Tạp chí Khoa học và Công nghệ ***49*** *(2) (2011) 107-115*

INVESTIGATION OF ARSENIC REMOVAL FROM GROUNDWATER BY NANO-DIMENSIONAL MnO_2 AND FeOOH COATING ON CALCINATED LATERITE

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Received March 15, 2010

ABSTRACT

The arsenic contamination in groundwater is real problem in Vietnam threatening health of millions people (M. Berg et al., 2001)[1]. The reason was concerned to natural processes happening in underlying layers of the basin areas including Hanoi in the North and Hochiminh, the biggest City in the South of Vietnam. The highest risk potential is determined in the areas of Mekong River, Red River and Ma River deltas. Therefore arsenic treatment for drinking water in Vietnam is recently urgent requirement [2].

Our investigation based on the advanced adsorption of nano-dimensional MnO_2 and FeOOH preparing in ethanol – water media [3]. The concentration of ethanol in solution played important role in nano-particles' formation and anticoagulation [10]. Dimension of MnO_2 particles was appropriately 50 nm diameter determined by TEM method; those of FeOOH particles were 30 nm long and 10 nm wide. The MnO_2 and FeOOH particles in colloidal solution then were coated on calcinated laterite grains to create high performance adsorption material for arsenic removal from groundwater. The materials surface was studied by SEM method.

The adsorption capacity of materials was determined. The maximum adsorption of arsenic on nano-MnO_2 coated material was 125.89 mg per gram and on nano-FeOOH coated material was 91.74 mg per gram. The optimum conditions for arsenic treatment as well as adsorbent's regeneration were investigated.

1. INTRODUCTION

For the purpose of the creation of high performance adsorption material, our investigation based onto two processes. The first was preparation of colloidal solution of nanodimensional particles of metals' oxide or hydroxide and the second was coating the prepared particles on denaturated laterite surface.

There are many chemical methods effectively used for nanomaterials preparation. Many authors prepared solid particles of transition metals' hydroxide and oxides in nanodimensional scale by the way of hydrolyzing metal-organic compounds in water solution [1,2] or applying deferent physical effect during hydrolysis of metals' ions [3] or using thermal and chemical disintegration suitable reagents [4, 5, 6].

In this article, the effects of organic solvents in water media were used for creation of nanndimensional MnO_2 and FeOOH from their inorganic salts. The pH of solution, concentration of the salts and reaction temperature were strong influenced on the quality of the product. Prepared nanodinsional particles were coated on denaturated laterite to create new high performance adsorption materials.

2. EXPERIMENT

2.1. Preparation of nanodimensional MnO_2 adsorbent

Tested organic solvents were ethanol, methanol, acetone and sodium stearate. All tested solvents proved their effect on nanodimensional MnO_2 formation; but ethanol was taken as a example solvent in this article.

The experimental process was realized in different ethanol concentration in both solutions of $MnSO_4$ and $KMnO_4$ from 0% to 100% and combined each others.

Working concentration of $MnSO_4$ solution was 3×10^{-2}M and $KMnO_4$ was 2×10^{-2}M. The procedure of MnO_2 nanoparticles formation was that: Slowly adding $KMnO_4$ solution one by one containing portion of ethanol as 0, 5, 10, 25, 50, 75 and 100% into the series of $MnSO_4$ solutions having the same volume and ethanol portion from zero to 100% respectively. The adding solution rate was 2.5 ml per min. During reaction time, the mixture was intensively stirred. Dark brown colloidal solution of nanodimensional MnO_2 was taken for particle size analysis and coating on denaturated laterite material.

The productivity of nanodimensional MnO_2 formation was calculated as percentage of mass ratio between amount of nanodimensional MnO_2 taken and theoretical amount upon reaction stechiometry.

Coating of nanodimensional MnO_2 on denaturated laterite was realized as below: Weigh suitable amount of dried denaturated laterite with size of 0.5 – 1.0 mm diameter and dropped into colloidal solution of MnO_2. Then softly shook the mixture in 60 min. When almost of MnO_2 particles adsorbed on the laterite surface, the solution became colorless. Rinsed off the solution, washed material by solution with the same ethanol portion and dried it through 4 hours in 105^0C.

