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ADSORPTION OF GASEOUS SUBSTANCES ON CHEMICAL AND ELECTROLYTIC MANGANESE DIOXIDE

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ABSTRACT *The adsorption of mercury , arsine, hydrocyanic acid and hydrogen sulfide on amorphous chemical manganese dioxide (CMD) and electrolytic manganese dioxide (EMD) has been investigated. Variables such as agitation time, pH, temperature, mass of adsorbent and concentration of adsorbate were studied. The adsorption process obeys a Freundlich type isotherm over the concentration range investigated. Wads of Luffa cylindrica Roem were used as substrate for CMD production. For gaseous substances this amorphous material showed better sorption capacity than EMD.*

KEY WORDS: manganese dioxide, pollutants, adsorption, isotherms

RESUMO *A adsorção de mercúrio, arsina e dos ácidos cianídrico e sulfídrico sobre o dióxido de manganês amorfo preparado químicamente (CMD) e o dióxido de manganês eletrolítico (EMD) foi estudado. As variáveis investigadas foram: tempo de agitação e de contato, pH, temperatura, massa do adsorvente e concentração do adsorvato. A reação obedece a isoterma de adsorção de Freundlich no intervalo de concentração estudado. Como substrato para a produção do dióxido de manganês utilizou-se aparas da bucha Luffa cylindrica Roem. Nos estudos com substâncias gasosas, este material amorfo mostrou capacidade de adsorção superior ao dióxido de manganês eletrolítico.*

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INTRODUCTION

There is a wide variety of manganese (IV) oxides whose structures have been extensively investigated. Among these oxides, most attention has been focused on electrolytic manganese dioxide for which the electrochemical and catalytic activity behaviour have been investigated[1].

X-ray studies showed that MnO_2 prepared by chemical reaction is amorphous with higher porosity than the electrolytic manganese dioxide[2]. Although progress has been made in the characterization of MnO_2 with respect to structure and electrochemical behavior, some aspects remain unexplained. The reason why certain forms of MnO_2, for instance, the γ modification, are highly reactive and may undergo electrochemical reduction at high rates, while other forms, for instance, the β modification, are relatively inactive, are still not fully understood[3].

One of the potential methods of removing pollutants from aqueous systems is the adsorption on iron, aluminum and manganese oxides.On the surface of manganese dioxide as much as 0.28 mole of lead ion can be adsorbed per mole of Mn(IV) at pH 6 as reported by Laitinen and Gadde[4]. The adsorption process of gaseous pollutants has different mechanisms from the aqueous phase, so that very little information is available for the mercury adsorption[5].

While there is no doubt that hydrous metal oxides are important sinks and modes of transport for heavy metals in the environment, the quantitative magnitude of this role is not known for a variety of natural waters[6].Hydrous oxides in aqueous solutions carry a surface charge which is very pH dependent. The pH of solution relative to the point of zero charge (PZC) affects the counter ion type adsorption of cations and anions. At pH values higher than PZC, cation adsorption is generally favored, whereas anion adsorption is favored by pH values less than PZC. (PZC of manganese dioxide is approximately 2,8)[7].

Manganese dioxide has been used as a sorbent for collection of radionuclides from water samples, collecting a known volume of water through identical MnO_2-impregnated cartridges connected in series[8]. Using this procedure the adsorption efficiency of an element and the activity were calculated. The redox mechanism was observed when two different oxidation states were investigated. After contact with MnO_2 plutonium(III) is oxidized to Pu(IV) and no higher oxidation states were observed[9]. The catalytic oxidation properties of manganese dioxide have also been investigated using organic (n-hexane or n-octane) compounds by gas chromatography.It was observed that doped EMD has a better catalytic activity[10].

The present research focuses upon the adsorption of toxic substances on manganese dioxide. The adsorption of mercury, mercuric ion, hydrogen sulfide, arsine, and hydrocyanic acid have been investigated.

EXPERIMENTAL

Chemicals

The reaction of 0.5 mol.l^{-1} $KMnO_4$ (250 ml) with wads (3.5g) of dry **Luffa cylindrica Roem** , 10 ml of 50% (m/v) of sodium silicate, and 10 ml of 1.5 mol.l^{-1} H_2SO_4 was employed for CMD production. The mixture was transferred to a 1000 ml flask with vigorous shaking and kept at room temperature. After 24 hours, 20 ml of 2 mol.l^{-1} H_2SO_4 were added with strong agitation. The filtration of this black gel like solution was performed using a vaccum pump and washing several times with distilled water.The amorphous CMD produced was dried at 80°C , powdered to 100 mesh,and dried again at 80°C for 2 hours.

