake only at high concentrations. Because of the small particles and the respective large specific surface, sorption is fast.

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1. Introduction

Pollution of ground and surface water with heavy metals is a major concern with respect to human health due to their extreme toxicity and to the fact of not being chemically or biologically degradable. Some of these metal ions are dangerous even at very low concentrations. Heavy metals may have natural origin such as leaching of underground minerals or they are introduced into the water streams as a result of anthropogenic and industrial activities. Metal processing facilities, mining operations, battery manufacturing, production of paints and pigments, glass production, etc. are responsible for emissions of metal ions among other contaminants. Inputs of heavy metals into bodies of water lead to a deterioration of water quality and cause an obvious necessity of purification and elimination of a variety of contaminating species [7].

Toxicity levels depend on the type of metal, its biological role, and the type of organisms that are exposed. Heavy metals linked most frequently to human health problems are lead, mercury, arsenic and cadmium. Other heavy metals, including copper, zinc, and chromium, are essential trace components required by the body in small amounts, but can be toxic in larger doses [16,27]. Various treatment techniques have been applied to remove metal ions from contaminated waters such as chemical precipitation [4], adsorption and ion exchange, membrane technology [25] and solvent extraction [23]. Over the last few decades, sorption has

gained importance as an effective purification technique used in wastewater treatment, and the removal of heavy metals is considered an important application of adsorption processes using a suitable adsorbent. A number of adsorbents such as polymeric materials, zeolites [20], activated carbon [13], clay minerals [21] and biosorbents [2,26] have been used in the adsorption process.

In recent years, many researchers have applied metal oxides for the adsorption of heavy metals from water systems [5,6,11,12]. Hydrous manganese oxide belongs to those metal oxides thought as natural scavengers of heavy metals in water systems. In the natural environment, trace metals, such as Cu, Pb, Ni and Zn, can be strongly associated with manganese oxides. Because of its large surface area, microporous structure, and OH functional groups capable of reacting with metals and other specifically sorbing ions; hydrous manganese oxides provide an efficient capture pathway for heavy metals [1]. Hydrous manganese oxide is one kind of surface acidic oxides, whose pHPZC (point of zero charge) value is about 1.5–4.5 and the charge of the hydrous oxide depends on the pH of the medium. Commonly, the surface charge of manganese oxide is negative, and it can be used as an adsorbent to remove heavy metals from wastewater [14]. However, pure hydrous manganese oxide as a filter media is not completely favorable. The fine particle size makes it very difficult to separate from the water phase or to infiltrate through. Nevertheless, coating manganese oxide to a media surface which can improve the solid/liquid separation may provide a promising adsorbent for heavy metals from wastewater.

Regarding these difficulties metal oxides have been combined with other materials because of their potential as effective sor-

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bents. Respective examples are the combination of hydrous oxides with materials such as activated carbon [8], zeolites [9] and sand [10] for metal ions removal.

Another kind of adsorbent materials possessing high adsorption capacity comprises metal oxide adsorbents with magnetic properties. The application of polymeric and inorganic magnetic micro-sorbents technology to solve environmental problems is a method that has received considerable attention in recent years [29,15,28]. Magnetic inorganic micro-sorbents can be used to adsorb contaminants from either aqueous or gaseous effluents and once the adsorption is carried out, the “loaded adsorbent” can be separated from the medium by a simple magnetic process. Clay materials and zeolites [17,18], activated carbon [22], carbon nanotubes [19] have been combined with iron oxide, such as maghemite or magnetite, to produce a magnetic adsorbent.

Magnetic micro-sorbents prepared from hydrous manganese oxide can be produced by means of the oxidation of manganese ions due to the action of an oxidizing agent in presence of magnetic particles such as magnetite. The advantage of such sorbent material is its very large specific surface and, therefore, the fast adjustment of sorption equilibria. The magnetic property allows the material to be easily recovered by magnetic separation methods after adsorption or regeneration, which overcomes the disadvantage of separation difficulties with common adsorbents.

