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Elaboration of Lamellar and Nanostructured Materials Based on Manganese: Efficient Adsorbents for Removing Heavy Metals

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Abstract

The lamellar and nanostructured manganese oxide materials were chemically synthesized by soft and non-toxic methods. The materials showed a monophasic character, symptomatic morphologies, as well as the predominance of a mesoporous structure. The removal of heavy metals Cd(II) and Pb(II) by the synthesized materials Na-MnO₂, Urchin-MnO₂ and Cocoon-MnO₂ according to the mineral structure and nature of the sites were also studied. Kinetically, the lamellar manganese oxide material Na-MnO₂ was the most efficient of the three materials which had more vacancies in the MnO₆ layers as well as in the space between the layers. The nanomaterials Urchin-MnO₂ and Cocoon-MnO₂ could exchange with the metal cations in their tunnels and cavities, respectively. The maximum adsorbed quantities followed the order (Pb(II): Na-MnO₂ (297 mg/g) > Urchin-MnO₂ (264 mg/g) > Cocoon-MnO₂ (209 mg/g), Cd(II): Na-MnO₂ (199 mg/g) > Urchin-MnO₂ (191 mg/g) > Cocoon-MnO₂ (172 mg/g)). Na-MnO₂ material exhibited the best stability among the different structures, Na-MnO₂ presented a very low amount of the manganese released. The results obtained showed the potential of lamellar manganese oxides (Na-MnO₂) and nanostructures (Urchin-MnO₂ and Cocoon-MnO₂) as selective, economical, and stable materials for the removal of toxic metals in an aqueous medium.

Keywords: Cadmium; lead; Wastewater; manganese oxide; kinetic; mesoporous structure

1. Introduction

The depletion of drinking water resources had been a global problem in recent years, due to water pollution by heavy metals mainly from intensive human activities. These pollutants were not biodegradable and toxic.¹ Moreover, all along the food chain, some of them were concentrated in living organisms, which posed major risks to the environment and human health.^{2–4} This contamination was certainly the most serious case among the problems posed by environmental pollution.^{5–7} Metal ions were more precisely cadmium and lead were general-

ly released without appropriate treatment during industrial processes,^{8,9} such as in metal factories, paint industries, battery production as well in the combustion of motor gasoline (lead), etc... Lead and cadmium were persistent metals in the subsoil. Consequently, lead contamination of soil and groundwater was a serious problem.¹⁰ Exposure to Pb(II) and as it was known worldwide could damage the nervous system and be carcinogenic to humans.^{11–14} It could also damage the kidneys, cellular processes, and the reproductive system.¹⁵ Toxic symptoms could occur in several ways, such as anemia, insomnia, headaches, muscle weakness, hallucinations, and kidney

damage.¹⁶ The United States Environmental Protection Agency had classified cadmium as a probable human carcinogen.¹⁷ Chronic exposure to cadmium posed serious risks, including kidney dysfunction and high levels of exposure leading to death.¹⁸ Environmental requirements were becoming increasingly stringent in the paint industry, as for all industrial activities.

Intensive research and development efforts were being used worldwide to develop effective processes to reduce or eliminate toxic metal ions in aqueous solutions using precipitation of several metals such as lead,¹⁹ cadmium²⁰ and magnesium.²¹ Still, they provided that this process was carried out at a pH between 8 and 11.^{18,22} Others have used polyamide membranes to remove Cd(II)²³ and Cu(II)²⁴ cations by reverse osmosis. Other processes had adopted elaborate materials such as zeolite,^{25,26} which had been used as an adsorbent to remove some heavy metals, but with adequate pretreatment systems for suspended solids removal before applying ion exchange. However, the application of these methods was limited due to their high energy costs, their complex operation and equipment, their secondary pollution, and the problem of regeneration. The adsorption technique had proven to be the most efficient process due to its simplicity, ease of implementation, and high efficiency over a wide range of concentrations.²⁷ Additionally, it was a cost-effective method for treating large quantities of wastewater containing low levels of pollutants.²⁸ Unlike many techniques based on oxidation/reduction reactions or photocatalytic reactions, adsorption remained a method that does not lead to the formation of products/by-products that may be more or less toxic, or that subsequently caused secondary contamination. For this purpose, several types of adsorbents had been used, either synthetic^{29,30} or natural such as calcium hydroxyapatite (CaHAP)³¹ and barium hydroxyapatite (BaHAP),³² perlite which has been used to remove cadmium and nickel ions in the aqueous medium.³³ Peat,³⁴ carbon nanotubes,³⁵ alumina,³⁶ mesoporous silica,³⁷ and clays^{38,39} had also been applied to remove or reduce some heavy metals at different concentrations. However, these adsorbents had several disadvantages. They were characterized by their low adsorption capacity, reactivity and long equilibrium time to remove heavy metals.^{40–42}

The manganese oxides materials existed widely in a large variety of forms in the upper crust. They were very important minerals because of their abundance and high reactivity. They were the strongest oxides in soils and were characterized by high sorption power.⁴³ They had a high capacity to remove several organic pollutants from soils and sediments.⁴⁴

In general, manganese oxides materials were characterized by a low point of zero charge (PZC),⁴⁵ a relatively large surface area, and strong acid sites, which gave them a high adsorption capacity and excellent oxidation

and catalysis activity.⁴⁶ Moreover, the layered manganese oxide structure (lamellar structure) was used as an effective adsorbent to remove several heavy metals.⁴⁷ These materials had a variable number of octahedral cationic vacancies within the MnO₆ layers, which were important and significant adsorption sites for metal cation.⁴⁸ The MnO₆ layers in this type of structure were assembled in the form of sandwiches separated from each other to form spaces of 7 Å (birnessite) or 10 Å (buserite), this generated a large part of the sorption sites.⁴⁹ Tunnel structures were generally made up of single, double or triple chains that were connected by their vertices to form tunnels of square or rectangular cross-section with inserted cations (H⁺ or K⁺).⁵⁰

The use of this type of material to remove metal cations was favorable and generally carried out by ion charge equilibrium exchange with cations inserted in tunnels that were characterized by a space of 4.6 Å.⁵¹ The removal of several metals, including arsenic (III) and (V) from aqueous medium, had been studied using materials based on manganese with a compact structure (hausmannite).⁵² Various studies had been carried out to remove several metals such as copper,⁵³ nickel,^{54,55} lead,^{56,57} cadmium²⁷ and zinc⁵⁸ ions using iron and modified manganese oxides as adsorbents. A research study reported that despite the high reactivity of iron oxides, the manganese oxides had shown an efficiency 40 times higher than iron oxides in the case of Pb(II) ions.⁵⁹ Indeed several studies have shown that the use of manganese oxides for the coating of some materials such as biochar (BC),⁶⁰ wool,⁶¹ and zeolite,⁶² allowed to increase their specific surface as well as the volume of the pores and consequently to favor the adsorption phenomenon. This showed the very important role of manganese oxides for the removal of metal ions from aqueous medium.

