

Creating nano composite $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ /laterite material applying to treat arsenic compound in groundwater

Chế tạo vật liệu nano composite $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ /đá ong ứng dụng xử lý asen trong nước ngầm

Research article

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This article presents nano composite $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ /laterite materials, which were successfully prepared by hydrometallurgical method. The materials were modified using urea as the nitrogen source. The particles size of the materials is from 20-30 nanometers. The obtained materials can not only absorb arsenic compounds but also enhance the ability of converting As (III) or As (V) into As^0 , which is removed from solution. Arsenic removal efficiency of these materials is high. Using sunlight in a hydraulic retention time, about 180 minutes, the arsenic value at the inflow was about 10 mg/L but the outflow was negligible. Covering $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nano on laterite have brought high economical efficiency, on one hand, it saved material and on the other hand, it can be continuously operated without the centrifugal separation of the nano material.

Bài báo này giới thiệu về phương pháp điều chế vật liệu nano $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ biến tính nitơ được phủ trên đá ong bằng phương pháp thủy luyện. Vật liệu nano thu được có kích thước 20-30 nm. Vật liệu thu được không những có khả năng hấp phụ các hợp chất của asen mà còn có khả năng khử As (III) hoặc As (V) thành As^0 khi được chiếu sáng. Sử dụng ánh sáng mặt trời chiếu vào hệ thống xử lý trong thời gian 180 phút có thể loại bỏ được gần như hoàn toàn asen ra khỏi nước mặc dù hàm lượng đầu vào là 10 mg/l. Việc phủ vật liệu $\text{TiO}_2\cdot\text{Fe}_2\text{O}_3$ nano lên đá ong đã mang lại hiệu quả kinh tế cao, một mặt nó tiết kiệm được vật liệu, mặt khác, vật liệu có thể sử dụng một cách liên tục mà không cần phải tách bằng phương pháp ly tâm.

Keywords: Fe_2O_3 , TiO_2 , nano, laterite, urea, arsenic, groundwater

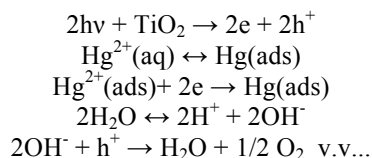
1. Introduction

Arsenic (As) contamination of water is a serious problem in not only Vietnam but also many countries around the world. According to WHO investigations, approximate numbers of 15 million Vietnamese people (about 1/5 of Vietnam population) can be under the risk of arsenic contamination coming from water source unstrictly treated. In order to treat arsenic contaminant in water, several treatment methods have been being developed, in which adsorption (Clifford & Ghurye, 2002; Stumm & Morgan, 1996), anion exchange (Ghurye et al., 1999), reverse osmosis (Sorg & Logsdon, 1978), and coagulation processes (Driehaus et al., 1998; Hering & Elimelech, 1996) are used. Alumina (Clifford & Ghurye, 2002) and hydrat-

ed iron oxide (Hering & Elimelech, 1996) are often used to treat arsenic by adsorption and coagulation methods.

The most common oxidation states of arsenic are -3, +3 and +5, which can be changed to each other via the redox reactions. Fe_2O_3 nano particles are well known as the very important adsorption material for arsenic removal (Savinaa et al., 2011; Sylvester et al., 2007). Nano TiO_2 is a photoactive material which is activated by the light with appropriate wavelength giving the electrons and holes (Hug et al., 2001). Heavy metals will be reduced by the electrons, and thereafter precipitate on the surface of material. For example:

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The aim of this study is finding the suitable conditions for synthesizing the composite materials of nano nitrogen-modified $\text{TiO}_2\text{Fe}_2\text{O}_3$ by using hydrometallurgical method. In these synthesized materials, nano Fe_2O_3 plays the role of adsorbing arsenic on the nano particle surface and nano nitrogen-modified TiO_2 can use the sunlight and undergoes the photoreactions forming the electrons source that supplies for reduction of As (III) or As (V) to As (0), which is then separated out of water. The efficiency of the synthesized materials for arsenic removal from underground water was tested and evaluated.