2.2. Preparation of nanodimensional FeOOH adsorbent

Working solution of $FeCl_3$ had concentration 0.5 M and hydrolyzing media were water solutions containing 0, 5, 10, 20, 50, 75and 100 % ethanol. The nanodimensional FeOOH was prepared by adding 10 ml iron chloride solution into 500 ml hydrolyzing media with the rate of 2 ml per min and solution was strong stirred. Then ammonia solution (5 M) was slowly added into hydrolyzing media until pH reached value of 4. The reaction temperature was kept in 80^0C during reaction process and continuously stirred. Dark brown colloidal solution of nanodimensional FeOOH was created. A part of colloidal solution was taken for size analysis and other part was used for coating nanodimensional FeOOH on laterite bearing material.

The coating process of nanoparticles of FeOOH was realized by the same way as coating of MnO_2 nanoparticles.

2.3. Arsenic adsorption test

Let MnO_2 or FeOOH coated materials contact with arsenic solution; then concentration of arsenic in water phase was determined along the sorption time or after the time when sorption reached equilibrium statd by atomic absorption spectrometry on.

3. THE RESULTS AND DISCUSSION

3.1. Nanodimensional MnO_2

3.1.1. Nanodimensional MnO_2 formation

Table 1. The effect of ethanol concentration in reagent solutions on nanodimensional MnO_2 formation (%)

EP_1 / EP_2	0	5	10	15	25	50	75	100
0	0	0	0	0	0.46	0.52	0.58	0.65
5	0	2.74	4.89	5.67	6.34	7.21	7.90	8.51
10	0	6.41	8.79	10.18	12.87	13.12	14.60	16.09
15	0.69	12.41	13.17	15.79	17.16	18.85	19.33	20.08
25	0.80	40.00	48.51	51.26	59.08	63.45	65.75	67.26
50	2.76	50.34	52.18	45.06	43.68	62.99	62.76	60.46
75	3.23	62.28	62.09	60.46	52.18	57.93	56.55	49.89
100	4.02	73.10	70.99	70.34	45.06	48.73	48.75	51.03

EP_1: Percentage concentration of ethanol in $MnSO_4$ solution and

EP_2: Percentage concentration of ethanol in $KMnO_4$ solution.

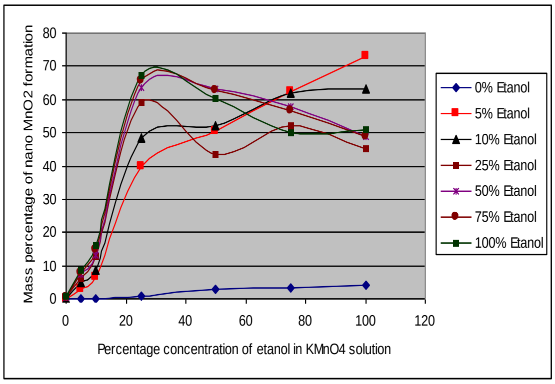


Figure 1. Influence of ethanol concentration in $KMnO_4$ solution on nanodimensional MnO_2 formation

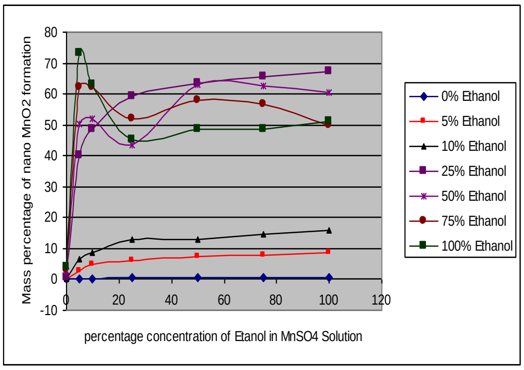


Figure 2. Influence of ethanol concentration in $MnSO_4$ solution on nanodimensional MnO_2 formation

Table 1 and figure 1 and 2 showed strong effect of ethanol concentrathon in reagents' solution on MnO_2 nanoparticles formation. There were two areas where effect of nanodimensional MnO_2 formation reached more than 60%. The first one lay in the area where concentration of ethanol in $KMnO_4$ solution from 25 to 50% and in $MnSO_4$ solution from 50 to 100%. The second one was 75 to 100% ethanol in $KMnO_4$ solution and 5 to 15% ethanol in $MnSO_4$ solution.