In this work, we investigated the possibility of removing Pb(II) and Cd(II) ions from the aqueous medium by three manganese oxide materials (marked as Na-MnO₂, Urchin-MnO₂, and Cocoon-MnO₂) with different lamellar structures and nanostructures. The composition, morphology, and distribution of the sites of each material were determined by different spectroscopic techniques. To better understand the removal process of Pb(II) and Cd(II) by manganese oxides materials, the effect of pH, kinetics and adsorption studies were examined. To study the stability of the materials, the total amount of manganese released during removal processes will be elucidated. These materials will be characterized by X-ray diffraction after interaction. To verify the reusability of the materials for the removal of Pb(II) and Cd(II), five successive cycles were performed, as well as examining their stability.

To better understand the removal process of Pb(II) and Cd(II) by manganese oxides materials the performing kinetic and adsorption studies were examined. Finally, these materials will be characterized after the interaction by X-ray diffraction. To study the stability of the materials,

the total amount of manganese released, and the amount of heavy metal removed will be elucidated.

2. Experimental Section

2. 1. Chemical Compounds

All chemicals used in this study were purchased from Sigma Aldrich (St. Louis, MO, USA) and were used without further purification. Solutions were prepared with demineralized water from the Adrona crystal water system (quality $\leq 0.05 \mu\text{S/cm}$).

2. 2. Synthesis of Na-MnO₂

Manganese oxide Na-MnO₂ was obtained by precipitation at room temperature. During stirring, 10 mL of hydrogen peroxide mixed with 2.16 g of sodium hydroxide dissolved in 90 mL of water was added dropwise to the manganese sulfate solution (MnSO₄ · H₂O) (2.535 g, 50 mL). The mixture remained agitated overnight at room temperature. The deep brown precipitate obtained after filtration was washed with water and ethanol. The product was recovered by filtration and dried at 50 °C.⁶³

2. 3. Synthesis of Urchin-MnO₂ Nanostructure

Urchin manganese oxide MnO₂ nanostructure was synthesized by the reflux method under acidic conditions.⁶⁴ 2 g of manganese sulfate (MnSO₄ · H₂O) was dissolved in 100 mL of distilled water. In a water bath and under vigorous stirring, 1 mL of sulfuric acid was added by dripping. After stirring, 66 mL of potassium permanganate (0.1 M) was added to the mixture. Stirring was maintained at 80 °C for 24 hours. The resulting black colored product was isolated and washed several times with water and absolute ethanol. Finally, the product obtained was dried at 60 °C.

2. 4. Synthesis of Cocoon-MnO₂ Nanostructures

Synthesis of manganese oxide type cocoon was based on the reduction of Mn(VII) and Mn(II) under ambient temperature conditions.⁶⁴ 100 mL of potassium permanganate KMnO₄ solution (0.1 M) was added dropwise under vigorous agitation to 150 mL of manganese sulfate solution (0.1 M). The resulting mixture was agitated for 6 hours. The resulting black colored product was isolated, washed several times with water and absolute ethanol, and dried at 60 °C.

2. 5. Chemical Analysis

The chemical composition of the three materials was determined by dissolving 0.1 g of sample with 1 g of hy-

droxylamine hydrochloride in 250 mL of the distilled water.⁶⁵ The resulting Mn, K, and Na content in the solution was determined by atomic absorption spectrometry device (Shimadzu AA-7000) (Shimadzu Corporation, Japon).

Manganese average oxidation state (AOS) was determined by potentiometric determination using sodium pyrophosphate. This method avoids errors related to mass and reagent concentration measurements, and the only parameters to be determined were equivalent volumes.⁶⁶ All chemical analysis was repeated three times, and the average was determined.

2. 6. Characterization

X-ray diffraction patterns were recorded on a Bruker D8 (Bruker, France S.A.S). Advance diffractometer equipped with a graphite monochromator, a Lynx-Eye detector, and parallel beam optics using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Phase identification and material structures were determined by the High Score software (XRD data processing software).

The morphology of the particles of the various synthesized samples was studied by scanning electron microscopy (JEOL Ltd Gemini 15-25, Japon).

The specific surface area analysis was performed using the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method from N₂ adsorption and desorption isotherms using Micromeritics Gemini VII system (Micromeritics Instruments Corporation, USA). 0.1 g of the sample was degassed before measurement at 110 °C for 3 hours under vacuum equilibrium.

2. 7. Batch Experiment of Cd(II) and Pb(II) Removal

The Cd(II) and Pb(II) ions removal experiments were performed by placing 100 mg of the synthesized material in a 50 mL of an aqueous solution containing 30 ppm of the Cd(II) or Pb(II) respectively as Cd(NO₃)₂ or Pb(NO₃)₂. The content was agitated (500 rpm) during the interaction. The metal cation removal experiments were performed under ambient conditions at different values of pH. The solution pH was adjusted using NaOH (0.1 M) or H₂SO₄ (0.1 M). The solution was filtered through a 0.45 μm membrane, and the residual concentration of the metal cation Cd(II) and Pb(II) concentration in the solution was analyzed using atomic absorption spectrophotometer (AAS). This allowed us to evaluate the removal efficiency of heavy metal (R%) using Eq. (1) and the adsorbed amount $q(t)$ in mg/g using Eq. (2). Measurements under the same conditions were proceeded three times.

$$R(\%) = \left(1 - \frac{C_r}{C_0}\right) \times 100 \quad (1)$$

$$q(t) = \frac{(C_0 - C_r) \times V}{m} \quad (2)$$

Where: m : mass of manganese oxide material (100 mg).

