Application of Nano Dimensional MnO$_2$ for

High Effective Sorption of Arsenic and Fluoride

in Drinking Water

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Abstract

Nano dimensional MnO$_2$ was prepared by oxidation-reduction reaction of permanganate and manganese sulfate in water – ethanol solution. The dimension of MnO$_2$ particles was controlled by ethanol concentration, one of most important parameter in the oxidation-reduction process. Nano dimensional MnO$_2$ particles then were coated on natural pyrolusite grains to create high performance sorption material. The adsorption capacity of arsenic and fluoride on the fresh prepared material in water solution was investigated. The result showed that the adsorption of arsenate anion is almost accord with Langmuir isothermal equation and maximum adsorption capacity reached up to approximately 84 mg per gram. In contrast to arsenic, adsorption of fluoride anion on the material was more suitable to Freundlich isothermal equation than the Langmuir one; however, its adsorption capacity is very high. The hypothesis of adsorption mechanisms was discussed. In both cases, there was no any Mn(II) cation in treated water detected.

Keywords: nano dimensional MnO$_2$, arsenic, fluoride adsorption

1. Introduction

Arsenic contamination in groundwater is known as a global problem. That is not only by its toxicity but mainly by its worldwide distribution. Bangladesh is the typical case of arsenic contamination of water under the Ganga River delta [2, 5]. Similar situation as Bangladesh, Vietnam has two big deltas of Mekong and Red Rivers which originate from mountainous region in southern-east of Himalaya mountain chain, where is rich in arsenide-sulfide ores [4]. There were many arsenic removal technologies applicable for drinking water as well as for wastewater treatment [12], but high performance one always was a challenge to scientists and technologists in the World. During recent years, investigations turned to using of natural minerals as adsorbents for arsenic removal from drinking water because of their wide distribution, more safety for human health than chemical removing methods [6]. Among most commonly used minerals are iron oxide/hydroxide containing minerals, such as hematite, laterite, goethite...[8]. Whereas pyrolusite, a mineral containing mainly manganese dioxide and iron(III) oxide, was less investigated and used for water treatment purpose, although manganese dioxide is a high potential adsorbent for effective treatment of arsenic and other toxic anion in water environment [9].

Beside arsenic, fluoride contamination in supplied water of large areas in the World is no less important problem threatens human health. Many supply water sources in the middle part of Vietnam are polluted by fluoride, which need to be treated. Beside well known as effective fluoride removing materials such as aluminum or zirconium compounds...[7, 11], based on our initial investigation, manganese dioxide indicated as a good material for fluoride removing reagent. Especially when dimension of the manganese dioxide particles reduced to nano size, their sorption of fluoride anion largely increased. That is the result why this investigation was carried out and its results would be published as a data base for other investigation in the future.

2. Materials and Methods

2.1. Nano dimensional MnO₂ material preparation

Nano dimensional MnO₂ particles preparation

The nanodimensional MnO_2 formation was carried out in water – ethanol media with ethanol concentration in both solutions of $MnSO_4$ and $KMnO_4$ from 0% to 80% and combined each others.

Working concentration of $MnSO_4$ solution was 3.10^{-2}M and $KMnO_4$ was 2.10^{-2}M. The oxidation-reduction reaction was developed by slowly adding of $MnSO_4$ water – ethanol solution into the $KMnO_4$ solution with the same volume. The adding solution rate was 2.5 ml per min. During the reaction, the mixture was intensively stirred. Dark brown colloidal solution of nanodimensional MnO_2 was formed. This solution was taken for particle size analysis on Laser Scattering

Particle Size Distribution Analyzer LA-950 (Japan) and for coating on carrying body of the material.

Nano MnO$_2$ coated materials

Nanodimensional MnO$_2$ carrying body is natural pyrolusite ore in grains formation with relative diameter of 0.5 – 1.0 mm. Coating of nanodimensional MnO$_2$ on pyrolusite grains was realized by soaking of the grains into colloidal solution of MnO$_2$ according to designed proportion. Then let the mixture stand for 12 hours at room temperature. When almost of MnO$_2$ particles adsorbed on the grains surface, the solution became colorless, and rinsed off. Nano MnO$_2$ coated grains then was washed by water – ethanol mixture with the same proportion as that in the original solution and dried for 4 hours at 105^{0}C. The new adsorption materials were recovered.

2.2. Investigation of arsenic adsorption capacity of the material

Let the adsorption material contact with arsenic solution of designed concentration for the time in which the adsorption reached equilibrium state. The arsenic concentration in water phase then analyzed by AAS – HVG equipment.

