Removal of Arsenic and Manganese in Underground Water by Manganese Dioxide and Diatomite Mineral Ores

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Abstract

A methodology has been developed for the removal of arsenic (As) and manganese (Mn) from underground water using natural manganese dioxide (MnO_2) and diatomite mineral basing on the adsorptive process. The results showed that 90-96% concentration of As and/or Mn had been removed from water samples by MnO_2 and diatomite adsorbent materials. After treating, the concentration of As and Mn is lower than Vietnamese underground water quality standard (0.05 mg/L for As and 0.1 mg/L for Mn). Natural MnO_2 and diatomite mineral are able to remove a total of As (III, V) without the oxidation reagents. The removal of As and Mn by using diatomite is more efficient than using MnO_2. Using the nature MnO_2 and diatomite mineral are extremely efficiency for removing As and Mn in the underground water.

Keywords: Arsenic, Manganese, Manganese dioxide, diatomite mineral, underground water, adsorptive method

Introduction

Arsenic contamination in underground water was found in various countries in the world as Bangladesh, India, China, Mexico, America and ect. About 40 million people of Bangladesh, 13 million people in America, are now at risk of arsenic contamination. arsenic concentration at higher level than WHO recommended value is found of 51% in the tube-wells in Bangladesh [1]. The geology of the Red river Delta in Vietnam, like the geology of Ganges river in Bangladesh, also has been finding the arsenic contamination in underground water in some provinces as Hanoi, Hatay, Namdinh, Hanam and etc. New investigations have shown potential problems related to the presence of arsenic in alluvial deposits in the Red river region and in tube wells pumping water from lower aquifer. This requires further study and careful assessment. In addition, manganese level above the admissible standards are found both in the Red river and Mekong river Delta [2].The arsenic contamination survey data in 351 tube wells, the results showed that 351 water samples in which 25% have 0,05 mg/l higher concentration of arsenic contaminated and 68% are 0,01 higher than permitted Vietnamese standard [3].Using arsenic and manganese contaminated water source for a long time will cause tiredness, affect nervous system, even stomach cancer and other internal organs [4,5].

To eliminate arsenic and manganese from water source, development of feasible technologies to their treatment process as well as house-hold scale is essential requirement in Vietnam [6, 7].Therefore, study and assessment of the nature MnO_2 and Diatomite mineral adsorptive abilities to treat Mn and As total in underground water was carried out. Those processing technologies are simple, low-priced, and easily-operated. Utilizing mobile and statically absorptive ability is a method of assessing the arsenic and manganese eliminating process from underground water by dermining the maximum adsorption capacity into the nature MnO_2 and diatomite mineral which is investigated with hopes to contribute a part of technology and science to solve this urgent problem.

Experimental

The MnO_2 and diatomite mineral were pulverized from available raw materials. Arsenic and manganese solutions were prepared by diluting the initially standard solution of 1 g/L concentration from Merck Chemical Co. Ltd. All other chemicals were of analytical reagent grade. An Atomic Absorption Spectrophotometer system (AAS) using graphite and flame techniques was used to measure As and Mn.

Determination of As and Mn by statically absorptive method

Adsorption isotherm is a kind of graphic representing the relation between 1/a and 1/c (inversion of adsorption capacity of adsorbent material and inversion of concentration of adsorbent at the level point). This diagram can present the maximal adsorption capacity and constant Longmuir K_L for every material. Basing on experimental result, the adsorptive isotherm of metal ions (As and Mn) and the maximal adsorptive capacity are established. The adsorption isotherm of As (V) on every material can be drawn and the maximum adsorption capability is of Arsenic. Therefore, adsorbent capacity of arsenic on different material is able to be assessed.

Preparation of sample (2.1)*:

Firstly, 1g of MnO_2 and /or diatomite mineral was poured in to a beaker, which previously contained 100 mL of a mixed solution of 0.1 mg/L arsenic and 4 mg/L manganese. The solution was mixed and stirred gently with constant speed for 3 hours. Filtering this solution, As and Mn were determined in extracted solution.

Secondly, 1g of MnO_2 and /or diatomite mineral was poured in to a beaker, which previously contained 100 mL of 0.1 mg/L arsenic solution or 1 mg/L manganese. Next, the solution was stirred gently with a constant speed for 72 hours. Filtering the solution, As and Mn were determined in that extracted solutions.

Determination of As and Mn by mobile absorptive method

Put 10 g materials (means 7.5 cm^3 for capacity) to column, which contained glass wool. The solution, having As and Mn is poured into the column with flow rate as 1.6 mL/min. After every 24 hour, check sample and analyze content of Arsenic and Manganese. This experiment is illustrated as the below figure 1.

