ADSORPTION OF Pb(II), Co(II) AND Cu(II) FROM AQUEOUS SOLUTION ONTO MANGANESE DIOXIDE (γ - MNO_2) NANOSTRUCTURE. I- Synthesis of γ -MnO_2 nanostructure and its adsorption to Pb^{2+}, Cu^{2+} and Co^{2+}

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SUMMARY

HẤP PHỤ Pb(II), Co(II) VÀ Cu(II) TỪ DUNG DỊCH NƯỚC BỞI MANGANESE DIOXIDE (γ - MnO_2) CẤU TRÚC NANO I- Tổng hợp MnO_2 và sự hấp phụ của MnO_2 đối với các ion Pb^{2+}, Cu^{2+} và Co^{2+}

Manganese dioxide (MnO_2) được tổng hợp bởi phản ứng oxy hóa-khử giữa $KMnO_4$ và C_2H_5OH tại nhiệt độ phòng. Bằng các phương pháp XRD, SEM, TEM và BET cho thấy manganese dioxide tổng hợp được có dạng γ - MnO_2 với kích thước vào khoảng 10 – 18 nm và diện tích bề mặt khoảng 65 m^2/g. Manganese dioxide (γ - MnO_2) được sử dụng như chất hấp phụ để hấp thu Pb(II), Co(II) và Cu(II) từ dung dịch nước. Bằng phương pháp phân đoạn tại nhiệt độ phòng (t~24^oC), các yếu tố ảnh hưởng đến sự hấp phụ Pb(II), Co(II) và Cu(II) đã được khảo sát như ảnh hưởng nồng độ đầu của các ion kim lọai, thời gian tiếp xúc và pH.

Keywords: *Manganese dioxide (γ - MnO_2), nanostructure, nanospheres, XRD, SEM, TEM and BET.*

1. INTRODUCTION

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment[1-3]. These pollutants enter the water bodies through wastewater from metal plating industries, batteries, phosphate fertilizer, mining, pigments and stabilizers alloys[1-7].

Various treatment techniques have been applied to remove metal ions from contaminated waters such as chemical precipitation, adsorption and ionic exchange, membrane technology and solvent extraction[4-7]. Adsorption technology is considered as one of the most efficient and promising methods for the treatment of trace amount of heavy metal ions from large volumes of water because of its high enrichment efficiency, and the ease of phase separation[4-10].

Recently, the adsorption properties of nanostructured metal oxides have been applied for environment pollution removal. Because of their huger specific surface area and many unsaturated atoms on surface, the adsorbability of nanomaterials to metal ions was very strong. Nanostrucrured manganese oxides have attracted increasing attention in view of their applications in batteries, molecular sieves, catalysts, and adsorbents [8-10].

In this study, we reported a simple method to synthesize MnO_2 nanostructure which was used as a low cost adsorbent for the adsorption of Pb(II), Co(II) and Cu(II) from aqueous solutions.

2. EXPERIMENTAL

2.1. Chemicals and Instruments

- Chemicals

Potassium permanganate ($KMnO_4$), ethyl alcohol (C_2H_5OH), $Pb(NO_3)_2$, $Cu(NO_3)_2.3H_2O$ and $Co(NO_3)_2.6H_2O$, HNO_3 and NaOH. All reagents used in the experiment were of analytical grade and pure of Merck.

Pb(II), Cu(II), and Co(II) were used as adsorbate. 1000 mg/l standard stock solution of each metal ions were prepared by dissolving $Pb(NO_3)_2$, $Cu(NO_3)_2.3H_2O$ and $Co(NO_3)_2.6H_2O$ respectively in distilled water. The concentration of metal ions in the aqueous solutions was analyzed by using AA-7000 atomic absorption spectrometer (Shimadzu Corporation).

- Instruments

X-ray Diffractometer D5000 made in Germany by Siemens with X-ray radiation: CuKα, λ = 1,54056 Å; Ultra High Resolution Scanning Electron Microscopy S – 4800; Transmission electron microscope; Physical absorption system Micrometrics Gemini VII.

Atomic Absorption Spectrophotometer (Spectrometer Atomic Absorption AA – 7000 made in Japan by Shimadzu.)

The pH measurements were done with a pH-meter (MARTINI Instruments Mi-150 Romania); the pH-meter was standardized using HANNA instruments buffer solutions with pH values of 4.01±0.01, 7.01±0.01, and 10.01±0.01.