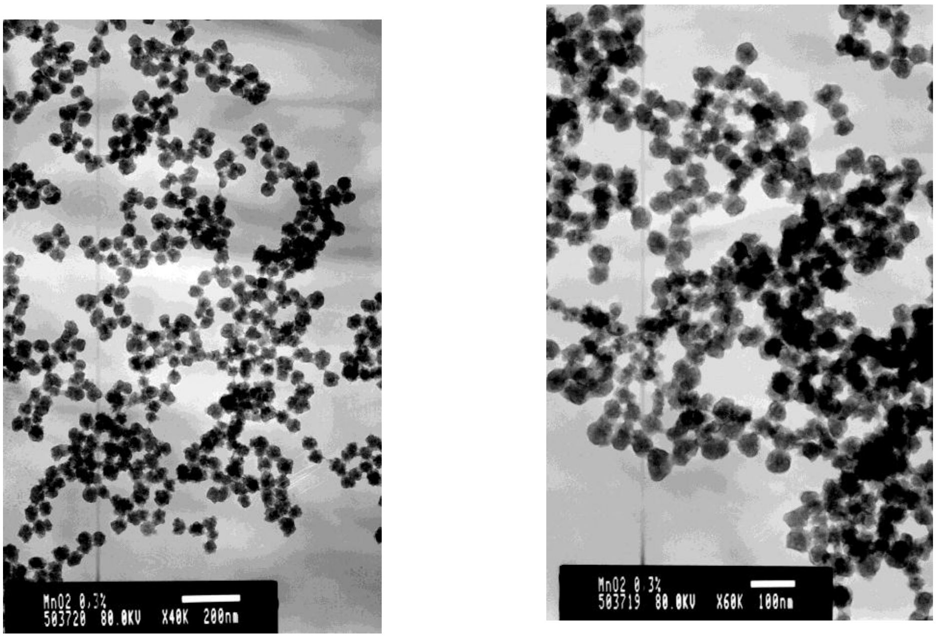


Figure 3. TEM image of nanodimensional MnO_2

Figure 3 showed TEM image of MnO_2 nanoparticles. The almost of MnO_2 particles have almost the same dimension of around 50 nm.

The effect of organic solvents on formation of elements existing in water solution was reviled [7] and applied in chemistry since a long time [8]. This effect on nanoscale particles formation may caused by changing 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 water structure, competition of hydration and solvation and for long chain molecule solvent, there appeared net-like of solvent molecules in water solution; that hampered molecules and ions association and crystals growing.

3.1.2. Nanodimensional MnO_2 adsorbent

Figure 4 and 5 showed surface of denaturated laterite before and after coating of MnO_2 particles.

On SEM images in the same scale we can easily recognize different surface picture of the material before and after coating nanodimensional MnO_2. Before coating, the surface of laterite was quite smooth; but after coating there ware nanocrystals of MnO_2 in barbed shape sphere distributed tight all over laterite surface.