2. Material and methods

2.1. Chemicals

In this research, chemicals are PVA; $(\text{NH}_2)_2\text{CO}$; NH_4NO_3 ; TiCl_4 ; $\text{Fe}(\text{NO}_3)_3$; laterite; $\text{NH}_2\text{OH.HCl}$; $\text{C}_2\text{H}_5\text{OH}$; methylene blue; Standard solution of AsO_4^{3-} .

2.2. Nano $\text{TiO}_2\text{Fe}_2\text{O}_3$ preparation

The compositions of chemical mixtures are listed in the Table 1. The chemical mixtures were vigorously stirred at 70°C in 24 hours, and then at 90°C in 12 hours, and followed by drying at 120°C in 12 hours. The obtained materials were calcinated at 250°C in 8 hours, and eventually calcinated at 600°C in 3 hours.

Table 1. The composition of chemical mixtures for nano $\text{TiO}_2\text{Fe}_2\text{O}_3$ preparation

Sample names	PVA (4%)	$\text{Fe}(\text{NO}_3)_3$ (1M)	TiCl_4 (0,5M)	$(\text{NH}_2)_2\text{CO}$ (1M)	NH_4NO_3 (1M)	% mol TiO_2
M1	180	60	0	450	60	0
M2	180	50	10	450	60	16,6
M3	180	45	15	450	60	25
M4	180	40	20	450	60	33,3
M5	180	30	30	450	60	50
M6	180	20	40	450	60	66,6
M7	180	10	50	450	60	83,3
M8	180	0	60	450	60	100

2.3. Cover nano $\text{TiO}_2\text{Fe}_2\text{O}_3$ material on laterite carrier

The process of covering material on laterite occurs in steps below:

First, calcine crushed laterite and sieve in the size of 1mm at 1000°C in 3 hours with heat acceleration velocity of $10^\circ\text{C}/\text{min}$. After that, wash it with 1 time distilled water till clear, then continue to wash with 3 times distilled water. Drying at 120°C in 8 hours. Producted sol gel solution add to laterite and continue to stir by stirrer with wings, keep at 90°C in 24 hours. Dry products, combust sol-gel at 250°C , continue to calcine at 600°C in 3 hours with heat acceleration velocity of $10^\circ\text{C}/\text{min}$.

2.4. Analysis

The synthesized materials were characterized by Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) methods to determine the particle sizes.

The photoactivity properties of the materials were investigated by degradation reaction of methylene blue. The testing steps are:

1. Add 0.1 gram of synthesized material in 100ml standard solution of methylene blue; (concentration = 100 mg/L)

2. Test the methylene blue degradation ability of material in the sunlight, or ultraviolet, or dark condition;
3. Sampling times: 30 min; 60 min; 90 min; 120 min; 150 min; 180 min.

Concentration of methylene blue in the solution was measured at the optical adsorption wavelength of 664 nm by UV-Vis Absorption Spectroscopy (Optizen 2120 UV/Shimadzu). The concentrations of arsenic in the samples taken before and after adsorption were determined by using Inductively Coupled Plasma Atomic Emission Spectroscopy (Perkin Elmer Optima 3300 DV).

3. Results and discussions

3.1. Nano $\text{TiO}_2\text{Fe}_2\text{O}_3$ preparation

SEM and TEM pictures show that the materials have generally uniform particles. The obtained materials with the different ratio of $\text{TiO}_2\text{Fe}_2\text{O}_3$ have the different particle sizes ranging from 12 to 30 nm. The most uniform and smallest particles belong to the samples which were synthesized with ratio of $\text{TiO}_2\text{Fe}_2\text{O}_3 = 1:1$.

