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Preparation of nano-structural MnO_2 in ethanol-water media coated on calcinated laterite and study of its arsenic adsorption capacity

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Abstract. Nano-dimensional MnO_2 were prepared in ethanol – water media from their inorganic salts by parallel redox reactions. The pH of solution, concentration of the salts and ethanol as well as reaction temperature were the key parameters for forming of nano-particles and anticoagulation. The MnO_2 particles in colloidal solution then were coated on calcinated laterite grains to create new adsorption materials. The structure and surface of materials were studied by TEM and SEM methods.

The arsenic adsorption ability of the material was investigated with imitative and real samples. In the optimum conditions, maximum arsenic adsorption capacity reached the value of 139 g per kg. Created material was stable in water media and easy to regenerate when it was saturated adsorption by arsenic.

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 nanostructure of metals' oxides and the second was coating the prepared nano-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 different physical effects during hydrolysis of metals' ions [3] or using thermal and chemical disintegration of suitable reagents [4,5].

In this article, the effects of organic solvent in water media were used for creation of nanodimensional MnO_2 from their inorganic salts. The pH of solution, concentration of the salts, the portion of organic solvent and reaction temperature were strongly influenced on the quality of the product. Prepared nanodimensional

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particles were coated on denaturated laterite to create new high performance adsorption materials.

Rinsed off the supernatant and washed material by solution with the same ethanol portion and dried it through 4 hours in 105°C.

2. Experiment

Preparation of nanodimensional MnO_2 adsorbent

The experimental process was realized with different ethanol concentrations from 0% to 100% in series solutions of $MnSO_4$ and $KMnO_4$.

Therefore, working solutions of Mn(II) are series of 0, 5, 10, ..., 100 % of ethanol in 3.10^{-2} $MnSO_4$ solution. Similarly, working solutions of Mn(VII) include series of 0, 5, 10, ..., 100 % of ethanol in 2.10^{-2} M $KMnO_4$ solution.

The procedure of MnO_2 nanoparticles formation was followed: slowly add series of $KMnO_4$ solutions one by one into the series of $MnSO_4$ solutions. The dropped rate of mixed reagent 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 stoichiometry.

Coating of nanodimensional MnO_2 on denaturated laterite was realized as below: weighed 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.

Arsenic adsorption test

Let MnO_2 coated materials contact with arsenic solution. Then concentration of arsenic in water phase was determined along the sorption time and after the time, when sorption reached equilibrium state by AAS (on the Spectrophotometer AA-6800, Shimadzu).

3. Results and discussion

Nanodimensional MnO_2 formation

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

EP_2 \ EP_1	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

Table 1 showed strong effect of ethanol concentration 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 laid in the area where concentration of ethanol in $KMnO_4$ solution was from 25 to 50% and in $MnSO_4$ solution was 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.

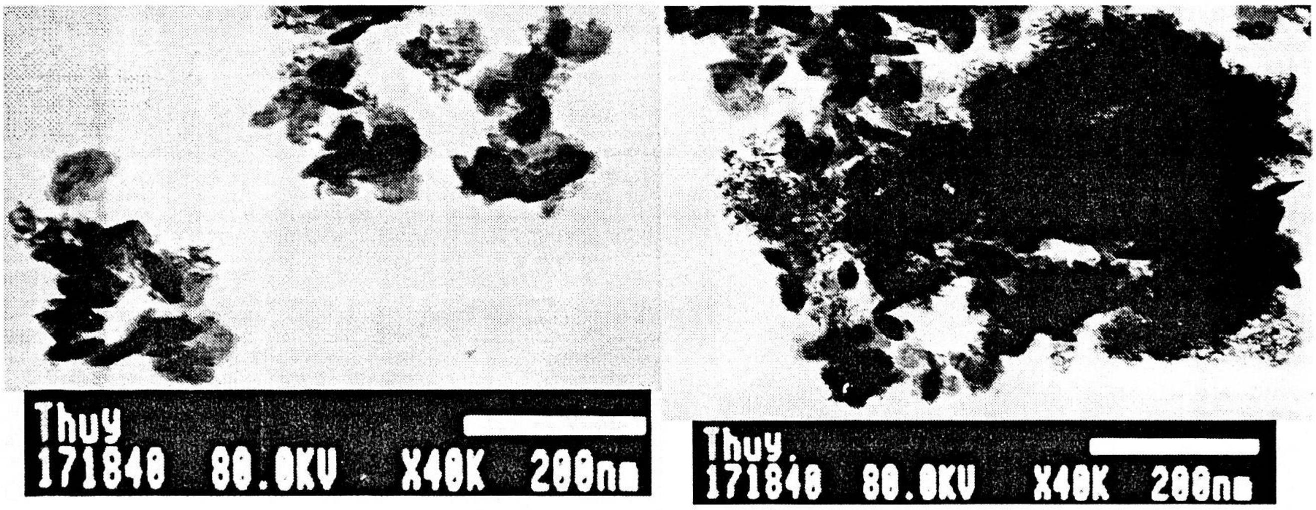

Fig. 1. TEM image of nanodimensional MnO_2.