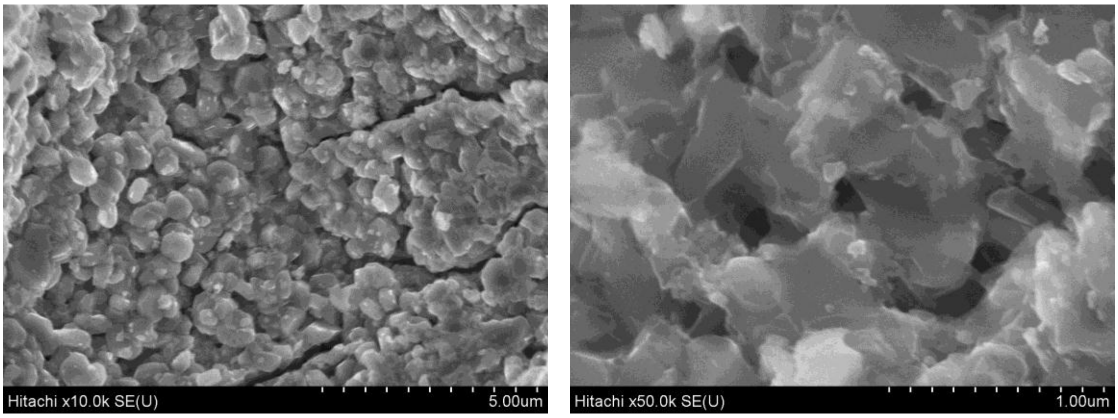


Figure 4. SEM image of denaturated laterite surface before nano MnO_2 coating

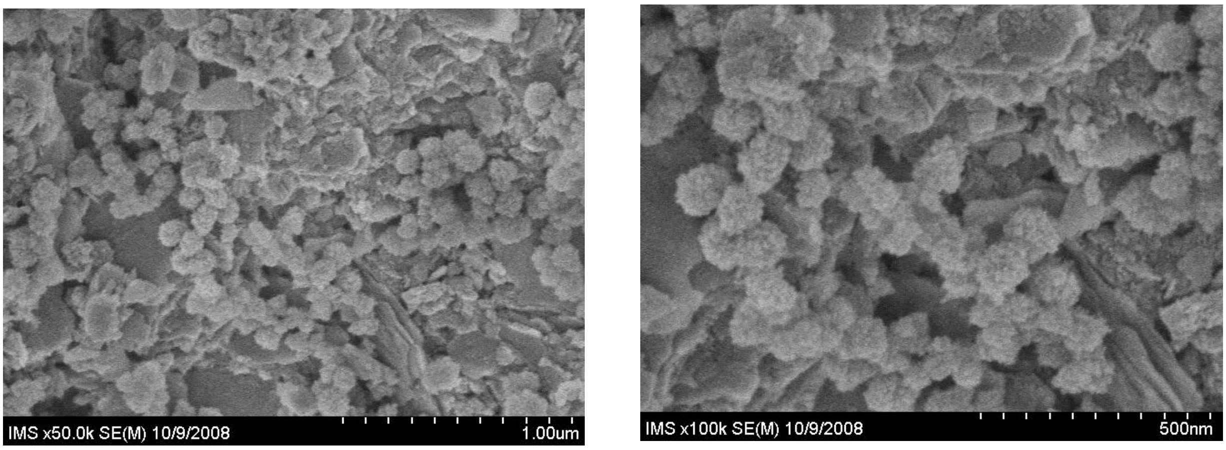


Figure 4. SEM image of denaturated laterite surface after nano MnO_2 coating

The clinging of MnO_2 nanoparticles on denaturated laterite surface was recognized for application purpose, but the essence of this phenomenon was not investigated so far. For example is there any chemical bond, binding energy, reformation of nanoparticles or inactivation…

3.1.3. Arsenic sorption equilibrium investigation

1 gram adsorbent was dropped into 250 ml arsenic solution of 1000 ppb concentration. The solution was stirred continuously. Periodically arsenic concentration was determined. The investigation results were showed in figure 5.

From figure 4, the equilibrium adsorption time was 8 hours determined, because the arsenic concentration in water phase was almost unreduced after 8 hours adsorption.

3.1.4. Arsenic adsorption capacity investigation

The Langmuir Isothermal Curve was established with the range of initial concentration from 0.00 to 100 ppm and the result was showed in figure 5.

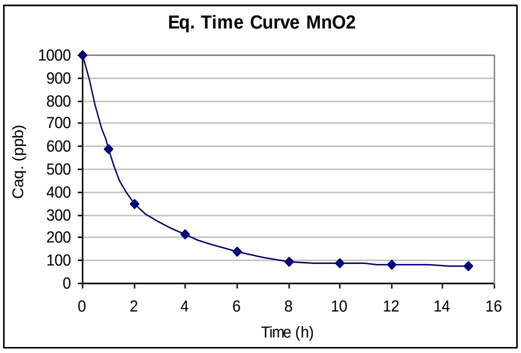


Figure 4. Reduction of arsenic concentration upon the sorption time

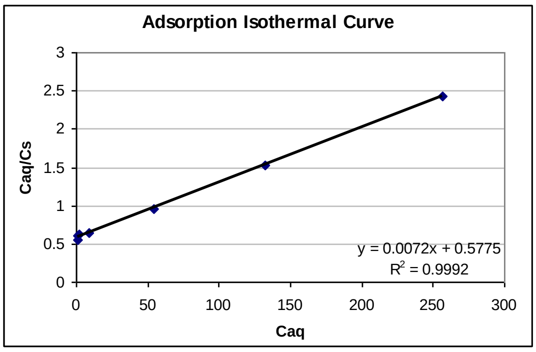


Figure 5. The Langmuir adsorption Isothermal Curve

From Langmuir Isothermal Equilibrium in the form of

$$\frac{C_l}{C_r} = \frac{1}{b.C_m} + \frac{C_l}{C_m}$$

where C_l and C_r is arsenic equilibration concentration in liquid and solid phase respectively; C_m is maximum concentration of arsenic in adsorbent. We can determine C_m (maximum adsorption capacity of adsorbent) by graphic method. The curve of relation between C_l/C_r upon C_l is linear curve with angle coefficient $1/C_m$ and inverse value of this coefficient is C_{max}.