Objectives of the work presented here were the reproducible production of stable manganese dioxide with magnetic properties, its physical and chemical characterization and investigations about equilibria and kinetics of the sorption of selected contaminants.

2. Materials and methods

2.1. Synthesis of manganese dioxide with magnetic properties (MMS)

Manganese dioxide was precipitated from MnCl_2 solutions by adding potassium permanganate according to:



To obtain a precipitate with magnetic properties (MMS), synthetic magnetite, Fe_3O_4 (Bayoxide E 8710) was added in a Fe_3O_4 : MnO_2 ratio of 1:1 during the precipitation.

For precipitation 14 mL of 1 M KOH and 23 mL of 0.2 M KMnO_4 were added to 500 mL of purified water under constant agitation. Once the pH of the suspension reached a value of about 12.40, 7 mL of 1 M $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ solution was slowly added within 5 min (1.4 mL/min). The suspension was continuously agitated for a period of 30 min. Once the reaction time was completed the solid was separated from the solution by using a hand magnet.

2.2. Chemicals

For the sorption experiments solutions of $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Ni}(\text{NO}_3)_2$ were prepared from standard solutions, analytical grade, in deionized water. The pH of the solutions was adjusted by adding 0.01 M HNO_3 or 0.01 M NaOH solutions. The presence of calcium was realized by adding CaCl_2 . All chemicals were analytical grade from Merck Comp., Germany.

2.3. Analyses

The magnetic properties of MMS were determined by means of alternating gradient magnetometer (AGM) measurements (Micro-mag 2900). The surface area was determined by BET measurements using a Quantachrome Autosorb-1 device. Further surface information of δ - MnO_2 and MMS was obtained by environmental scanning electron microscopic (ESEM) analysis. Atomic absorption

(VARIAN SpectraAA-220-FS) was applied for measuring the total manganese contents of the magnetic samples. For pH measurements a standard Metrohm pH meter was used.

The ζ potential of the solid particles was measured using a Zetasizer 5000 (Malvern Instruments Ltd.) micro electrophoresis apparatus at room temperature, 25 °C. Sufficiently diluted suspensions of the magnetic adsorbent (MMS) were prepared with constant ionic strength (0.01 M NaNO_3). Titration was carried out by adding small amounts of 0.1 M HNO_3 or NaOH solution. The same procedure was made for magnetite and δ - MnO_2 used for the synthesis of the MMS.

Determination of the particle size distribution was carried out by means of a computerized system, Eye Tech (CIS 100) (Ankersmid Ltd., Netherland), that allows the measurement of particle sizes in the range of 0.1–3600 μm . For the measurements cells of 1 cm/1.5 mL were used and the samples were directly taken from the suspension without any previous treatment.

2.4. Sorption experiments

For determination of the equilibrium of sorption of metal cations or metal oxo anions samples of 1 L of solution were prepared with initial metal concentrations between 0.08 and 1 mg/L (corresponding to 0.71–8.9 $\mu\text{mol/L}$ (Cd^{2+}), 1.36–17 $\mu\text{mol/L}$ (Ni^{2+}) and 0.386–4.83 $\mu\text{mol/L}$ (Pb^{2+})) to simulate trace contaminations. Initial pH values were adjusted by means of HNO_3 or NaOH . The solutions were contacted with 5 mg MMS in the experiments with cadmium and nickel and with 1.25 mg in the experiments with lead. The samples were shaken on a shaker (VKS 75 Edmund Bühler GmbH) at 100/min for 3 h. After this period the pH was measured and samples were taken.

To study sorption kinetics 10 mg of MMS were contacted with 200 mL of solution of given initial concentration and pH value in a 400 mL Erlenmeyer. The suspension was stirred by means of a magnetic stirrer (IKA Labortechnik) at 500/min. At preset time intervals samples were taken and analysed to follow the development of sorption.

3. Characterization of the adsorbent

3.1. Physical properties

Fig. 1 shows an ESEM photograph of δ - MnO_2 and of the magnetic adsorbent. The crystalline structure of MMS is due to the presence of magnetite.

The particle size distribution is shown in Fig. 2.