Figure 1 showed TEM image of MnO_2 nanoparticles. The almost of MnO_2 particles have the same dimension with the length approximate 60 nm and the width 20 nm.

The effect of organic solvents on formation of chemical elements existing in water solution was revealed [6] and applied in chemistry since a long time ago [7,8]. This effect on nanoscale particles formation may caused by changing of 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.

Nanodimensional MnO_2 adsorbent

Figure 2 and 3 described the surface of denaturated laterite before and after coating of MnO_2 particles.

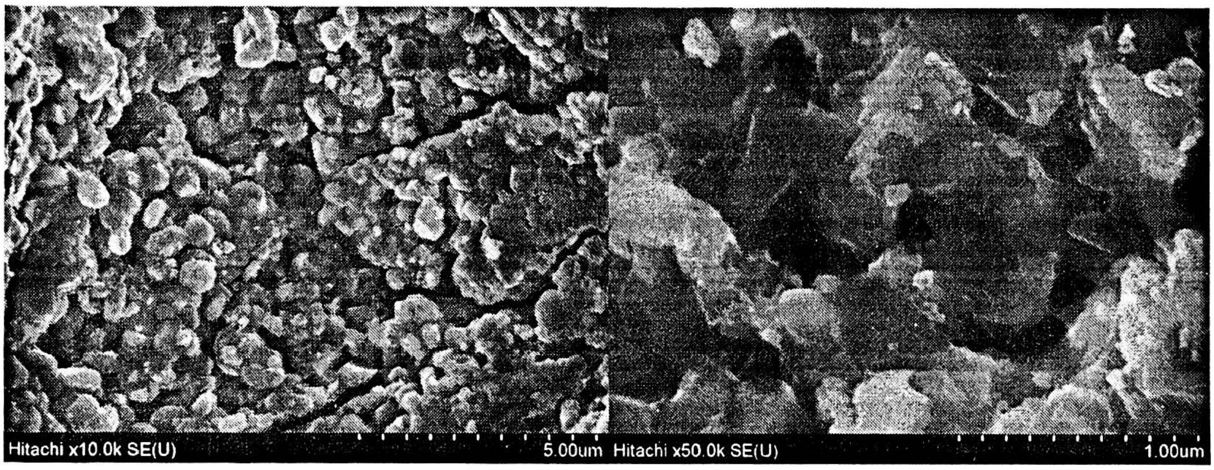

Fig. 2. SEM image of denaturated laterite surface before nano MnO_2 coating.

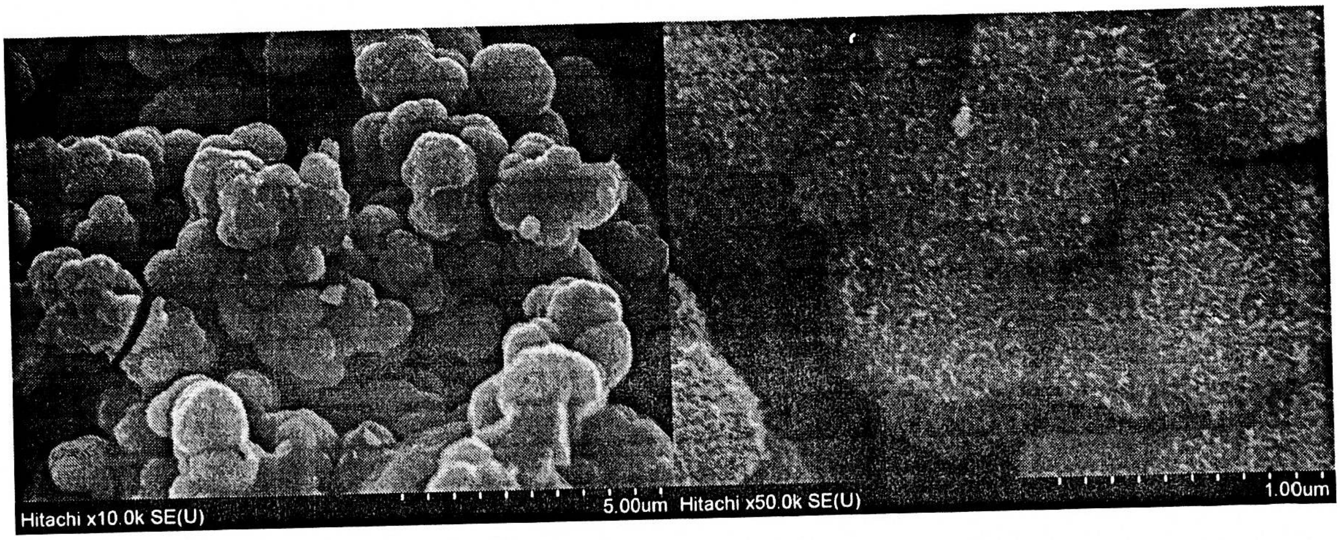

Fig. 3. SEM image of denaturated laterite surface after nano MnO_2 coating.