2.3. Investigation of fluoride sorption capacity of the material

The fluoride sorption investigation was carried out by the same procedure as that for arsenic investigation but all experiments were developed in plasticware to avoid fluoride corrosion of glassware. The equilibrium concentration of fluoride in water phase was determined by photometric method by SPANDS method [1].

2.4. Materials regeneration

There were a lot of reagents would be used for desorption of arsenic and fluoride from sorbent; but for drinking water treatment, only acid or alkaline solution should be chosen. So the regeneration of exhaust material was studied by means of column washing with dilute acid or alkaline solution of different concentration. Desorbed anions were analyzed and the regenerated materials were tested again for their sorption capacity.

3. Result and discussion

3.1. The effect of ethanol concentration on nano MnO$_2$ formation

Table 1. The effect of ethanol concentration on nanodimensional MnO$_2$ formation (%)

EP$_2$ \ EP$_1$	0	20	40	60	80
0	1.2	22.8	46.3	51.7	55.8
20	11.6	33.6	61.2	78.4	86.6
40	34.5	51.1	64.8	68.4	82.8
60	22.6	46.2	56.4	62.1	64.5
80	18.2	26.7	41.5	48.6	58.7

EP$_1$: Percentage concentration of ethanol in MnSO$_4$ solution and EP$_2$: Percentage concentration of ethanol in KMnO$_4$ solution

Table 1 illustrated the effect of ethanol concentration on MnO_2 nanoparticles formation. It seems that ethanol concentration in Mn^{2+} solutions increased the nano MnO_2 fractions also increased. While increase of ethanol concentration in MnO_4^- solutions, the nano MnO_2 productivity increased in lower ethanol percentage area but turned to decrease in higher percentage concentration of ethanol. Based on the experimental observation and theoretical high oxidative potential of permanganate ion, the unregulated phenomenon was result of pre-oxidation-reduction between permanganate and ethanol at higher concentration area occurred before adding of Mn(II) ions. This process create initial MnO_2 particles and they play as a precipitate centers to form bigger particles in oxidation-reduction reaction between permanganate and Mn(II) later. Therefore, the optimal ethanol concentrations in $MnSO_4$ solution were from 60 to 80% and in $KMnO_4$ solution were from 20 to 40% were recommended.
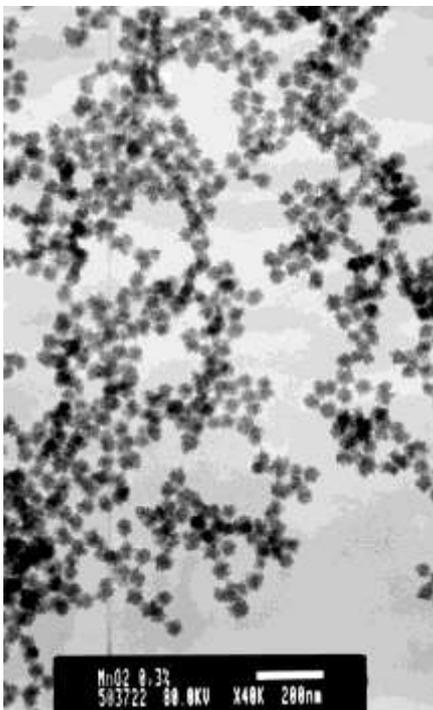

Figure 1. TEM image of nano MnO_2 particles in the solution

Figure 1 showed TEM image of MnO_2 nanoparticles. The MnO_2 particles in this case have almost the same shape of spongy barbed spheres with dimension of 30 - 50 nm.

The effect of organic solvents on existing formation of elements in water solution was reviled [3] and applied in chemistry since a long time ago [10]. This effect on nanoscale particles formation may caused by changing of the property and structure of solution. The changing property of solution may include firstly dielectric coefficient and surface tensity. The changing structure of solution was concerning to changing of water structure, competition of hydration and solvation and long chain molecules of the solvent in water may create a net-like of solvent molecules in the solution; that hampered association of precipitate molecules to grow biger crystals.

3.2. Nanodimensional MnO_2 coating sorbent

Figure 2 showed surface of natural pyrolusite coating MnO_2 particles. At the SEM image, that is easy to recognize the nanoparticles of MnO_2 distributed all over pyrolusite grain surface with the same spherical shape and diameter as those appeared in the solution (figure 1). The loading rate of nano MnO_2 on pyrolusite was determined approximately 3.0 mg/g.