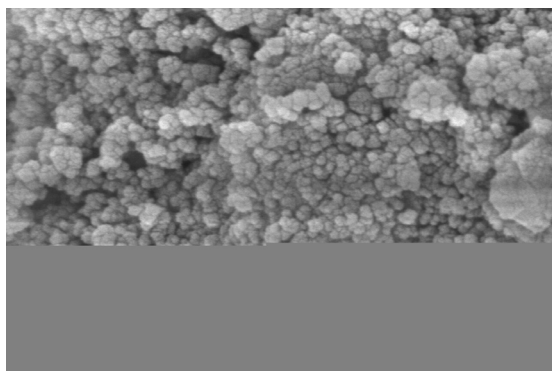


Figure 1. SEM picture of sample M2

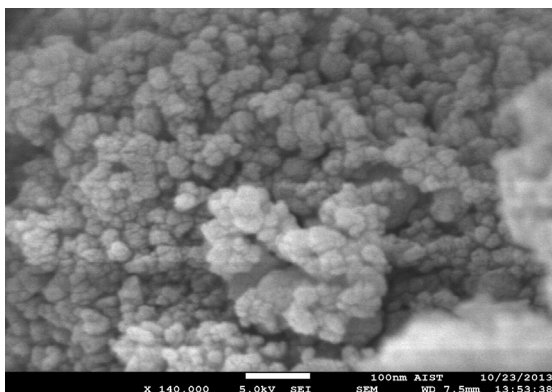


Figure 2. SEM picture of sample M3

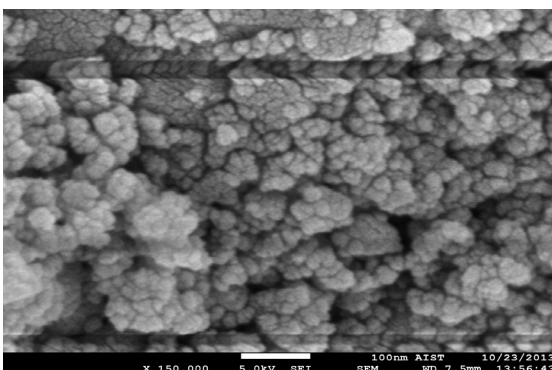


Figure 3. SEM picture of sample M4

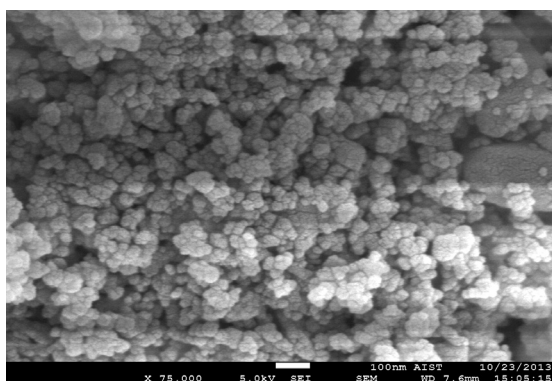


Figure 4. SEM picture of sample M5

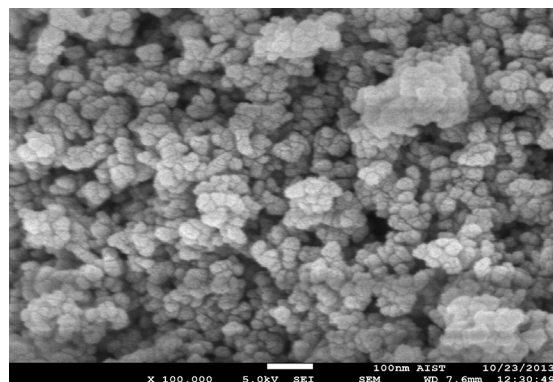


Figure 0. SEM picture of sample M6

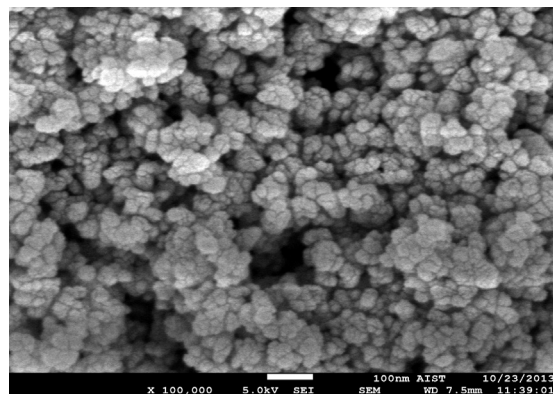


Figure 6. SEM picture of sample M7

To obtain the oxide materials with the particles at nano scale by hydrometallurgical method, the important thing is to get the hydroxide which is small in size, and separated and unaggregated in form. The hydrolysis of urea is at 70 - 90°C. The urea hydrolysis process very slowly occurs forming NH_3 , CO_2 products, and specially OH^- for slow co-precipitation of Ti^{4+} , Fe^{3+} in the form of $\text{Ti}(\text{OH})_4$ and $\text{Fe}(\text{OH})_3$ avoiding their aggregation. Moreover, the addition of polyvinylalcohol (PVA) can also reduce the aggregation ability of hydroxide particles. In the solution containing Ti^{4+} , Fe^{3+} and PVA, the composite reaction of Ti^{4+} , Fe^{3+} combining with OH^- group in the polymer are present resulting in the network broken of this organic polymer.

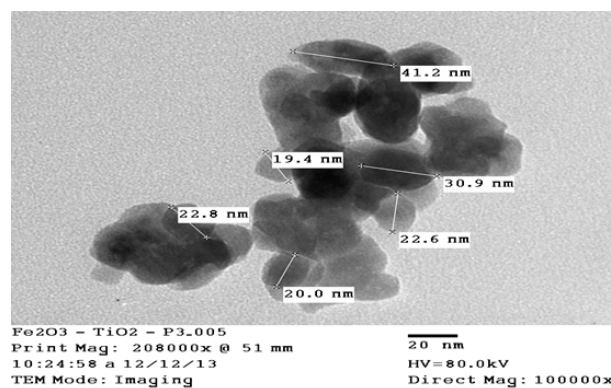


Figure 7. TEM picture of sample M5

As the state is coming to limitation, the tiny oxide particles are formed beside the network (Qin et al., 2008a; Wu et al., 2010). The presence of ammonia and nitrate ions in