V : Volume of the solution used (50 mL).

C_0 and C_r were the initial and residual concentrations of metal ions (cadmium or lead).

3. Results and Discussion

3.1. XRD of MnO_2 Lamellar and Nanostructures

The diffractograms (Figure 1) of the synthesized manganese oxides, namely: Na-MnO_2 , Cocoon-MnO_2 , and Urchin-MnO_2 , showed that materials were different and therefore, they don't had the same crystalline structure.

The diffractogram of the Cocoon-MnO_2 material (Figure 1) had a very low-intensity signal. This could be

explained by the low crystallinity of the material. The poor crystallinity of the material was due to its synthesis at room temperature. The increase in the synthesis temperature made it possible to improve the material crystallinity but also to generate different morphologies.^{64,67} Nevertheless, the diffractogram revealed the presence of two diffraction peaks at $2\theta = 37^\circ$ (311) and 65° (440), which had been indexed for the MnO_2 type structure. It was deduced that the sample was in a weakly crystalline state with $\alpha\text{-MnO}_2$ crystallographic forms.⁶⁸ This material was characterized by a crystalline structure as $\text{K}_2\text{Mn}_4\text{O}_9$ (Table 1).

For the Urchin-MnO_2 material, the diffractogram showed several well-defined and symmetrical peaks indicating that the material was well crystallized. The peaks observed, at $2\theta = 12.8^\circ$ (101), 17.8° (200), 28.6° (201), 37.4° (211), 41.6° (310), 49.5° (411), 59.9° (512), 65° (020) and 69.7° (514), could easily be indexed with cryptomelane ($\text{KMn}_8\text{O}_{16}$) with a space group (I2/m(12) (JCPDS sheet No 44-1386).⁶⁴ This material had a tunnel structure whose cation K^+ was present in these cavities.⁶⁹

The last diffractogram of Na-MnO_2 material, as shown in (Figure 1) had well-defined with symmetrical diffraction peaks (001) and (002) (JCPDS card #01-073-9669).⁷⁰ They indicated that material was single-phase mineral and well crystallized. This phase corresponds to the family of birnessite type sodium manganese, which has a layered structure with crystal water and Na^+ between the MnO_6 octahedral sheets.⁷¹ This oxide had a basal spacing of 0.714 nm along the c -axis with a single crystal water sheet between the MnO_6 octahedral sheets. The diffraction peaks could be easily indexed as a monoclinic structure (space group: C2/m).⁷² From the diffractograms, we noticed that the various synthesized oxides had slightly wide peaks. These materials had slightly different surface areas. The chemical formula, structures, the Mn (AOS) of each material were illustrated in Table 1. The spacing between layers for Na-MnO_2 and the size of the tunnels for Urchin-MnO_2 was calculated from the 2θ values of the peaks using a value of $1.541 \text{ \AA}$ (copper anticathode wavelength).

Figure 1. X-ray diffractograms of the synthesized manganese oxides materials.

Table 1. Crystalline parameters and composition of manganese oxide materials (Na-MnO_2 , Cocoon-MnO_2 , and Urchin-MnO_2).

Material	Chemical formula*	d (Å)	Mesh parameters (Å)*	Structure*	Composition in element (ppm)**	(AOS) of Mn
Na-MnO_2	$\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot (\text{H}_2\text{O})_{1.5}$ (Birnessite)	7.14	$a = 5.1750$ $b = 2.8490$ $c = 7.3380$	Monoclinic	[Mn] = 388.87 [Na] = 75	3.580
Cocoon-MnO_2	$\text{K}_2\text{Mn}_4\text{O}_9$	–	$a = b = 11.2950$ $c = 21.870$	Hexagonal	[Mn] = 704.16 [K] = 34.79	3.650
Urchin-MnO_2	$\text{KMn}_8\text{O}_{16}$ (Cryptomelane)	4.85	$a = b = 9.840$ $c = 2.850$	Tetragonal	[Mn] = 637.86 [K] = 33.765	3.730

* determined by HighScore software. ** determined by atomic absorption spectroscopy (AAS).

Figure 2. SEM images of (a) Na-MnO₂, (b) Urchin-MnO₂, and (c) Cocoon-MnO₂.

3. 2. SEM of MnO₂ Lamellar and Nanostructures

Scanning electron microscopy (SEM) was used to study the detailed surface morphology of the different synthesized materials. As seen in (Figure 2), the morphology of the materials was different.

The different SEM images showed that the surface morphology of these different materials was highly dependent on the preparation technique. Figure 2 showed that the Na-MnO₂ material (Figure 2 a) was composed of thin sheets which were agglomerated together to form particles several micrometers in size. The nanostructured material (Urchin-MnO₂) obtained at 80 °C (Figure 2 b) had an urchin morphology and composed of a large number of nanorods with different sizes intertwining each other while the material obtained at room temperature (Figure 2 c) had a cocoon-shaped morphology composed of micro-spheres.⁶⁴

3. 3. Isotherm BET

All the characteristics of each material, including pore volume, pore size and specific surface area were determined using conventional nitrogen isothermal analysis. From Eq. (S1) we could determine the specific surface area of each material. The evolution of $\frac{1}{Q[(\frac{P_0}{P}) - 1]}$ with $\frac{P}{P_0}$ was linear (Figure 3).

Figure 3 showed the BET isothermal models for the three materials. The results of this study showed a high correlation between relative pressures $\frac{P}{P_0}$ and $\frac{1}{Q[(\frac{P_0}{P}) - 1]}$ that

allowed us to determine the specific surface area of each material. According to Table 2, the three materials were characterized by a large specific surface area ranging from 30 to 44 m²/g. These results showed that a large specific BET surface area provided an effective adsorbent. The BET surface of the Na-MnO₂ material was the lowest of the

Figure 3. BET isotherm of materials Na-MnO₂, Cocoon-MnO₂, and Urchin-MnO₂.