The maximum adsorption capacity was determined of 138.89 mg arsenic per 1 gram of adsorbent. The maximum adsorption capacity of denaturated laterite was only 0.48 mg arsenic per 1 gram adsorbent and those of MnO_2 reached to value of approximately 2,00 mg arsenic per gram adsorbent [9].

In competition of C_{max} of denaturated laterite and common precipitation MnO_2, the C_{max} of nano MnO_2 coated material was sharply increased (from 70 to 290 times higher). There were no other reasons than nanodimensional effect of prepared MnO_2 particles.

3.2. Nanodimensional FeOOH

3.2.1. Nanodimensional FeOOH formation

FeOOH particles with nanoscale were preparation according to procedure mentioned at experiment part. Their TEM image was presented on figure 6. The uniform needle shape nanocrystals of FeOOH picture were found clearly and their dimension was about 40 × 10 nm.

Ethanol concentration in hydrolyzing solution strongly influenced on nanodimensional FeOOH formation. In the range of 0 to 20% ethanol, mass percentage of nano FeOOH created sharply increased and reached more than 75%, then slowly decreased when concentration of ethanol was 20 to 80% and lightly increased again after 80%. In solution of 100% ethanol, the nano FeOOH formation was not better than this in 10% ethanol solution. So hydrolyzing medium was chosen as 20% ethanol in water for our application. Other organic solvents were tested but the results were presented in other publication.

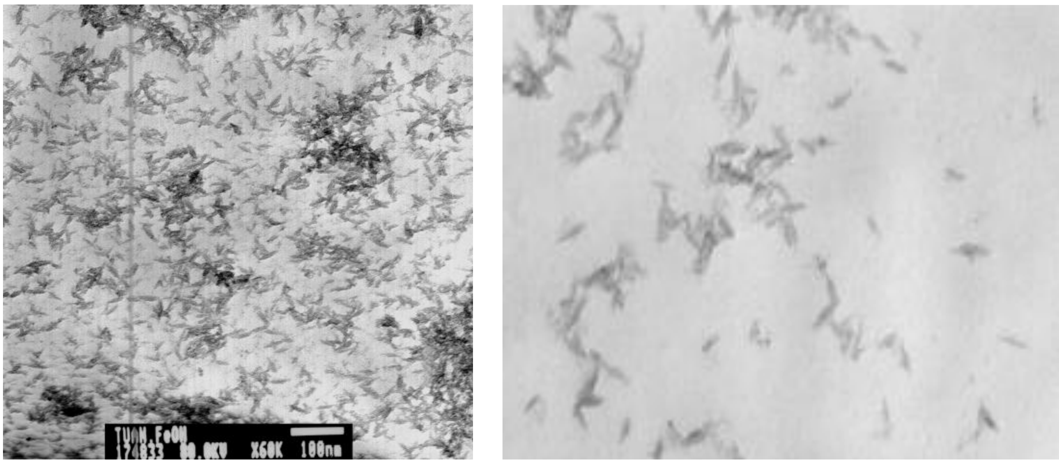


Figure 6. TEM image of FeOOH nanoparticles

3.2.2. Nano FeOOH adsorbent

The procedure of nano FeOOH coating on denaturated laterite was done by the same way as MnO_2 coating. The SEM image of adsorbent surface was showed in figure 8.