The figure shows a distribution between 0.5 μm and 5 μm with a maximum of the volume distribution at 2 μm .

Fig. 3 shows the magnetization curves of MMS, δ - MnO_2 and magnetite (Fe_3O_4). The magnetic saturation of δ - MnO_2 is very small. Magnetic saturation of MMS is smaller than that of magnetite, however, sufficiently high to allow the particles to be removed from a solution by using a magnetic field.

Data about the magnetization, the contents of manganese, and the specific surface are summarized in Table 1.

3.2. Chemical properties

The sorption properties are dominated by the protonation/deprotonation of the surface, i.e. by the point of zero charge, pH_{PZC} . Fig. 4 shows the electrophoretic mobility of the particles as a function of pH. According to the development the point of zero charge of the surface is in the range of $\text{pH} = 2.5$. This value is in accordance to data from literature for pure δ - MnO_2 [3,24]. As a consequence, the magnetic adsorbent MMS acts predominantly as a cation

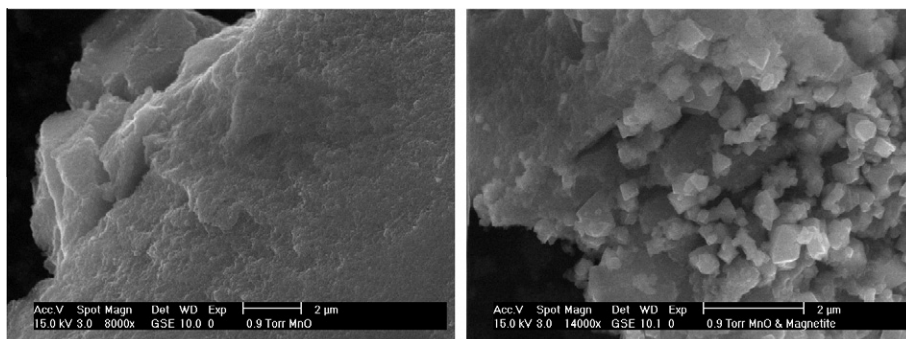


Fig. 1. Environmental scanning electron microscope (ESEM) photographs of pure δ -MnO₂ (left) and MMS (right).

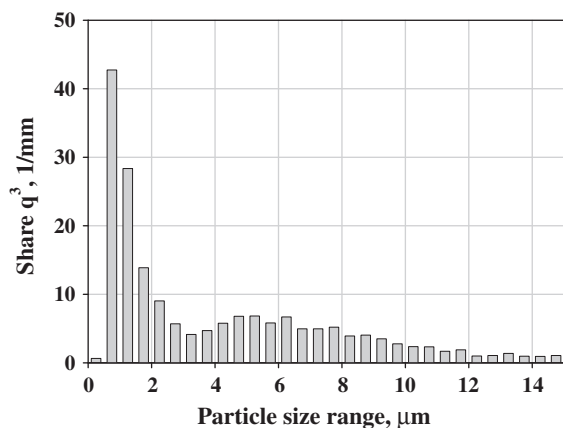


Fig. 2. Particle size distribution of magnetic sorbent.

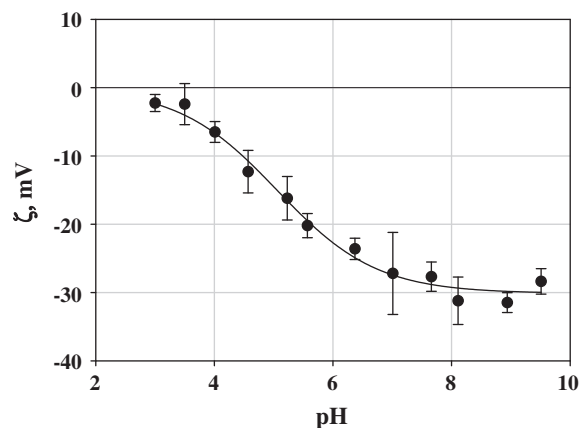


Fig. 4. Development of zeta potential of MMS particles as a function of pH.