Clinging of MnO$_2$ nanoparticles on the surface of carrying grain body is important factor for application purpose, because nanoparticles were almost
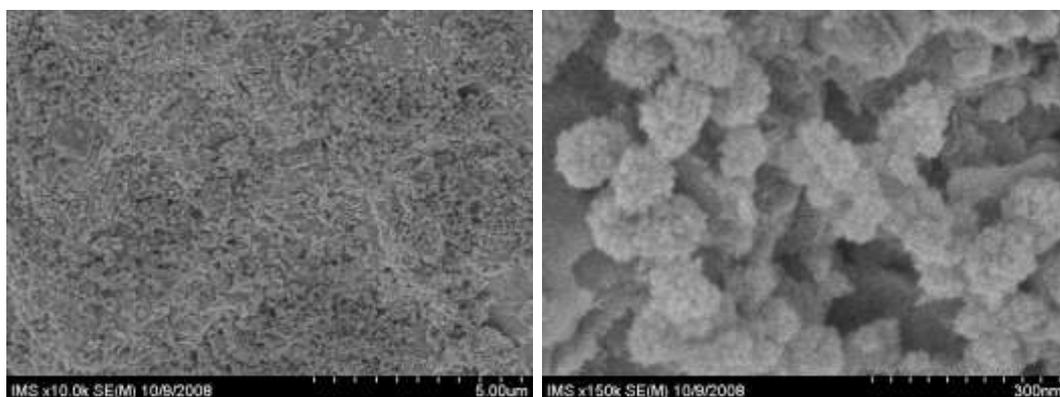

Figure 2. SEM image of nanodimensional MnO$_2$ particles coated on calcinated clay surface

impossible use for sorption and removal of pollutants from water environment. The barrier is the lack of effective separation methods; but the essence of this situation was not seriously investigated yet. So successfully coating MnO$_2$ nanoparticles on pyrolusite grain was important achievement for application of nano particles in environmental pollution treatment.

3.3. Arsenic and fluoride adsorption capacity investigation

The adsorption equilibrium of arsenate anions on nano MnO$_2$ coated material was almost established after 180 min contact of solid and liquid phases. In the case of arsenite, the adsorption equilibrium time was almost the same as that for arsenate. The analytical result also showed that, all arsenite anions changed into arsenate ones after contact time and there was no Mn^{2+} ion in the water phase detected. This means all arsenite was oxidized to arsenate state by dissolved oxygen or additional catalyzing of manganese dioxide. And the oxidation rate in this case was in general higher than adsorption rate. Therefore, adsorption process of arsenic finally occurred only between arsenate anions on adsorbent surface. The adsorption isothermal curve of arsenate was carried out by experiments mentioned in section 2.2 with arsenic concentration in the range of 0.00 to 500.00 mg/L and the ratio of adsorption material and arsenic solution for all experiments was 1.0 g/100 ml. The experimental results showed that, adsorption process was closely according to the Langmuir adsorption isotherm than other one (figure 3).
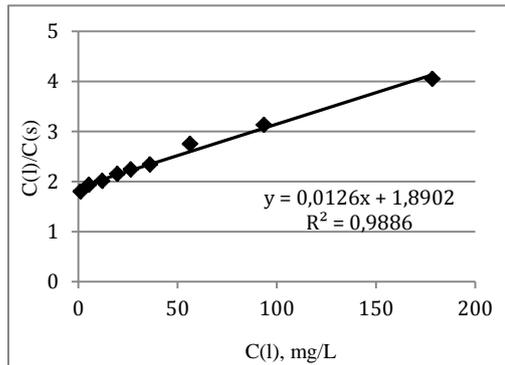
Based on the Langmuir adsorption isotherm equation,

$$\frac{C_l}{C_s} = \frac{1}{bC_{max}} + \frac{1}{C_{max}}C_l$$, the maximum

adsorption capacity of arsenic was determined of 83.34 mg/g. In comparison of maximal adsorption (8.67 mg/g) of MnO_2 produced by electrolysis oxidation coating on the same carrying body, the maximum adsorption of nano MnO_2 material was about ten times higher.

Figure 3. The Langmuir adsorption isothermal curve of arsenic on nano MnO_2 material

For fluoride anions, the investigation results showed that, the adsorption of fluoride ions on the nano MnO_2 material reached equilibrium state only after about 60 min. Figure 4 and 5 illustrated adsorption process of fluoride on the material applying to Langmuir and Freundlich isothermal equations. From figure 4 and 5, the isothermal curve was more closely according to the Freundlich adsorption equation than the Langmuir one. Following Langmuir adsorption equation, from the data illustrated at figure 4, the maximum adsorption capacity was calculated and gained the average value 21.74 mg/g. This value is very high in comparison with almost well known fluoride adsorption materials. Application of Freundlich isothermal equation, $lnC_s = lnK_f + (1/n)\ lnC_l$, (experiment data showed in figure 5), the values of K_f and n were calculated and these were 0.644 and 1.425 respectively.