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 needle shape distributed tightly all over laterite surface.

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...

Arsenic adsorption 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 4.

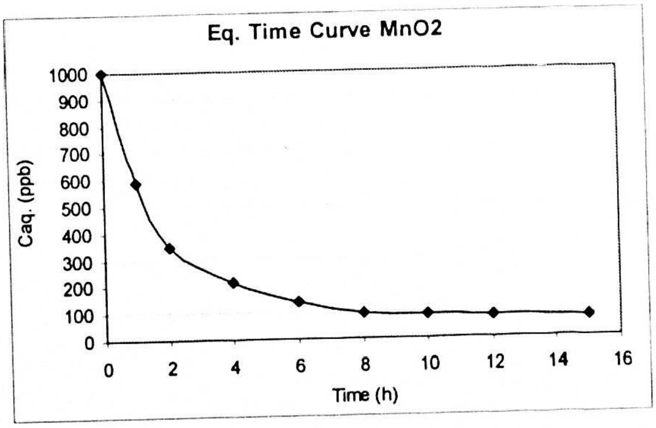

Fig. 4. Reduction of arsenic concentration upon the sorption time.

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.

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.

From Langmuir Isothermal Equilibrium in the form of

$$\frac{C_{aq}}{C_s} = \frac{1}{b.C_m} + \frac{C_{aq}}{C_m}$$

where C_{aq} and C_s 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_{aq}/C_s upon C_{aq} is linear curve with angle coefficient $1/C_m$ and inverse value of this coefficient is C_{max}.

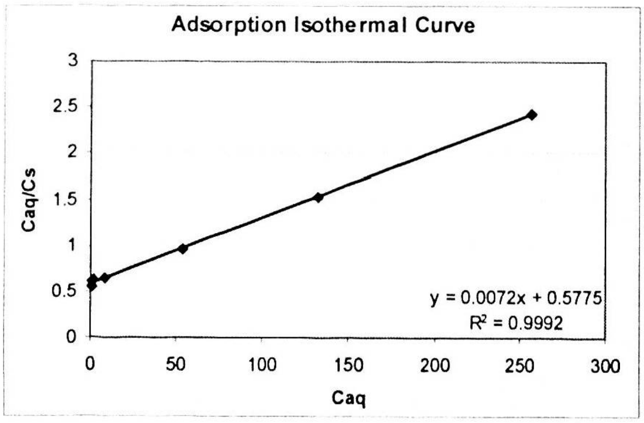

Fig. 5. The Langmuir adsorption Isothermal Curve.

Our research resulted in the C_{max} of denaturated laterite and common precipitation MnO_2 were only 0,48 mg and 2,00 mg arsenic per 1 gram adsorbent respectively (similar of [9]) , while the C_{max} of nano MnO_2 coated material reached to value of 138,89 mg/g.

In competition, the maximum adsorption capacity of nano MnO_2 coated material was sharply increased to 70 and 290 times higher than two mentioned adsorbents. It can be explained as the result of nanodimensional structure effect of prepared MnO_2 particles.

Conclusion

Effect of organic solvents on nanoparticles of metals hydroxide or 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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Điều chế MnO_2 có cấu trúc nano trong môi trường nước-etanol với chất mang laterit biến tính nhiệt và nghiên cứu khả năng hấp phụ Asen của nó

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Mangan dioxit (MnO_2) có cấu trúc nano đã được điều chế từ các dung dịch muối Mn vô cơ trong môi trường nước-etanol nhờ thực hiện phản ứng oxy hóa-khử đồng thời. Các yếu tố chính quyết định sự hình thành dạng nano MnO_2 là pH, nồng độ muối và hàm lượng dung môi hữu cơ trong dung dịch. Tiếp đó, nano MnO_2 vừa điều chế được mang lên các hạt laterit biến tính để tạo ra một vật liệu hấp phụ mới. Khả năng hấp phụ asen của loại vật liệu mới này đã được nghiên cứu và khảo sát trên các mẫu giả và mẫu thực tế. Kết quả cho thấy hấp phụ cực đại đối với asen đạt trên 138g asen/1 kg vật liệu. Vật liệu rất bền trong môi trường nước và có thể tái sinh một cách dễ dàng khi đã hấp phụ no asen.