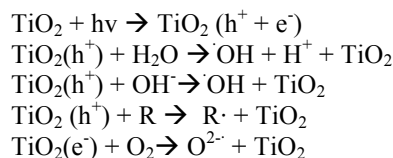
the solution, on one hand, prevents the aggregation. On the other hand, introducing nitrogen source into the system can modify the materials making them to be active at both ultraviolet and visible light (Hongqi Sun, 2008; Qin et al., 2008b).

3.2. Photoactive ability of Fe₂O₃.TiO₂ materials

The obtained materials were tested their ability of giving the electrons and holes in the light conditions as predicted or not.

The results show that all obtained materials are able to remove methylene blue. The material containing only Fe₂O₃ (M1) has quite low percentage of methylene removal. The adsorption maybe the only process taking place in the case of material M1 and resulting in low methylene blue removal. As the ratio of TiO₂ in the materials is increased, the percentage of methylene removal of

materials also increases, especially the pure TiO₂ material (M8) having 97% of methylene removal after 120 min of treatment. This means that the removal of methylene blue is probably contributed by two processes: adsorption and photocatalytic reaction, in which the photocatalytic ability of the materials plays more important role than that of adsorption ability. The photocatalytic process can be described as the steps below (Qin et al., 2008a; Qin et al., 2008b; Wu et al., 2010):



The products formed in the process are very strong oxidative, and they oxidize the organic compounds to CO₂ and H₂O.