Table 2. Isotherm parameters for BET models.

	Constant C	S_{BET} (m ² /g)	Q_m	R ²
Na-MnO ₂	75.1	30.5 ± 1.7	0.457	0.9999
Urchin-MnO ₂	52.9	44.3 ± 3.0	0.705	0.9998
Cocoon-MnO ₂	41.1	43.9 ± 3.3	0.709	0.9998

three materials, this weakness may be attributed to sodium insertion into the material.

Adsorption/desorption studies of N₂ were performed to characterize the pore size distribution of the three materials, the resulting isotherms and Barrett-Joyner-Halenda (BJH) pore size distribution diagrams were presented in Figure S1. According to the International Union of Pure and Applied Chemistry Classification (IUPAC),⁷³ the curve corresponding to the Na-MnO₂ material had a type V shape with a type H3 hysteresis loop

attributed to mesoporous solids. In contrast, the two materials Urchin-MnO₂ and Cocoon-MnO₂, their curves had a type II shape that corresponded to non-porous rather than macroporous solids.

The pore size classification suggested by the IUPAC⁷⁴ was adopted. Analysis of the BJH pore distribution of the Na-MnO₂ material showed that mesopores ($d > 50$ Å) had about 52% of the total porous surface area. These results showed the predominance of mesopores in the Na-MnO₂ material. This parameter would be a factor and an essential element for the removal of metal ions. The two materials Urchin-MnO₂ and Cocoon-MnO₂, mesoporous, had 52% to 54% of the total area (Table S1). The average pore diameters for the two materials (Urchin-MnO₂ and Cocoon-MnO₂) were slightly small compared to Na-MnO₂ (Table S1). It was also noted from Figure S1 that the pore volume was distributed according to all pore sizes studied. All these parameters allowed having the materials with a high affinity of adsorption of heavy metals. During this study, we also surveyed the average diameters of the adsorption and desorption pores of the BJH model, as well as the cumulative volume of adsorption/desorption, the results obtained were illustrated in Table S1.

4. Pb(II) and Cd(II) Removal by Manganese Oxides Materials

4. 1. Effect of Contact Time on the Removal Efficiency of Heavy Metals

The equilibrium study between the adsorbate (liquid phase) and the adsorbent (solid) was achieved with a speed that depended not only on the rate at which the components diffused into the adsorbent and in the fluid, but also

on the adsorbent-adsorbate interaction. The time-dependent study of the adsorption of a compound on an adsorbent allowed us to examine the influence of contact time on its retention. The effect of contact time for the interaction studies between Pb(II), Cd(II), and the synthesized materials in an aqueous medium under ambient temperature conditions were given in Figure 4.

Figure 4 demonstrated that the prepared materials had a very high removal efficiency. The removal of lead ion could rapidly achieve the equilibrium within 15 min allowed to have a removal efficiency of 97.44, 93.15, and 98.77% for Na-MnO₂, Urchin-MnO₂, and Cocoon-MnO₂, respectively. In the case of Cd(II) ions, the materials also showed high reactivity to this metal cation during contact. The highest yield was up to 99% for Na-MnO₂ material during 30 minutes of interaction, while in the case of Urchin-MnO₂ and Cocoon-MnO₂, the yields were 55.33% and 80.26% respectively.

Several parameters could be discussed to explain the behavior of Pb(II) and Cd(II) ions during interaction with synthesized materials such as the specific surface area, the acid-base properties of the materials, and certainly their composition and Mn (AOS). In this work, we determined the Mn (AOS) for each material using a specific dosage. The results showed that the materials had an oxidation degree average about 3.5. Therefore, the manganese oxide material was a mixture of Mn(III) and Mn(IV) with Mn(IV) dominated (Table 1). Studies had been done to examine the effect of oxidation degree on the removal efficiency of heavy metals.⁴⁹ The results showed that adsorption capacity increased with increasing oxidation degree. This significant correlation may indicate that samples with a high degree of oxidation contained more octahedral cationic vacancy sites, which were primarily responsible for heavy metals sorption. According to the BET isotherm

Figure 4. Effect of contact time on (a) Pb(II) and (b) Cd(II) removal by Na-MnO₂, Urchin-MnO₂ and Cocoon-MnO₂ ([Pb(II)]_{initial}=[Cd(II)]_{initial} =30ppm).

performed for the three synthesized materials, we had found that these oxides had high specific surfaces (Table 2). This parameter was an essential factor in the properties of an adsorbent. The pore diameter could make possible to enhance metal ions elimination. Also, as noticed previously that the Na-MnO₂ material was characterized by the largest pore diameter ($d = 66.63 \text{ \AA}$) compared to the two types of manganese oxides (Table S1). Higher yields recorded for the two metal ions were also enhanced at high pH, which was attributed to the formation of MOH⁺ (M = metal cation) species with the increase in pH. Therefore, the formation of MOH⁺ species conducted to higher adsorption. S. Wan et al. have shown that manganese oxides can trapped metal ions, specifically Pb(II) and Cd(II) ions, by electrostatic forces and formation of inner-sphere complexes,⁷⁵ rendered it an efficient material for the removal of metal ions in the aqueous medium.