Temperature-controlled shaker (Model KIKA R 5) was used for equilibrium studies.

2.2. Synthesis of MnO_2 nanostructure

MnO_2 nanostructure was synthesized via the reduction – oxidation between

$KMnO_4$ and C_2H_5OH at room temperature for 4h by adding gradually $KMnO_4$ saturated solution to the mixture of C_2H_5OH and H_2O. The effect of reaction time as well as the ratio between H_2O and C_2H_5OH to the structure and size of crystal was studied. After the reaction was completed, the solid precipitate was washed with distilled water, and then dried at 80^0C for 12h to get the product.

Characterization of the products: Phase identification was carried out by X-ray diffraction. The surface morphology of the samples was monitored with SEM and transmission electron microscope. The specific surface area was evaluated by nitrogen adsorption–desorption isotherm measurements at 77 K.

2.3. Adsorption study

Adsorption experiment was prepared by adding 0.1 g MnO_2 to 50 mL heavy metal ion solution in a 100 mL conical flask. Effect of pH of the initial solution was analyzed over a pH ranges from 2 to 6 using HNO_3 0.1M or NaOH 0.1M solutions. The adsorption studies were also conducted in batch experiments as function of contact time (20, 40, 60, 80, 100, 120, 150, 180, 210, 240 minute) and metal ions concentration (from 100 mg/L to 500 mg/L) for maximum adsorption. Atomic Absorption Spectrophotometer (Spectrometer Atomic Absorption AA – 7000) was used to analyze the concentrations of the different metal ion in the filtrate before and after adsorbent process.

Adsorption capacity was calculated by using the mass balance equation for the adsorbent [10-12]:

$$q = \frac{(C_o - C_e).V}{m}$$

where q is the adsorption capacity (mg/g) at equilibrium, Co and Ce are the initial concentration and the equilibrium concentration (mg/L), respectively. V is the volume (mL) of solution and m is the mass (g) of adsorbent used.

3. RESULTS AND DISCUSSION

3.1. Characterization of manganese dioxide

The phase and purity of the products were firstly examined by XRD. Fig. 1 shows a typical XRD pattern of the as – synthesized samples. Curves (a) and (b) are the XRD patterns of the two products obtained for 3h and 4h. Curves (c) and (d) are the XRD patterns of the two products btained for 5h and 6h, respectively. All reflection peaks can be readily indexed to Hexagonal γ - MnO_2 phase. However, the as – prepared sample achieved clearly crystal structure for 5h.

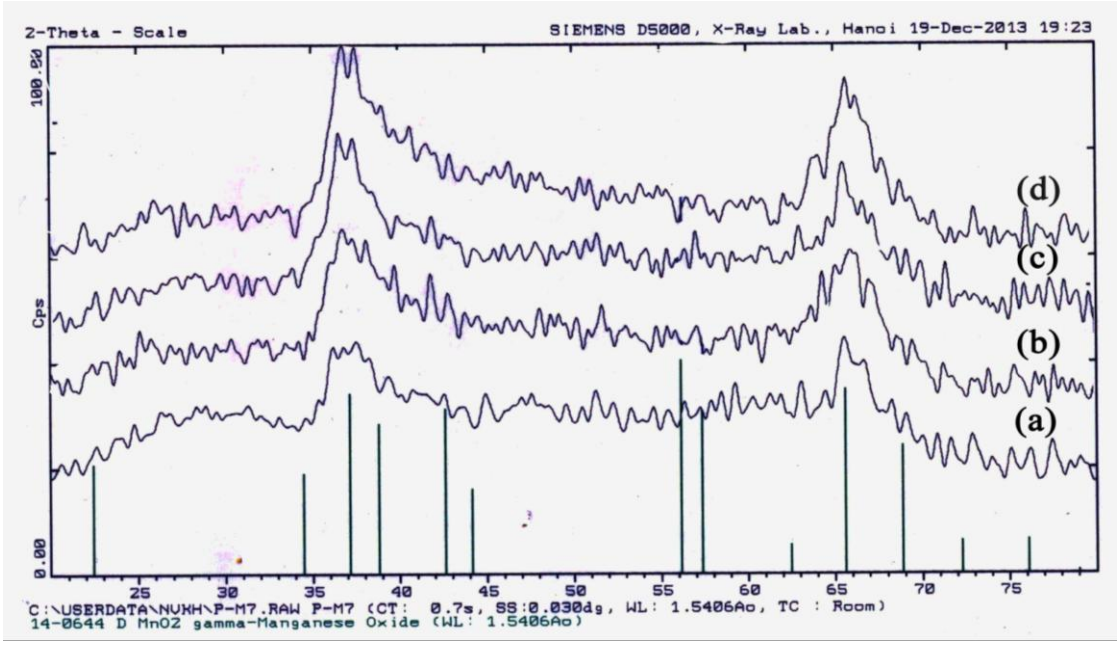
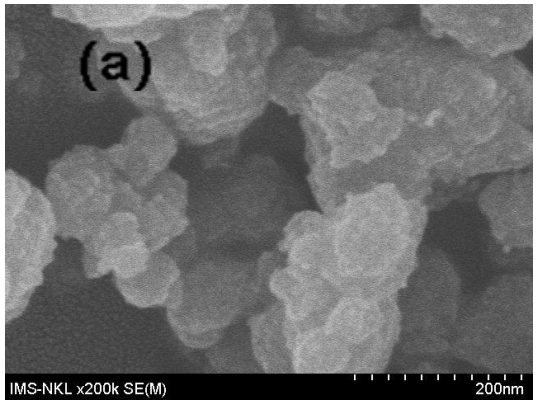