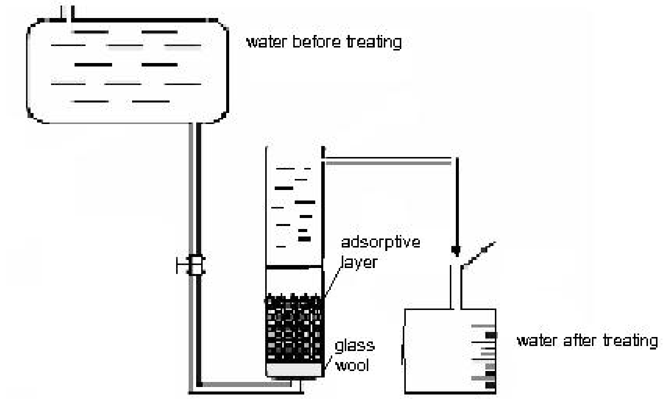

Figure 1. Sketch of As and Mn treated system by adsorptive method

Results and discussion

Investigation of the adsorptive ability of MnO_2 for removing arsenic and manganese in under ground water by mobile adsorptive method

The experimental condition for Manganese treatment:

The material is of 1mm for the diameter. The weight is 10 g. Input Manganese content (Co) is 1 mg/L. Flow rate through glass tube is 1.6mL/min. Mnd1-00; Mnd1- 02, …, Mnd1-20 are the sample mark, corresponding to adsorbent reduction time. The results in table 1 showed that about 99% of Mn ion has been removed after 1day. Indicating that almost Mn was adsorbate into MnO_2 ore. The concentration of Mn after treatment is lower than Vietnamese standard limit. The treatment productivity is of 99.9%.

Table 1. The result of treatment of Manganese by MnO_2 ore.

Time (hour)	Sample mark	Output concentration of Mn C_1 (mg/L)
0	Mnd_1-01	1
2	Mnd_1-02	0.7
4	Mnd_1-04	0.5
8	Mnd_1-08	0.3
12	Mnd_1-12	0.1
16	Mnd_1-16	0.06
20	Mnd_1-20	0.01

Table 2. The result of Arsenic treatment by MnO_2 ore.

Time (hour)	Sample mark	Output concentration of As C_1 (mg/L)
1	Asd1-01	0.100
2	Asd1-02	0.100
10	Asd1-10	0.093
20	Asd1-20	0.091
48	Asd1-48	0.060
120	Asd1-120	0.057
168	Asd1-168	0.058
240	Asd1-240	0.051

The experimental condition for Arsenic treatment:

The condition for As treatment is quite similar. As initial concentration (C_0) is 0, 1 mg/l. Asd1-01, Asd1-02 ... Asd1-240 is the sample mark, corresponding to adsorbent reduction time. The results in table 2 shows that the concentration of As has not much been removed after 10 days for using MnO_2 ore. This result indicated that almost As was not adsorpted into MnO_2.

Investigation of the adsorptive ability of MnO_2 and diatomite ore for removing arsenic and manganese in the under ground water by statically adsorptive method

For determination of Manganese: Sample using diatomite natural coded Do-Mn-03 and another using manganese dioxide coded M-Mn-03. Soak 1g materials into 100mL of Manganese solution which has 4mg/L of concentration. The procedure is described above (2.1*). The results in table 3 indicated that Mn was well treated by MnO_2 and diatomite natural. It means MnO_2 and diatomite ores are very good at treating Mn in the water. MnO_2 is not only oxidized but also adsorbent material.

Table 3. The result of statically adsorptive process for treating of Mn by some materials.			The result of statically adsorptive process for treating of As by some materials (C_0 = 0,1mg/l).			
Name of material	Sample symbol	Mn concentration after treating C_1 (4 mg/l)	Name of materila	Symbol sample	Output of As C_1 (mg/l)	Treatment productivity (%)
Diatomite	Do-Mn -03	<0.01	Diatomite	Do-As-03	0,0054	94,62
MnO_2 ore	M-Mn -03	<0.01	MnO_2 ore	M-As-03	0,0031	96,95

For determination of Arsenic: The condition for As removal is similar as Mn. 100mL Arsenic with concentration of 0,1mg/L is stirred with constant speed in 3 hours. Result in table 4 showed that the absorbent ability of As into MnO_2 was very good. Processing efficiency was nearly 97% and concentration of arsenic in sample after treatment was below Vietnamese standard. Arsenic is well treated by diatomite due to the high As adsorption capacity of diatomite. Possibility, diatomite natural was made up of many other mineral materials like Al_2O_3, Fe_2O_3, betonies and ect.