The comparative study on the performance obtained during the interaction of oxides with Pb(II) and Cd(II) (Figure S2) showed that the Na-MnO₂ material had a significant affinity for (Cd(II) and Pb(II)) removal in an aqueous medium. On the other hand, the Urchin-MnO₂ and Cocoon-MnO₂ materials had more affinity for Pb(II) than Cd(II). Several parameters can explain the difference between the yields recorded for Cd(II) and Pb(II). When the lamellar materials (Na-MnO₂) interacted with the Pb(II) and Cd(II) ions, the Pb(II) ions occupied the inter-layer MnO₆ and surface sites,⁷⁶ while the Cd(II) mainly occupied the sites above and below the octahedrons of MnO₆.^{65,77} The removal efficiency for each metal ion depended strongly on its hydrolysis constant. Indeed, this elimination capacity increased with the hydrolysis constants⁷⁸ of Pb(II) and Cd(II), which were respectively $10^{-7.7}$ and $10^{-10.1}$. The cationic exchange was better at low pK value.⁷⁹ The pH of the medium studied (pH = 6.5) was less

than the pK of Pb(II) and Cd(II) (7.7 and 10.1), indicating that the hydroxylation cations were formed by hydrolysis induced by the surfaces of the manganese oxide.⁸⁰ The metal valency, as well as its hydrated radius ($r_{\text{hydrated}} = r_{\text{ion}} + 2r_{\text{H}_2\text{O}}$ with $r_{\text{H}_2\text{O}} = 0.138 \text{ nm}$) was also an important parameter in adsorption phenomenon.⁵⁹ Indeed, the higher the valency of the cation, the higher the affinity of the material towards this cation. For equal valence, the cations with a high volume that will be fixed first (Pb(II) ($1.19 \text{ \AA}$) > Cd(II) ($0.95 \text{ \AA}$)).

4. 2. Effect of pH on the Removal Efficiency of Heavy Metals

To investigate the effect of pH on the removal efficiency of metal ions by different materials, the adsorption of Pb(II) or Cd(II) ions was studied in the pH range of 2.0 to 9.0. The evolution of removal efficiencies of Pb(II) and Cd(II) pH solution after 30 min interaction were shown in Figure 5.

For the different materials, the removal percentages of the two metal ions were favored by the increase in pH from 2.0 to 9.0. This behavior may be explained by the increase in the number of negatively charged sites on the surface of the materials, which promoted the diffusion process of the metal ions and thus facilitated their removal by the different types of manganese oxide material. At lower pH values (pH = 2), the lamellar material maintained its adsorptive power with yields of 83% and 71% in the case of Pb(II) and Cd(II) respectively. The slight decrease in removal efficiencies of Pb(II) and Cd(II) ions by the different materials may be due to the effect of competition between H⁺ ions and metal ions.⁸¹ The highest removal > 94% in the case of Pb(II) was recorded at pH = 6.5. In the case of Cd(II) and above this pH, the highest efficiencies were achieved with the lamellar material Na-MnO₂ with a value

Figure 5. Effect of pH on the removal efficiency of metal ions by manganese oxide materials.

of 97%. In comparison, the two nanostructured materials recorded efficiencies of 56% and 81% for Urchin-MnO₂ and Cocoon-MnO₂, respectively. At values of pH $\geq$ 6.5, the removal efficiencies of metal ions were increased and remained almost stable up to pH = 9, which reflected the effect that under alkaline conditions, the concentration of H⁺ protons was changed and the material, therefore, maintained its performance and removal capacity. In addition to these pH values, the two phenomena of adsorption and precipitation could be the predominant mechanisms for removing the two metal ions.⁸¹ In effect, the further treatment during this study was carried out at a free pH (6.5).

4. 3. Study of Manganese Oxides Stability During Interaction with Metal Cations

During metal ion removal processes, manganese oxides could release manganese ions. To evaluate the manganese oxides stability, it was necessary to determine the Mn released by the different materials at different pH solutions. Figure 6 showed the percentages of manganese released in the case of interaction between the different materials and two metal ions Pb(II) and Cd(II).

From Figure 6, we noticed that during the removal of the two metal ions, the percentages of Mn released decreased with the pH increased from 2.0 to 9.0. At acidic pH values (2.0–4.0), the materials released more manganese. This release was probably due to the dissolution of manganese ions during the removal of metal ions. In pH $\geq$ 6.5, the manganese released by materials during interaction with Pb(II) and Cd(II) was low or even negligible. These results showed very high stability of the materials in neutral and alkaline pH. The greatest stability was recorded for the Na-MnO₂ lamellar material. For example, at pH = 6.5, in the case of Na-MnO₂ lamellar material, the percentages of manganese released were very weak (0.013% (0.123 mmol/Kg) and 0.31% (2.822 mmol/Kg) during Pb(II) and Cd(II)

adsorption respectively). The Urchin-MnO₂ material released a very small amount of 0.93% (4.034 mmol/Kg) of the total manganese during Pb(II) removal, whereas in the case of cadmium, a release rate of 6.08% (26.422 mmol/Kg) was recorded. The highest amount of released manganese was obtained in the case of the Cocoon-MnO₂ material (6.3% (66.787 mmol/Kg) during the removal of Pb(II) and 7.09% (75.22 mmol/Kg) during the removal of Cd(II)). The results obtained showed that for the two nanostructures Urchin-MnO₂ and Cocoon-MnO₂ that the maximum amount of total manganese released decreased with increasing Mn AOS⁴⁷ (Mn AOS: Urchin-MnO₂ (3.730) > Cocoon-MnO₂ (3.650)).

This study indicated that manganese oxide materials presented high stability. The high stability of these materials was strongly due to the stabilizing power and binding strength of the Na⁺ and K⁺ cations present in the structure of the three materials.⁸² The best stability among the different structures was recorded in the case of the lamellar structure (Na-MnO₂), which presented a very low amount of the manganese release. This result confirmed that the use of Na-MnO₂ material with a lamellar structure compared to nanostructures responded to several requirements such as fast elimination kinetics and high reactivity to both heavy metals and also the factors of stability. This parameter is an essential factor in the use of materials in the form of the adsorbent. Na-MnO₂ material can be used in more advanced applications and more precisely in the industrial sector for the treatment of contaminated waste by heavy metals.

4. 4. Adsorption Kinetics

The sorption kinetics of Pb(II) and Cd(II) on manganese oxide materials was evaluated, and the results were shown in Figure 7. The adsorption equilibrium was achieved within 30 min. The kinetics data were fitted according to pseudo-first order (Eq. (4)) and pseudo-second

Figure 6. Percentages of manganese released by manganese oxides during interaction with Pb(II) and Cd(II) at different pH solution.

order (Eq. (5)) equations. The adsorbed quantities q_{exp} , the order of the constants K and regression coefficients R^2 were shown in Table S2.

$$\ln(q_e - q_t) = -Kt + \ln(q_e) \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{(k \times q_e^2)} + \left(\frac{1}{q_e}\right)t \quad (5)$$

With:

$q_e(\text{mg/g})$ and $q_t(\text{mg/g})$ were the adsorbed quantities of Pb(II) or Cd(II) at equilibrium and time t (min).