Brown granular EMD, sample n° 9, International Common Sample with surface area of $45m^2$ BET was purchased from Trona Chemicals (USA). All solutions were prepared using doubly distilled deionized water. Analytical-reagent grade chemicals were used without further purification.

Procedure:

Figures 1 and 2 show the apparatus used for adsorption studies of hydrogen sulfide, arsine, hydrocyanic acid and mercury on manganese dioxide.

Hydrogen sulfide evolution and adsorption. The following chemicals were added to flask A, and to tubes B and C respectivelly:

A) 10 ml of 12 $mol.l^{-1}$ HCl (Merck) and variable amounts of FeS (ferrous sulfide-technical grade-Aldrich).
B) 0.500 g of Manganese dioxide and pieces of glass wool.
C) 10,0 ml of As(III) solution (996 μg/ml), prepared from As_2O_3 (Aldrich-USA).

After 45 minutes of reaction at room temperature, tube B was disconnected from A, and the filtration of solution in tube C was performed using quantitative filter paper. The remained arsenic(III) in tube C was transferred to an erlenmeyer flask and determined by titration with standard iodine solution according to the procedure of Skoog et al[11] .

Hydrocyanic acid adsorption. The adsorption studies of hydrocyanic acid on MnO_2 was performed using the following chemicals:

A) 10 ml of 6 $mol.l^{-1}$ HCl (Merck) + variable amounts of KCN (Merck).
B) glass wool + 0.500 g of MnO_2.
C) 10 ml of 0.25 $mol.l^{-1}$ NaOH (Reagen).

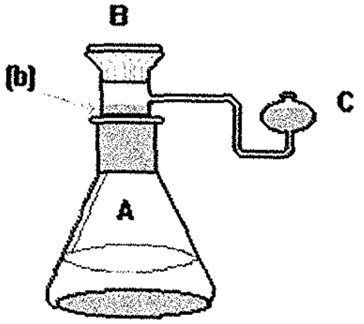
After 75 minutes, tube B was disconnected from A and the HCN concentration in tube C was determined by UV-VIS spectrophotometry with the pyridine and barbituric acid method [12].

Arsine generation and adsorption. The adsorption of AsH_3, generated by reduction of standard As(III) solution with $SnCl_2$ and Zn (powder) in acidic medium, on CMD and EMD were studied with the following chemicals:

A) 5 ml of 12 $mol.l^{-1}$ HCl + 5 ml of 0.01 $mol.l^{-1}$ KIO_3 (Aldrich) + 0.2 ml of 0.001 $mol.l^{-1}$ $SnCl_2$ (Merck). After the initial reduction of As(III), 1.5 g of Zn (powder-Merck) were added into the the flask to AsH_3 generation.
B) 0.500 g MnO_2 + glass wool wetted in 1 $mol.l^{-1}$ lead acetate (Reagen).
C) 10 ml of 0.1 $mol.l^{-1}$ TRIS (tris(hydroxymethyl)aminomethane-Sigma) + 0.5 ml of 0.002 $mol.l^{-1}$ $AgNO_3$ (Aldrich). The arsine after reaction with Ag^+, was determined by differential pulse polarography using a solution of 0.1 $mol.l^{-1}$ TRIS and HCl as supporting electrolyte[13].

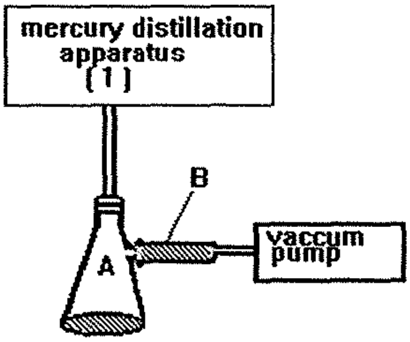
To the polarographic cell containing 2 ml of pure mercury and 10.0 ml of supporting electrolyte, 1.0 ml of sample collected in flask C was added. Deaeration was performed with pure nitrogen for 15 minutes and the polarogram recorded from 0 to -1.6 volts with the following apparatus and conditions: Polarograph (Radelkis-Hungary-OH-107), a platinum wire as reference electrode, scan rate (2 $mV.sec^{-1}$), pulse amplitude (50 $mV.sec^{-1}$), and sensibility of 0.2 μA.