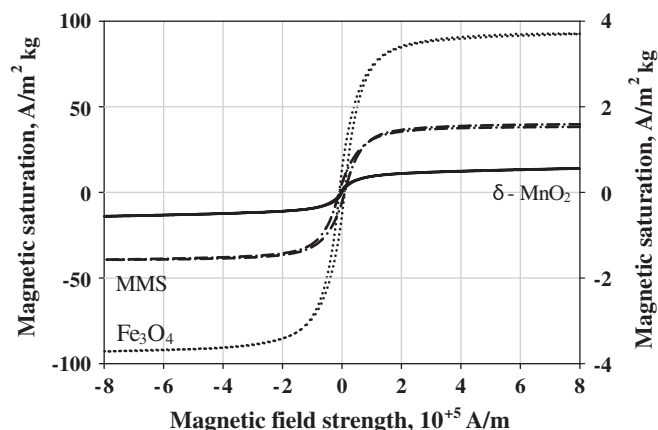


Fig. 3. Magnetization of Fe₃O₄, and MMS (left hand side ordinate axis), δ -MnO₂ (right hand side ordinate axis).

Table 1
Contents of Mn²⁺, BET surface and magnetic saturation of Fe₃O₄, δ -MnO₂ and MMS.

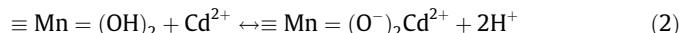
Material	Fe ₃ O ₄	δ -MnO ₂	MMS
Mn ²⁺ , g/g MMS	–	–	0.47
BET, m ² g ⁻¹	5	240	126
Magnetic saturation, Am ² /kg	90–95	0.3–0.4	36–40

exchanger. At pH > pH_{PZC} parts of the surface groups are still protonated, but the degree of protonation decreases gradually with increasing pH. Corresponding to the pH-dependent protonation, therefore, some anion exchange is possible at pH > 2.5.

4. Sorption equilibria

4.1. Heavy metal cations

Sorption of heavy metal cations predominantly occurs at pH values above the point of zero charge. It develops as an exchange of e.g. Cd²⁺ metal ions for hydrogen ions from the surface groups:



The number of dissociated –OH groups depends on the pH of the liquid phase. As a consequence, the sorption capacity depends on pH and increases with increasing pH.

Fig. 5 shows isotherms from the sorption of cadmium ions onto MMS from pure solutions for initial pH values between 5 and 8 and demonstrates the increase of capacity with increasing pH value. Because of the small amounts of adsorbent the shift of pH due to sorption was in the range of ± 0.15 pH units and therefore almost negligible. As a consequence, the state of protonation/deprotonation of the surface was approximately the same for each series.

Similar results have been obtained for the sorption of Ni²⁺ and Pb²⁺ ions.

The Langmuir relationship has been applied for evaluation of the equilibrium data:

$$q = q_{\max} \frac{K_L c}{1 + K_L c} \quad (3)$$

The equilibrium parameters q_{\max} and K_L deduced from the experiments are summarized in Table 2.

The sorption also depends on the background composition of the water. Fig. 6 shows isotherms from the sorption of cadmium

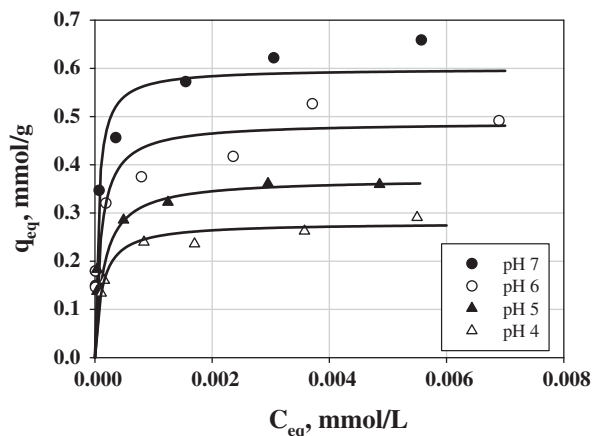
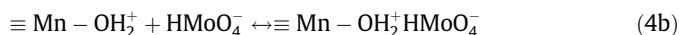
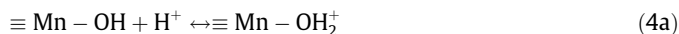