As results presented above, the arsenic anions adsorbed on the nano MnO_2 adsorbent complied closely with the Langmuir adsorption isotherm. This means
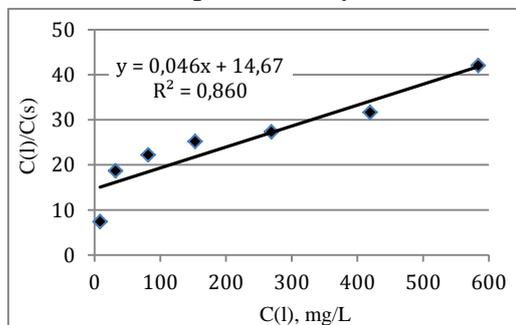

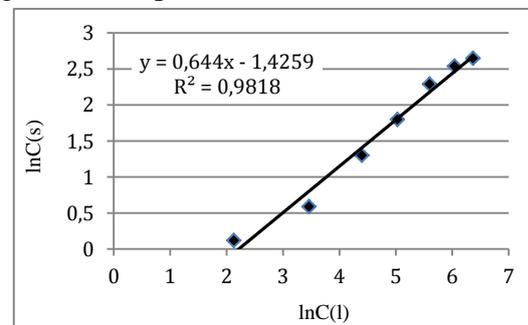*Figure 4. The Langmuir adsorption isothermal curve of fluoride on the material*

Figure 5. The Freundlich adsorption isothermal curve of fluoride on the material

most arsenate anions created a monomolecular layer and covered around the infinitesimal MnO_2 bodies which formed high porous barbed spherical particles (as showed in figure 1 and 2). The difficulty of diffusion process of unwieldy arsenate anions into porous barbed particles was most probably the reason why the adsorption equilibrium of them took the long time up to 180 min or longer. Whereas, in the case of simple fluoride anions, the equilibrium adsorption time was only around 60 min. The well known fact is that, fluoride anions are strongest electronegative ones and trend to dimerize; those result in formation of multilayer adsorption of fluoride in the material. That partly explained why the adsorption mostly complied with Freundlich isotherm than the Langmuir one. The adsorption mechanism of this case was more complicated. There may were the coordinate bond directly between fluoride anion and central Mn atom, the oxygen and hydrogen bridge bonds, the polymerization of fluoride anions…These problems need to further investigate.
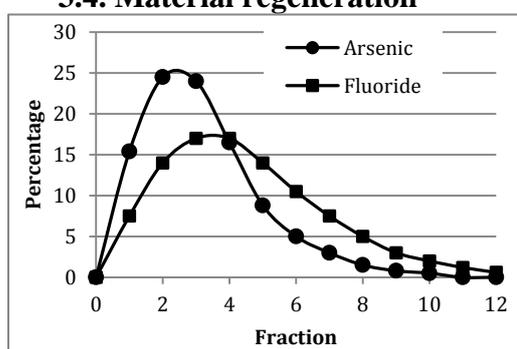
3.4. Material regeneration

Figure 6. The percentage of washed arsenic and fluoride from exhaust materials

The exhaust material was regenerated in the column and washing reagent was ammoniac or sodium hydroxide solution. Figure 6 illustrated the percentage of arsenic and fluoride in continuous washing fractions using 0.01M NaOH solution with flow rate of 2.5 ml/min.cm^2. It showed that adsorbed arsenic was easier desorbed than fluoride anions. The investigation also showed the maximum adsorption capacity of regenerated material after third period still reached about 75% in comparison with fresh one, and sodium hydroxide solution with concentration more than 0.05M could damage active surface of the material.

4. Conclusion

The nanodimensional MnO_2 particles could be prepared by oxidation-reduction reaction between $MnSO_4$ and $KMnO_4$ in water – ethanol solution. The concentration of ethanol in the initial solutions played important role in formation efficiency of the nano particles. Nano MnO_2 particles seemed to be formed by the clusters of infinitesimal needle-shape bodies and were almost spherical shape with very high porosity in internal structure. Nano particles were coated on almost surface area of carrying grains and created excellent adsorption material for treatment of several pollutants in water environment.

Investigation of arsenic and fluoride adsorption on nano MnO_2 coated on pyrolusite showed that, the arsenic adsorption was closely according to Langmuir

adsorption isotherm and took long time to achieve equilibrium state. This phenomenon could be explained by low diffusion rate of unwieldy arsenate anion into porous MnO_2 particles. In contrast to arsenate, fluoride anions adsorbed on the material more complied with Freundlich isotherm and adsorption equilibrium time was only about 60 min. This difference was resulted from origin and special properties of fluoride ions. There were problems concerning to nano scale material need to further investigate.

The exhaust materials could be regenerated by alkaline solution with low concentration. The adsorption capacity of the regenerated materials was lightly degreased after used periods.

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