Gauge adsorbent isotherm and determine maximal adsorption capacity of As and Mn onto some materials

To make the calculation of adsorptive of material, it is necessary to identify the maximal adsorption capacity of substance on materials basing on adsorbent isotherm. Figure 2 is illustration of adsorbent isotherm of As onto MnO_2 while figure 3 is that of As onto Fe_2O_3/diatomite natural. Adsorbent isotherm of Manganese on MnO_2 ore is in figure 4 and figure 5 is that into diatomite natural.

Study results showed that As treatment efficiency was high up to 80% with adsorbent capacity calculated by Longmuir formula 1:

$$A_m=2,08\text{mg/g } (y=1,535x+0, 48) \qquad (1)$$

The adsorptive of Fe_2O_3/Diatomite is dependent on ·OH group, which adhesion onto diatomite surface, can be replaced As in that. The adsorbent ability of arsenic into diatomite is higher than that intoMnO_2. The maximal adsorbent capacity (am) can be calculated by formula 2

$$A_m = 2,5 \text{ mg/g } (y= 20{,}03x + 0{,}406) \quad (2)$$

Figure 4 can be explained that MnO_2 is oxidability and minus chargeable, therefore, it can be attracted Mn2+ ion and created Mn_2O_3. Maximal adsorption capacity calculated by Longmuir formula 3:

$$A_m=12{,}7 \text{mg/g } (y= 10{,}29x + 0{,}079) \quad (3)$$

Therefore, the adsorptive of Diatomite natural onto Mn is apparent (Fig. 5). At the moment of investigation, Oxidized Mn^{2+} and dissolved oxy possibly appeared in this solution, even low concentration of Mn^{2+}.

It is due to adsorption and flocculation ability of Diatomite or Mn $(OH)_4$ which was created through oxidization process which played an important part for Mn oxidization process. Adsorbent capacity of Mn is calculated by Longmuir formula 4:

$$A_m=15,15 \text{ mg/g } (y= 7{,}508x + 0{,}066) \quad (4)$$

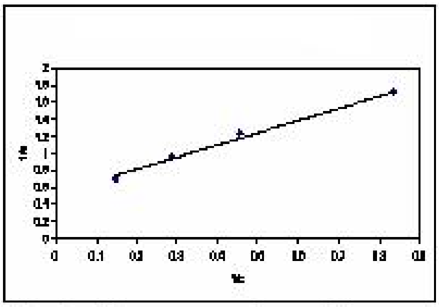

Fig.2: Adsorption isotherm of As into MnO_2

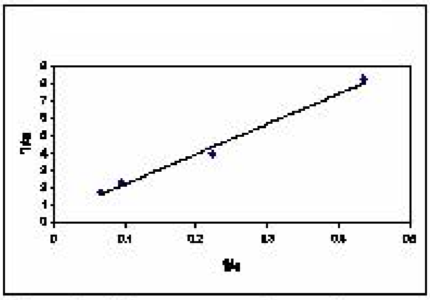

Fig. 3. Adsorption isotherm As into 1%Fe_2O_3 diatomite

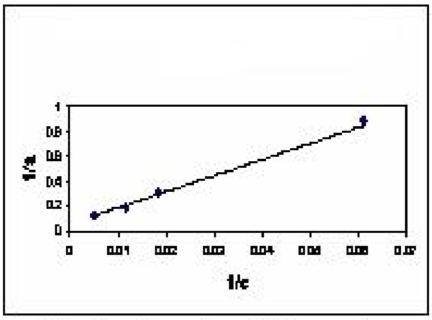

Fig. 4. Adsorption isotherm of MnO_2 for Mn

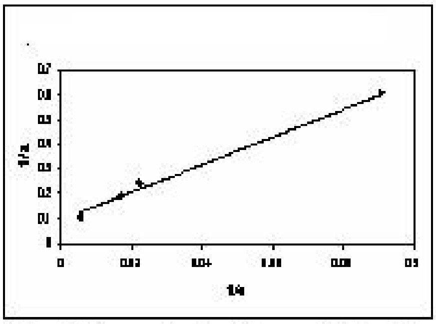

Fig. 5. Adsorption isotherm of Mn into diatomite

Conclusion

The adsorptive ability of MnO_2 for manganese removal in underground water by mobile adsorptive method is very good. Using 10 g material, it can treat 1mg/L Mn with the treatment productivity is of 99.9%.This method can not applied to As case.

The adsorptive ability of MnO_2 and diatomite ore for arsenic and manganese removal in underground water by statically adsorptive method is excellent. It means MnO_2 and diatomite ores are very good for Mn treatment in the water. Manganese dioxide is not only oxidized but also adsorbent material. Arsenic is well treated by diatomite due to the high As adsorption capacity of diatomite.

Those above results proved that natural manganese dioxide, diatomite mineral were potential adsorbent materials which could be applied to treat Mn and As in water source. Using manganese dioxide and diatomite mineral would concurrently treat both Mn and As in the supply water.

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