Fig. 5. Isotherms of the sorption of Cd^{2+} ions at different pH values.

ions in the presence of different amounts of calcium. As becomes obvious, there is a competitive sorption of calcium ions. However, substantial influences occur only at concentrations much higher than that of the heavy metals. As a consequence, the figure demonstrates the preferred sorption of the heavy metal species. No theoretical evaluation was made for these ternary systems.

4.2. Metal oxoanions

Sorption of anions predominantly occurs at pH values below the point of zero charge. It develops as a consecutive sorption of protons in a first step, to generate positive surface charges, followed by the sorption of metal oxoanions, e.g. molybdate species in the second step:



As is obvious the number of protonated $-\text{OH}$ groups depends on the pH of the liquid phase. Therefore, the sorption capacity will increase with decreasing pH value of the solution.

To study the sorption of molybdate anions 250 mL samples containing 2 mg/L Mo (corresponding to 0.0024 mmol/L Mo) at different initial pH values were contacted with 2.5 mg MMS. Fig. 7 shows the resulting equilibrium loadings as a function of equilibrium pH. The development shows that the amount of anions that can be sorbed are in the same order of magnitude as those of cations.

Table 2

Equilibrium parameters for sorption of Cd^{2+} , Ni^{2+} , and Pb^{2+} .

Ion	pH	q _{max} , mmol/g	K _L (L/mmol)	R ²
Cd^{2+}	4	0.280	8524	0.99
	5	0.371	6627	0.97
	6	0.488	10,181	0.88
	7	0.599	18,609	0.94
Ni^{2+}	4	0.125	2494	0.85
	5	0.312	1837	0.98
	6	0.601	1135	0.93
	7	0.623	1481	0.99
Pb^{2+}	4	0.723	7509	0.98
	5	1.02	13,949	0.98
	6	2.18	2825	0.91

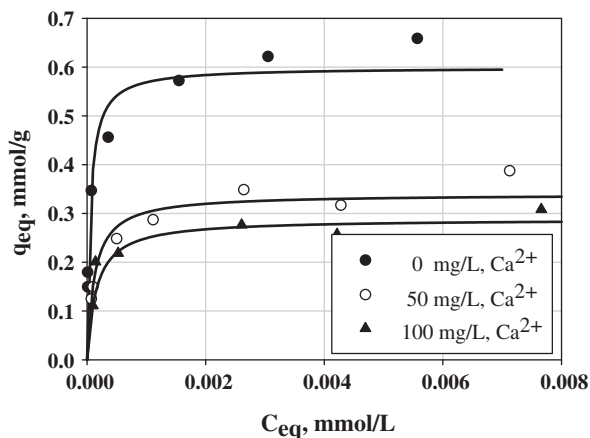


Fig. 6. Isotherms of the sorption of Cd^{2+} ions in the presence of Ca^{2+} ions.

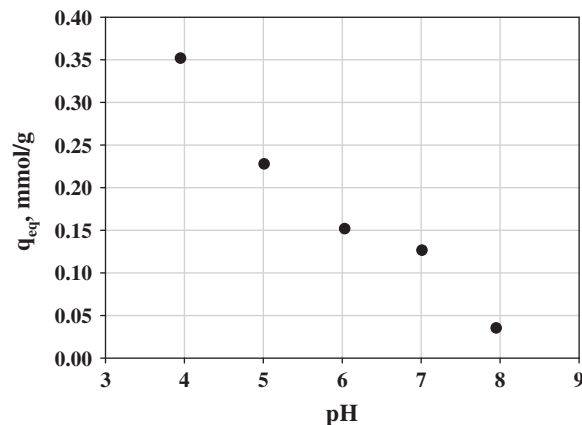


Fig. 7. Sorption of molybdate anions onto MMS at different pH values.