K : rate constant of the pseudo-first order model (min^{-1}).

k : rate constant of the pseudo-second order model ($\text{mg.g}^{-1}.\text{min}^{-1}$).

Figure 7 and Table S2 showed that the second-order R^2 values are very high and were all higher than those ob-

tained with the pseudo-first order model. The quantities fixed at equilibrium q_e were closed to the values obtained experimentally for the two metals. The adsorption process of Pb(II) and Cd(II) followed the pseudo-second order model. This model suggested the existence of chemisorption with the formation of a monomolecular layer.⁸³ In fact, the pseudo-second order constant (K) gave an idea of the affinity of the material towards metal ions.⁷⁷ Based on the results shown in Table S2, we could deduce that the three materials used have a higher affinity for Pb(II) than for Cd(II).

4. 5. Influence of the Initial Concentration of Metal Ions on the Removal Efficiency of Manganese Oxides

The influence of the initial concentration of metal ions on manganese oxide removal efficiencies was carried

Figure 7. Adsorption kinetic diagram of (a) Pb(II) and (b) Cd(II) on Na-MnO₂, Urchin-MnO₂ and Cocoon-MnO₂.

Figure 8. Influence of the initial concentration of metal ions on the removal efficiencies of Pb(II) and Cd(II) by manganese oxides.

out with different metal ion concentrations ranging from 30 to 800 ppm for 30 minutes of interaction. The results obtained were shown in Figure 8.

The examination of Figure 8 showed an increase in the removal efficiency of metal cations with increasing concentration. High removal capacities were recorded for Pb(II) for all three materials due to their high affinity toward this metal. For an initial concentration of 800 ppm of Pb(II), Urchin-MnO₂ and Cocoon-MnO₂ materials were able to absorb 160 mg/g, while Na-MnO₂ adsorbed a larger amount of 190 mg/g. For the same initial concentration of Cd(II), the three materials removed an amount ranging from 140 to 160 mg/g with the highest amount recorded for Na-MnO₂.

4. 6. Isotherm Models

In this study, the adsorption equilibrium was modeled using three mathematical laws Langmuir, Freundlich, and Temkin, which represented the equilibrium relationship between the amount of metal cation in the liquid phase (C_e) and that adsorbed on the material (q_e).

Adsorption studies were conducted for 30 minutes at different initial concentrations of Pb(II) and Cd(II) metal ions and 100 mg of the material. The isotherms were given in Figure S3. The following equations represented the models of each isotherm applied in this study:

$$\text{Langmuir isotherm: } \frac{C_e}{q_e} = \left(\frac{1}{b \times q_m} \right) + C_e \left(\frac{1}{q_m} \right) \quad (6)$$

$$\text{Freundlich isotherm: } \log q_e = \log K_F + \frac{1}{n} (\log C_e) \quad (7)$$

$$\text{Temkin isotherm: } q_e = \left(\frac{RT}{b_T} \right) \ln K_T + \left(\frac{RT}{b_T} \right) \ln C_e \quad (8)$$

For the Langmuir isotherm, another parameter could also be expressed as a constant representing the separation factor defined by Eq. (9).

$$R_L = \frac{1}{1 + b \times C_0} \quad (9)$$

A separation factor $R_L > 1$ indicated that the adsorption was unfavorable, if $R_L = 1$ the adsorption was described as linear, the adsorption was considered to be favorable when $0 < R_L < 1$ and a zero separation factor ($R_L = 0$) indicated that the adsorption was irreversible.⁸⁴

With:

C_e : the equilibrium concentration of substrates in the solution (mg/L).

q_e : the adsorption capacity at equilibrium (mg/g).

q_m : the maximum amount of adsorption (mg/g).

b : the adsorption equilibrium constant (L/mg).

K_F : a constant representing the adsorption capacity.

n : the constant showing the adsorption intensity.

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

T : absolute temperature in (K), K_T : Temkin constant in (L mg⁻¹).

C_0 : the initial concentration of the adsorbate (mg L⁻¹).

Figure S3 showed the most appropriate isotherms for the three materials Na-MnO₂, Urchin-MnO₂, and Cocoon-MnO₂. In table S3 all parameters of the isotherms for the two metals were given. After studying the isothermal adsorption of Pb(II) and Cd(II) ions by manganese oxides,

Table 3. Comparison of Pb(II) and Cd(II) adsorption capacities of Na-MnO₂, Urchin-MnO₂, Cocoon-MnO₂ and other reported adsorbents.

Sorbent	Adsorption capacity (mg/g)	Conditions	References
Pb(II)			
K-Birnessite	164.30	pH = 5, T° = 25 °C	85
Al ₂ O ₃ -supported iron oxide	28.98	pH = 5, T° = 27 °C	86
Fe ₃ O ₄ nanoparticles	83		87
TiO ₂ nanoparticles	159	pH = 7, T° = 25 °C	
Cocoon-MnO ₂	209		
Urchin-MnO ₂	264	pH = 6.5, T° = 25 °C	<i>This study</i>
Na-MnO ₂	297		
Cd(II)			
Birnessite	34	pH = 7, T° = 25 °C	88
Synthetic zeolites	50.8	pH = 6, T° = 25 °C	89
Activated carbon cloth	146	pH = 6, T° = 25 °C	90
Cocoon-MnO ₂	172		
Urchin-MnO ₂	191	pH = 6.5, T° = 25 °C	<i>This study</i>
Na-MnO ₂	199		

it could be seen that the best description of the adsorption phenomenon was obtained with the Langmuir model with a high correlation coefficient R^2 (Table S3). This applied model allowed us to determine the maximum adsorption quantity q_m (mg/g) for all materials interacting with the two metal cations (Table S3). For Pb(II), the maximum quantities adsorbed were 297 mg/g (Na-MnO₂), 264 mg/g (Urchin-MnO₂), and 209 mg/g for the material Cocoon-MnO₂. For Cd(II), the adsorbed quantities were 199 mg/g (Na-MnO₂), 191 mg/g (Urchin-MnO₂), and 172 mg/g (Cocoon-MnO₂). In addition, the developed lamellar materials and nanostructures had shown a high adsorption capacity compared to other types of adsorbents (Table 3).