Fig. 1. XRD image of prepared sample (γ - MnO_2) at different shaking speed: (a) at 480 rpm, (b) at 600 rpm, (c) at 720 rpm, (d) at 840 rpm.

The morphologies and structure information were further obtained from SEM and TEM images. Fig 2a, 2b and 2c showed SEM image of the as – prepared γ - MnO_2 which was synthesized at the different ration between H_2O and C_2H_5OH: (a) H_2O : C_2H_5OH = 2:1 (sample M1), (b) H_2O : C_2H_5OH = 1:1 (sample M2), (c) H_2O : C_2H_5OH = 1:2 (sample M3). As a results, γ - MnO_2 nanospheres with nanostructure were formed in the alcohol ($KMnO_4$: C_2H_5OH = 1:2). It is clear that the flocculation occurred in the water solution (Fig 2a). The Fig 2c also shows that the products of γ - MnO_2 consisted of a large amount of uniform nanospheres, with size of about 10 nm. Fig. 2d shows the TEM image of the as – prepared γ - MnO_2 nanospheres (sample M3) and the TEM image further demonstrate that the obtained product has a uniform sphere morphology. The TEM image also provides the size of γ - MnO_2 nanospheres from 10 to 18 nm. The BET surface area of the as – synthesized product (sample M3) was determined to be about 65 $m^2.g^{-1}$.



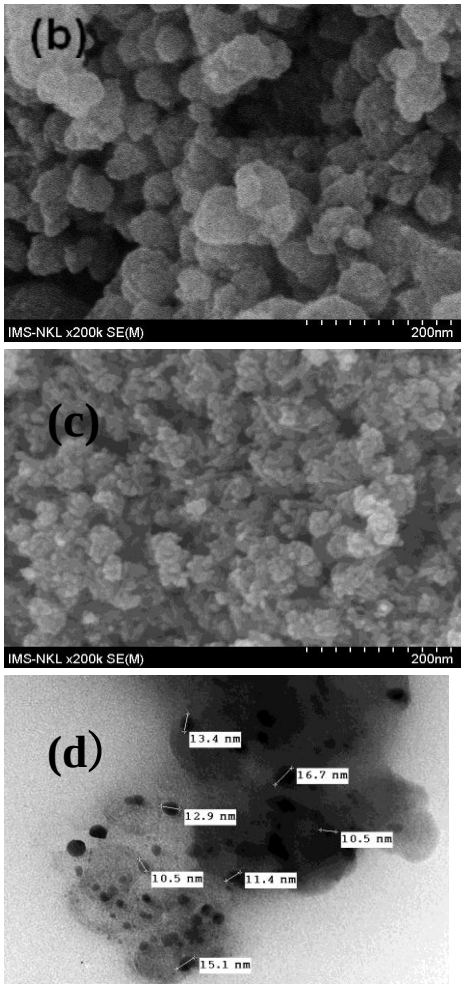


Fig. 2. (a), (b), (c) - SEM image of γ - MnO_2 at the different ration between H_2O: C_2H_5OH
(a) sample M1, (b) sample M2,
(c) sample M3;
(d)- TEM image of γ - MnO_2 sample.