5. Sorption kinetics

Fig. 8 shows the development of sorption of Cd^{2+} ions in the above-mentioned stirrer device. Fig. 8a shows results from experiments with an initial Cadmium concentration of 8.4 and 9 $\mu\text{mol/L}$ and different amounts of sorbents. As expected, higher amounts of sorbents result in lower equilibrium concentrations left in solution. In all three cases Cd^{2+} -uptake is fast and more than 90% of the total amount sorbed binds to the MMS within the first ten minutes. However, it can also be seen that in the case of the highest amount of sorbent used, corresponding to the lowest equilibrium concentration, a part of the sorption process takes place between 10 and 30 min.

The likely reason for this is that the uptake process is mainly determined by interparticle mass transfer through the stagnant liquid film surrounding each particle. In the case of low Cd^{2+} concentrations in solution the driving force for this process gets small resulting in a prolonged approach of the equilibrium state.

Fig. 8b presents results from experiments with different initial concentrations and 10 mg/L MMS. In all cases the initial pH was about seven. What can be seen from Fig. 8b is that despite the difference in the starting concentration in all cases the uptake is practically finished within the same time of 10 min. Again this result strengthens the assumption of the dominance of film kinetics. Given the average particle diameter of only around 2 μm this result is of no surprise, because of the very short distances the ions have to diffuse inside the particles.

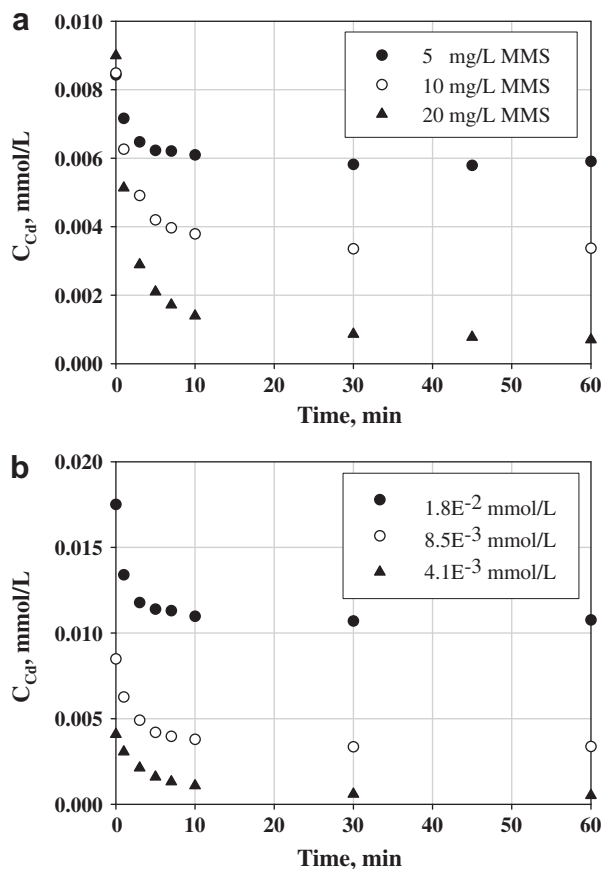


Fig. 8. (a) and (b) Rate of sorption of Cd²⁺ onto MMS at different amounts of sorbent (top) and different initial concentrations (bottom).

6. Conclusions

Synthesis of δ -MnO₂ with magnetic properties led to a micro-sorbent material with amphoteric properties. Its point of zero charge is about 2.5. Therefore, it can predominantly be applied for removal of cations. Sorption experiments revealed that health-relevant heavy metals are strongly preferred over alkaline earth ions from a background composition of the water to be treated. Because of the large specific surface, sorption develops very fast even in the range of trace concentrations. Despite of the low point of zero charge, even sorption of oxoanions is possible. Mag-

netization of the hybrid material is smaller than that of magnetite, however, still in a range where a simple solid-liquid separation is possible by applying standard magnetic separation devices. The respective experiments have, however, not yet been carried out. Furthermore, no information is still available on a possible regeneration and re-use of these adsorbents.

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