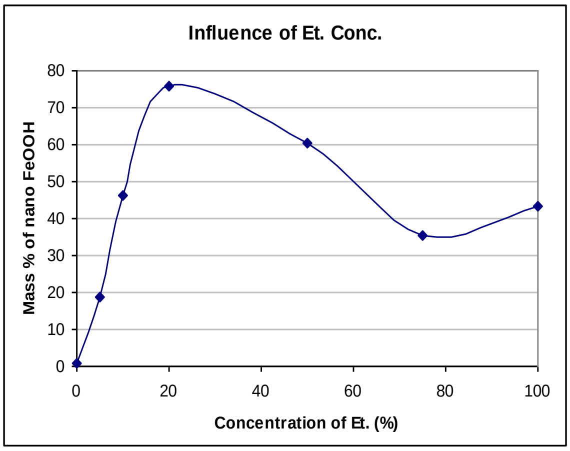
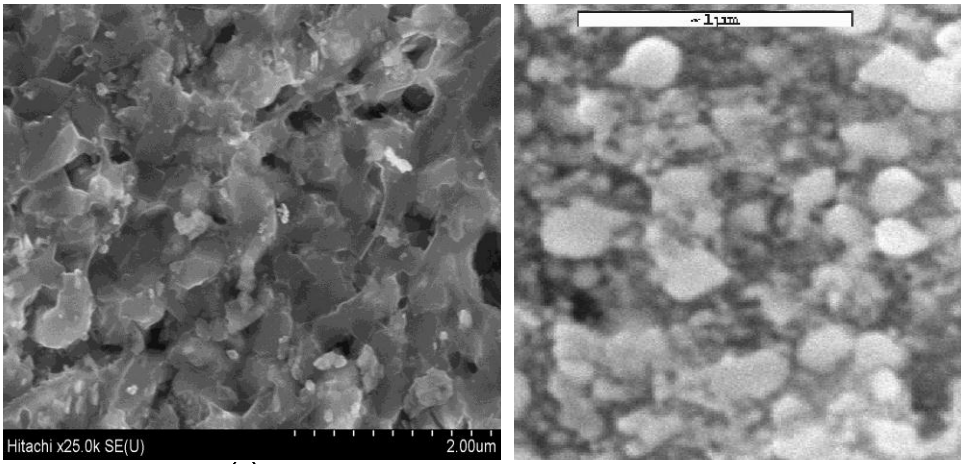


Figure 7. Influence of Ethanol concentration on nano FeOOH formation

3.2.3. Arsenic adsorption equilibrium and adsorption capacity investigation

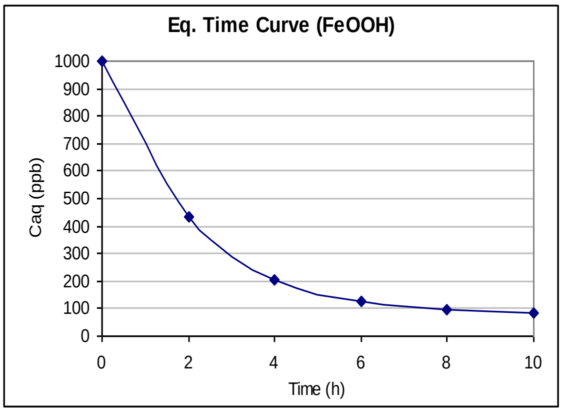
Upon the adsorption time in the range of 0 to 10 hours, arsenic concentration in liquid phase decreased. After 6 hour, the concentration of arsenic reached the level about 100 ppb from 1000 ppb initiated and then almost didn't drop yet (figure 9). So 6 hours adsorption was recognized as adsorption equilibrium time.

The maximum adsorption capacity (C_{max}) was determined from Langmuir Isothermal Equation by graphic method. The determination process was done similarly for MnO_2 coated material. From the isothermal curve in figure 10, the value of parameter $1/C_m$ was 0.0109, so the C_{max} value was determined of 91.74 mg arsenic per 1 gram adsorbent respectively.



(a) (b)

Figure 8. Laterite surface before (a) and after (b) coating nano FeOOH



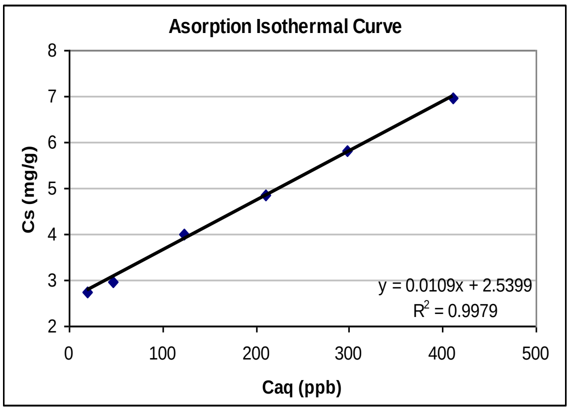


Figure 9. Adsorption equilibrium tine

Figure 10. Adsorption isothermal curve

4. CONCLUSION

Effect of organic solvents on nanoparticles of metals oxide formation during chemical precipitation was used for developing effectivity of nanodimensional materials preparation. This is the important way for chemists to expand their activity into nanoscience and nanotechnology.

Coating nanodimensional particles on very common materials could create high performance sorption materials useful for removal toxic substances in drinking water and other environmental objects.

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