Mercury adsorption. The conventional mercury purification and distillation apparatus was modified for mercury adsorption on MnO_2. A 100 mm length and 10 mm of internal diameter PVC



A = 125 mL flask
[b] = glass wool impregnated with lead acetate
C = solution of TRIS and silver nitrate

Figure 1. Apparatus used for arsine generation



B = 10 cm length and 1 cm internal diameter PVC tube with manganese dioxide
A = 500 mL collecting flask
[1] = conventional mercury distillation apparatus

Figure 2. Apparatus for mercury adsorption

tube was connected between the collecting flask and the vaccum pump (Figure 2). Pieces of dry **Luffa cylindrica Roem** were used at the extremity and the CMD inside the tube was changed every 48 hours of continuous operation. The mercury concentration, after washing the CMD with nitric acid, was determined by cold vapor atomic absorption spectrometry (CVAAS) according to the procedure of Akif et al[14] , with the following conditions: Atomic absorption spectrometer (CG AA 7000 ABC) and a mercury hollow cathode lamp as source, $\lambda = 253.7$ nm. Carrier gas used was pure nitrogen (White Martins). $SnCl_2$ (Merck) was used as 10% (m/v) solution (12.0 g of $SnCl_2 . 2 H_2O$ was weighed into a 100 ml flask, dissolved by 18 ml of diluted HCl (1:1), and diluted to the mark with distilled water).

Mercuric ion adsorption. The adsorption of 7.4 $\mu g.ml^{-1}$ of Hg^{2+} solution, prepared from $Hg(NO_3)_2$-Aldrich, on MnO_2 was performed using a 500 ml flask with a thermometer. A mechanical mixer was used for agitation, and the system was immersed in a thermostatic bath.The mercuric ion solution was transferred to the flask, the pH adjusted to 4.5, and the experiment started when MnO_2 was added to the solution. In previous paper[10] it was observed that EMD particles were stronger than CMD in liquid solution. Due to these better physical characteristics the adsorption studies of Hg^{2+} were performed on EMD.

RESULTS AND DISCUSSION

Table 1 shows the (%) adsorption of H_2S on CMD and EMD, based on the theoretical mass of H_2S generated. In this table, 100% adsorption means that no H_2S reacted with the standard solution of As^{3+}, keeping the original concentration of As^{3+} in flask C.The following reactions are related to the adsorption of H_2S indicated by $(H_2S)_{ads.}$

Flasks A). $FeS (s) + 2 HCl \rightarrow H_2S (g) + Fe^{2+} + 2 Cl^-$

B) $H_2S (g) + MnO_2 (s) \rightarrow (H_2S)_{ads.} / MnO_2$

C) $H_2S (excess) + As^{3+} \rightarrow As_2S_3 (s)$

Due to the high concentration of As^{3+} used (996 $\mu g.ml^{-1}$), the remaining As^{3+} in flask C was accordingly titrated with iodine, and the H_2S sorbed on MnO_2 was calculated by the difference of (H_2S) in flasks A and C.

Table 2 shows the HCN adsorption on MnO_2 , with the following reactions in flasks A, B, and C respectivelly:

A) $KCN + HCl \rightarrow HCN (g) + KCl$

B) $HCN (g) + MnO_2 (s) \rightarrow (HCN)_{(ads.)} /MnO_2$

C) $HCN (g) (excess) + NaOH \rightarrow NaCN + H_2O$

The spectrophotometric method of barbituric acid was employed for (CN^-) determination. The difference among the total cyanide concentration and the CN^- that remained in flask A plus the cyanide collected in flask C represents the $(HCN)_{(ads.)}$

Table 3 shows the adsorption of arsine on MnO_2 and the following reactions could be considered:

Table 1.Percentage (m/m) of hydrogen sulfide adsorption on MnO_2 (*)

sample number	mass of FeS (g) used	theoretical mass of H_2S generated (mg)	(%) adsorption on CMD	EMD
1	0.500	194	100	95
2	0.850	329	100	84
3	0.925	358	100	81
4	0.950	368	96	78
5	1.000	384	87	75

(*) % adsorption based on theoretical mass of H_2S generated. Average of three determinations with an estimated error of ± 6 % .