The description of the adsorption of Pb(II) and Cd(II) by the Langmuir model that the adsorption of these ions by the materials was done by the formation of a monolayer on the external surface of the adsorbent. Thus, this concordance could be explained by the homogeneity of the adsorption sites on the surface of these materials. Indeed, during the interaction, there would be a direct contact of metal ions on the surface of the materials up to the coverage of the monolayer. Based on the calculated R_L values, all values were between 0 and 1, indicating favorable adsorption.

In the structure of synthesized manganese oxides of the birnessite type (A_xMnO₂·zH₂O) (with A = Na⁺ (case: Na-MnO₂)), either Na⁺ and H⁺ ⁹¹ or Mn²⁺, two proton or (Mn(III)OH)²⁺ were located on each side of a vacant cationic site to obtain local charge balance of material.⁴⁷ The analysis of sodium (Na⁺) in solution during the removal of Cd(II) and Pb(II) confirmed this hypothesis. The result indicated that Na-MnO₂ material released a quantity of Na⁺ ions during removal processes (Figure S4).

As shown in X-ray diffractogram, the two materials Urchin-MnO₂ (KMn₈O₁₆) and Cocoon-MnO₂ (K₂Mn₄O₉) had two different structures, with K⁺ ions inserted into their cavities. The removal of Cd(II) and Pb(II) occurred by exchanging K⁺ from the tunnel site and also on the external surface of the materials.⁹² The exchange between the metal ions and the K⁺ caused it to be released into the solution during the metal removal process (Figure S5).

5. Analysis of the Adsorption Mechanism

5.1. X-ray Diffraction

The characterization by X-ray diffraction of the materials after interaction with metallic cations was important to determine the totality of structures formed. The diffractograms before and after interaction with Pb(II) and Cd(II) were illustrated in Figure 9.

After the interaction of the manganese oxide materials with Pb(II) and Cd(II), the diffractograms of each material were not similar. The peaks obtained from each material were analyzed to determine the phases formed. The crystallographic parameters of each phase were represented in Table 4.

In the case of Na-MnO₂, after interaction with Pb(II) and Cd(II), a slight decrease in the intensity of some peaks occurred. The identification of the phases formed made it possible to determine the MnO₂ manganese oxide phase and the appearance of new PbO phases observed at $2\theta = 30.66^\circ$ (110), 64.40° (002) and for the Cd(OH)₂ phase was indexed in two peaks located at $2\theta = 50^\circ$ (231), 53.64° (002) indicating that the Pb(II) and Cd(II) ions had been inserted into the material. The iden-

Figure 9. X-ray diffractograms of manganese oxides before and after interaction with (a) Pb(II) and (b) Cd(II).

Table 4. Crystallographic parameters of the structures formed after interaction of Pb(II) and Cd(II) ions with the materials.

	Phases formed	Mesh parameter (Å)	Crystal system
Na-MnO₂ (Before interaction)	Na _{0.55} Mn ₂ O ₄ ·(H ₂ O) _{1.5} (Birnessite)	a = 5.1750 b = 2.8490 c = 7.3380	Monoclinic
Na-MnO₂ (After interaction: Pb(II))	PbO	a = 3.9744 b = 3.9744 c = 5.0220	Tetragonal
	Na _{0.55} Mn ₂ O ₄ ·(H ₂ O) _{1.5} (Birnessite)	a = 5.1750 b = 2.8490 c = 7.3380	Monoclinic
Na-MnO₂ (After interaction: Cd(II))	Cd(OH) ₂	a = 5.6700 b = 10.2500 c = 3.4100	Monoclinic
	Na _{0.55} Mn ₂ O ₄ ·(H ₂ O) _{1.5} (Birnessite)	a = 5.1750 b = 2.8490 c = 7.3380	Monoclinic
Urchin-MnO₂ (Before interaction)	KMn ₈ O ₁₆ (Cryptomelane)	a = b = 9.840 c = 2.850	Tetragonal
Urchin-MnO₂ (After interaction: Pb(II))	Pb ₂ Mn ₈ O ₁₆	a = b = 9.8900 c = 2.8620	Tetragonal
	KMn ₈ O ₁₆ (Cryptomelane)	a = b = 9.840 c = 2.850	Tetragonal
Urchin-MnO₂ (After interaction: Cd(II))	Cd(OH) ₂	a = 5.6700 b = 10.2500 c = 3.4100	Monoclinic
	KMn ₈ O ₁₆ (Cryptomelane)	a = b = 9.840 c = 2.850	Tetragonal
Cocoon-MnO₂ (Before interaction)	K ₂ Mn ₄ O ₉	a = b = 11.2950 c = 21.870	Hexagonal
Urchin-MnO₂ (After interaction: Cd(II))	Pb ₂ MnO ₄	a = b = 12.7700 c = 5.1300	Tetragonal
	K ₂ Mn ₄ O ₉	a = b = 11.2950 c = 21.870	Hexagonal
Cocoon-MnO₂ (After interaction: Cd(II))	Cd(OH) ₂	a = 5.6700 b = 10.2500 c = 3.4100	Monoclinic
	K ₂ Mn ₄ O ₉	a = b = 11.2950 c = 21.870	Hexagonal

tification of the phases formed for the nanostructured material Urchin-MnO₂ after interaction with Pb(II) ions (Figure 9 a) and Cd(II) ions (Figure 9 b), showed the existence of the characteristic phase (KMn₈O₁₆) of Urchin-MnO₂ with the occurrence of Pb₂Mn₈O₁₆ and Cd(OH)₂ (Table 4). For Cocoon-MnO₂, the characteristic phase of this material still existed with the formation of the Pb₂MnO₄ phase (Table 4) in the case of interaction with Pb(II) ions (Figure 9 a) and Cd(OH)₂ in the case of