3.2. Effect of pH on adsorption of heavy metals

The pH is one of the imperative factors governing the adsorption of the metal ions. The effect of pH was studied from a range of 2 to 6 under the precise conditions (at optimum contact time of 120 min, 240 rpm shaking speed, with 0,1g of the adsorbents used, and at a room temperature of 24^0C). From figure - 3, with γ - MnO_2 used as adsorbent, it was observed that with increase in the pH (2 - 6) of the aqueous solution, the adsorption percentage of metal ions (lead, cobalt and copper) all increased up to the pH 4 as shown above. At pH 4, the maximum adsorption was obtained for all the three metal ions, with 98.9% adsorption of Pb (II), 54.1% of Co(II) and 41.3% adsorption of Cu(II).

The increase in adsorption percentage of the metal ions may be explained by the fact that at higher pH the adsorbent surface is deprotonated and negatively charge; hence attraction between the positively metal cations occurred [12].

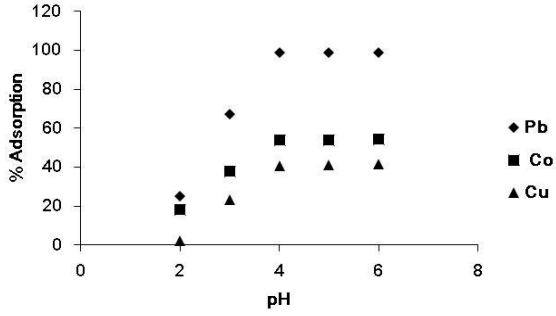


Fig. 3. Effect of pH on the adsorption of heavy metals by γ - MnO_2 nanostructure (Time = 120 min, agitation speed = 240 rpm, Mass = 0.1 g and Temp = 24^0C)

3.3. Effect of contact time on adsorption of heavy metals

The relationship between contact time and the adsorption percentage of heavy metals from aqueous solution with γ - MnO_2 adsorbent is shown in figure - 4. The effect of contact time was studied at a room temperature of 24^0C, at intervals of 20 min. From the obtained result, it is evident that the adsorption of metal ions increased as contact time increases. The adsorption percentage of metal ions approached equilibrium within 80 min for Pb (II), 120 min for Co (II) and 180 min for Cu(II); with Pb (II) recording 92.47% adsorption, Co (II) 81.51% and Cu(II) 89.24% adsorption. This experiment shows that the different metal ions attained equilibrium at different times.

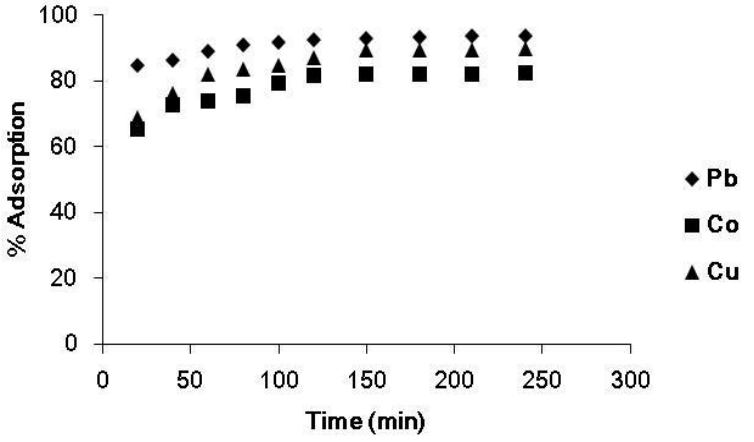


Fig. 4. Effect of contact time on adsorption of heavy metals by γ - MnO_2 nanostructure (pH = 4, agitation speed = 240 rpm, Mass = 0.1 g and Temp = 24^0C)

The results of adsorption performance were shown that the pH of aqueous solution, adsorption time have a great influence on the adsorption performance.

4. CONCLUSION

Manganese dioxide γ - MnO_2 was successfully synthesized via the reduction–oxidation reaction between $KMnO_4$ and C_2H_5OH at room temperature. The results showed that γ - MnO_2 was about 10 – 18 nm in size and the BET surface area was about 65 m^2/g. The feasibility of γ - MnO_2 used as a low cost adsorbent for the adsorption of Pb(II), Co(II) and Cu(II) from aqueous solutions

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