Table 2.Percentage (m/m) of HCN adsorption on MnO_2 (#)

sample number	theoretical mass of HCN generated (mg)	(%) adsorption on CMD	EMD
1	49	100	100
2	313	100	100
3	326	96	85

(#) % adsorption based on the theoretical mass of HCN generated. Average of three determinations with an estimated error of ± 6 % .

Table 3.Percentage (m/m) of AsH_3 adsorption on MnO_2 (*)

Sample number	theoretical mass of AsH_3 generated (mg)	% adsorption on CMD	EMD
1	26	100	100
2	63	100	100
3	158	98	90

(*) % adsorption based on theoretical mass of AsH_3 generated. Average of five determinations with an approximate error of ± 4 %.

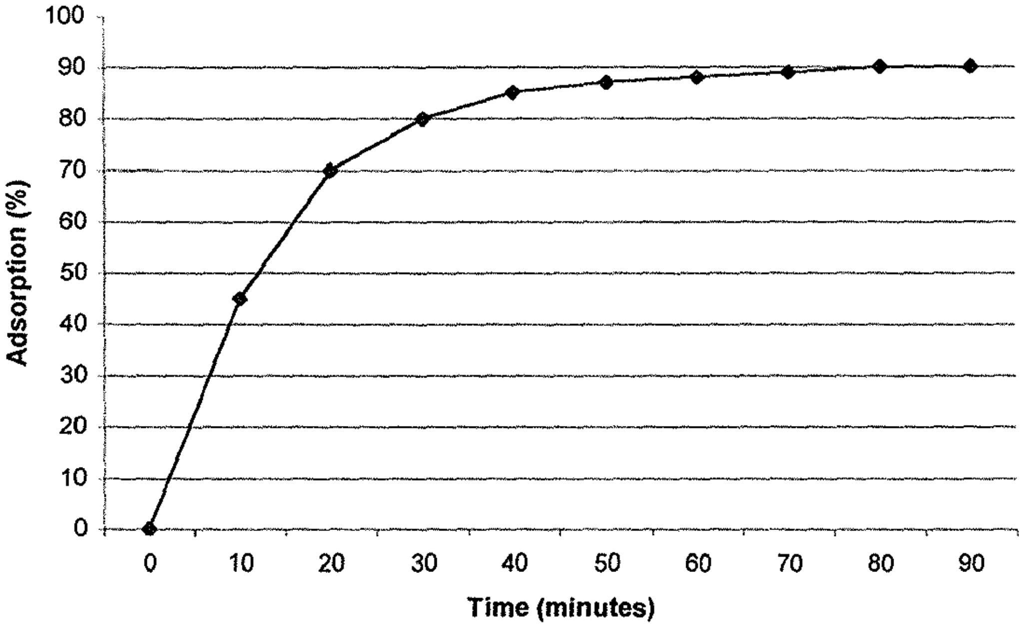
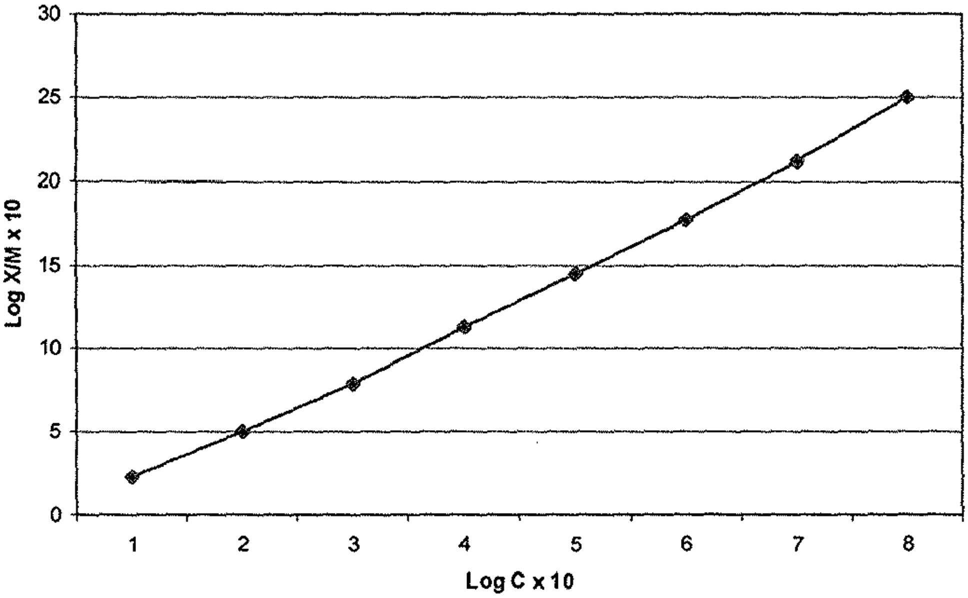