Cd(II) (Figure 9 b). All diffractograms of the materials after interaction showed that the intensity of some peaks decreased while others disappeared. This deformation was due to the insertion of metal cations in the vacant octahedral sites and in the interlayer space between the MnO₆ layers (case of Na-MnO₂) or in the cavities (case of Urchin-MnO₂ and Cocoon-MnO₂) which created a disorder in the materials.²⁷ Based on the results obtained, it could be said that the removal of metal ions after interac-

tion with the materials was achieved either by insertion as MO oxide (PbO) or by adsorption as $M(OH)_2$ hydroxide ($Cd(OH)_2$) or by the formation of new phases such as Pb_2MnO_4 and $Pb_2Mn_8O_{16}$. As shown, subsequent studies reported that the analysis of materials after interaction with Cd(II) ions by X-ray photoelectron spectroscopy (XPS) showed that Cd(II) was adsorbed on MnO_2 as CdO and $Cd(OH)_2$.²⁷

6. Stability and Reusability of the Na-MnO₂

In this study, the lamellar material Na-MnO₂ showed the highest removal efficiency of metal ions at different pH values, a high removal capacity as well as a very high stability compared to nanostructured materials. In this context, the reusability of this material for the removal of Pb(II) and Cd(II) ions was studied. Five successive adsorption cycles were investigated. After each cycle, the nanomaterial Na-MnO₂ was recovered by filtration, washed with water and dried, it was used in the subsequent cycle. As shown in Figure 10, the nanomaterial Na-MnO₂ could remove 97.26% Pb(II) and 97.44% Cd(II) in the initial cycle. A gradual decrease in removal efficiencies from 97.26% to 78.05% and 97.44% to 69% were observed after five reuses for Pb(II) and Cd(II) respectively. It was clear that the reusable capability of the nanomaterial Na-MnO₂ decreased slightly with an increase in the number of cycles. But in general, Na-MnO₂ was maintained at a relatively high removal efficiency.

The slight decrease in heavy metal removal efficiency could be due to the dissolution or release of a low concentration of manganese ions and the change in morphology of the material by reducing its available active sites. Simul-

taneously, AAS was employed to measure Mn concentration in the solution after each cycle (Figure 10, black line). Therefore, after 5 cycles of use the percentage of Mn released from the material was less than 0.1% and 0.48% in the case of Pb(II) and Cd(II) respectively, indicating good stability of Na-MnO₂.

7. Conclusions

XRD and SEM analysis showed that the prepared manganese oxides: Na-MnO₂, Urchin-MnO₂, and Cocoon-MnO₂ were composed of a monophase characteristic of each structure elaborated, these oxides had particular morphologies. Studies of adsorption/desorption of N₂ of the materials showed that their structures were composed of a mixture of pores with a predominance of mesopores of more than 53% of the total porous surface. This study showed that structure and morphology had a direct effect on the elimination of metal cations Pb(II) and Cd(II). All materials (lamellar: Na-MnO₂ and nanostructures: Urchin-MnO₂ and Cocoon-MnO₂) showed a high reactivity towards both metals with a high yield of more than 90% for a very short duration (less than 15 minutes) at free pH (6.5). These materials also demonstrated high stability during the removal process. In the case of the Na-MnO₂ lamellar material, the removal efficiency of metal cations was very high above 99%, and the release rates of manganese were lower than 0.4%. The reusability of the lamellar material Na-MnO₂ showed that it could be used more than 5 cycles without loss of performance and stability. The lamellar material Na-MnO₂ was very efficient, had a high removal capacity was very stable and suitable for several uses for the removal of metal ions.

Figure 10. Stability and reusability of Na-MnO₂ to remove Pb(II) and Cd(II) (Conditions: initial concentration of metal ions= 30 ppm, t = 30 min for each cycle).

Supporting Information

The equation (S1), pore size distributions of three MnO₂ (lamellar and nanostructures), comparative study of Cd(II) and Pb(II) removal efficiencies. Langmuir isotherm plot for Pb(II) and Cd(II) adsorption, Amount of Na⁺ released during the removal of Pb(II), and Cd(II) ions by Na-MnO₂. Amount of K⁺ released during the removal of Pb(II) and Cd(II) ions by Urchin-MnO₂ and Cocoon-MnO₂. Porous structure parameters of each material, Adsorption coefficients of Pb(II) and Cd(II) of the pseudo-first-order and pseudo-second-order models. Isotherm parameters for Langmuir, Freundlich, and Temkin models.

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Conflicts of Interest

The authors declare no conflict of interest.

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Povzetek

Z netoksičnimi metodami smo sintetizirali lamelarne in nanostrukturirane manganove okside. Materiali so bili enofazni z značilnimi morfologijami in pretežno mezoporozno strukturo. Preučevali smo možnosti odstranjevanja težkih kovin Cd(II) in Pb(II) s sintetiziranimi materiali Na-MnO₂, u-MnO₂ (v obliki morskih ježkov) in c-MnO₂ (v obliki zapredkov). Z vidika kinetike je bil najučinkovitejši od treh preizkušenih materialov lamelarni Na-MnO₂ ki ima več praznin v plasteh MnO₆ kot tudi med posameznimi plastmi. Nanomateriala u-MnO₂ in c-MnO₂ sta izmenjevala katione v tunelih in vdolbinah. Maksimalne adsorbirane količine so si sledile za Pb(II): Na-MnO₂ (297 mg/g) > u-MnO₂ (264 mg/g) > c-MnO₂ (209 mg/g) in za Cd(II): Na-MnO₂ (199 mg/g) > u-MnO₂ (191 mg/g) > c-MnO₂ (172 mg/g). Na-MnO₂ je izkazoval najboljšo stabilnost med strukturami in sproščal le male količine mangana. Rezultati kažejo potencial lamelarnih (Na-MnO₂) in nanostrukturiranih (U-MnO₂ in C-MnO₂) manganovih oksidov kot selektivnih, ekonomičnih in stabilnih materialov za odstranjevanje toksičnih kovin v vodnem mediju.

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