Figure 3. Dependence of contact and shaking time for Hg^{2+} adsorption on Electrolytic Manganese Dioxide (EMD)



X/M = concentration ratio of adsorbate (Hg^{2+}) and adsorbent (EMD). C = Hg^{2+} concentration in solution determined by cold vapor atomic absorption spectrometry using $SnCl_2$ as reducing reagent.

Figure 4. Freundlich adsorption isotherm of Hg^{2+} on Electrolytic Manganese Dioxide (EMD)

A). $As^{3+} + 3\ Zn(s) + 6\ HCl\ (aq.) \rightarrow AsH_3\ (g) + 3\ ZnCl_2 + 3\ H^+$

B). $AsH_3\ (g) + MnO_2\ (s) \rightarrow (AsH_3)_{(ads.)}/MnO_2$

$H_2S\ (g) + Pb^{2+} \rightarrow PbS\ (s) + 2\ H^+$

C). $6\ Ag^+ + AsH_3\ (g) \rightarrow As^{3+}\ (aq.) + 6\ Ag(s) + 3\ H^+$

$As^{3+} + 3\ e = As(s)$ $E = -0.45$ volts (polarographic cell)

As^{3+}(aq.) is an electroactive substance and its concentration was determined by differential pulse polarography . The lead acetate used in (B) was to prevent MnO_2 from sulphide contamination[15]. For instance, this method was used in determination of arsenic in bituminous coal with high sulfur concentration.

The adsorption studies of elemental mercury were carried out using the classical mercury distillation apparatus, and the following reactions could be considered:

B) distilled mercury collecting flask: $Hg\ (l) \leftrightarrow Hg\ (g)$

A) $Hg(g) + MnO_2\ (s) \rightarrow (Hg)_{(ads.)}/MnO_2$

$(Hg)_{(ads.)}/MnO_2 + \text{diluted } HNO_3 \rightarrow Hg(l) + H_3O^+ + NO_3^- + MnO_2\ (s)$

The concentration of Hg(l) was determined by CVAAS. The mercuric ion adsorption on MnO_2 represented by $(Hg^{2+})_{(ads.)}$ was performed with the following reactions:

$Hg^{2+}\ (aq.)\ (pH = 4.5) + MnO_2\ (s) \rightarrow (Hg^{2+})_{(ads.)}/MnO_2$

$(Hg^{2+})_{(ads.)}/MnO_2 + \text{diluted } HNO_3 \rightarrow Hg^{2+}(aq.) + H_3O^+ + NO_3^- + MnO_2\ (s)$

$Hg^{2+}\ (aq.) + SnCl_2 \rightarrow Hg(l) + Sn^{4+} + 2\ Cl^-$

The concentration of mercury was also determined by CVAAS. Figure 3 shows the dependence of shaking and contact time for Hg^{2+} adsorption on EMD. The adsorption efficiency increased at higher temperature (60°C) if compared with room temperature(25°C). At 60°C and pH 4.5 , that is slightly higher than the PZC of MnO_2, the adsorption process is very high from time zero until 30 minutes of reaction. It was also observed that in liquid media the adsorption efficiency of EMD was better than CMD. However, Freundlich isotherm were followed for both adsorption process (Figure 4).

The studies performed using manganese dioxide as adsorbent and gaseous substances as adsorbates showed some differences between CMD and EMD. Due to its porosity, the sorption efficiency of H_2S , HCN , AsH_3, and Hg were higher on CMD. On the other hand, EMD has better physical characteristics and efficiency for adsorption in liquid media. It was also observed that the adsorption of Hg^{2+} on MnO_2 changes the pH quickly. Starting at 4.5, the pH increases to 6.5 after 30 minutes of adsorption.

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