Table 2. The results of photoactive ability of the synthesized materials using methylene blue

Sample/time	Percentage of methylen blue removed (%)			
	30 min	60 min	90 min	120 min
M1	16,7%	26,7%	24,5%	27,1%
M2	24,1%	25,6%	26,4%	32,7%
M3	23,8%	24,6%	32,2%	32,3%
M4	26,4%	30,2%	32,9%	33,1%
M5	31,9%	32,3%	32,9%	33,9%
M6	32,9%	35,7%	41,6%	43,7%
M7	33,9%	41,4%	55,6%	63,9%
M8	34,7%	62,6%	86,6%	97%

From the research results, it can be clearly seen that the obtained nano materials have high photoactive abilities. It also means that the synthesized materials can be the source supplying the electrons for reduction process in the light conditions.

3.3. Ability of arsenic removal

The abilities of materials for arsenic removal were investigated under the conditions: the input arsenic concentra-

tions of 200 ppb, 1000 ppb and 10000 ppb; 1g of material per 1L; 1 hour of action time; and different light conditions: dark, sunlight, and ultraviolet.

The results obtained from the investigation of arsenic removal with input concentration of 200 ppb are shown in the Figure 8.

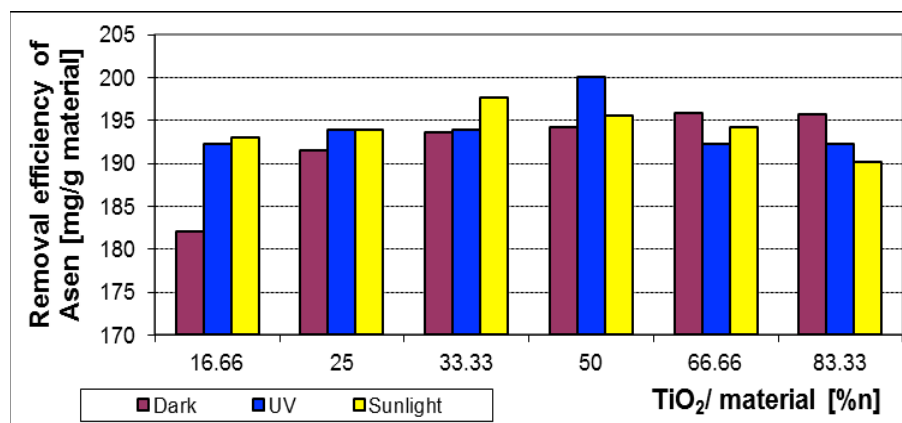


Figure 8. Efficiency of synthesized material on removing arsenic in the different light conditions. Input arsenic concentration of 200 ppb

It can be seen that in the dark condition the arsenic removal ability of the materials increases as the amount of TiO₂ in the materials is increased. This can be explained by the fact that TiO₂ also has ability of arsenic adsorption. The material with TiO₂/Fe₂O₃ ratio of 2:1 has the maximum arsenic amount adsorbed. In the sunlight condition, the highest ability of arsenic removal belongs to the material with TiO₂/Fe₂O₃ ratio of 1:2. From the comparison between two cases (dark and sunlight conditions), it can be confirmed that the arsenic removal of the materials occurs via not only adsorption process, but also via photo activity process.

The results of arsenic removal in ultraviolet condition show that the material with TiO₂/Fe₂O₃ ratio of 1:1 has the highest efficiency approaching almost 100% in case of input arsenic concentration of 200 ppb. This is also the highest result in comparison among three light conditions (dark, ultraviolet, and sunlight) investigated.

3.4. Effect of time on arsenic removal

Arsenic removal efficiency of the materials as a function of time was investigated under the conditions: time period of 30 – 180 minutes; the input arsenic concentrations of 1000 ppb and 10000 ppb; 1g of powder material per 1L, 1kg laterite and 1 kg TiO₂.Fe₂O₃/laterite; and different light conditions: dark, UV and sunlight.

Figure 9 shows that in dark condition the arsenic amount removed increases as the investigation time is increased. After 60 min, 1gram of synthesized material can remove 0.98 mg of arsenic. Prolong the investigation time results in the maximum amount of arsenic removed, which is about 1.01 mg/1 gram of material. So, it can be seen that the removal of arsenic in the dark condition is just because of the adsorption process (Savinaa et al., 2011; Sylvester et al., 2007).

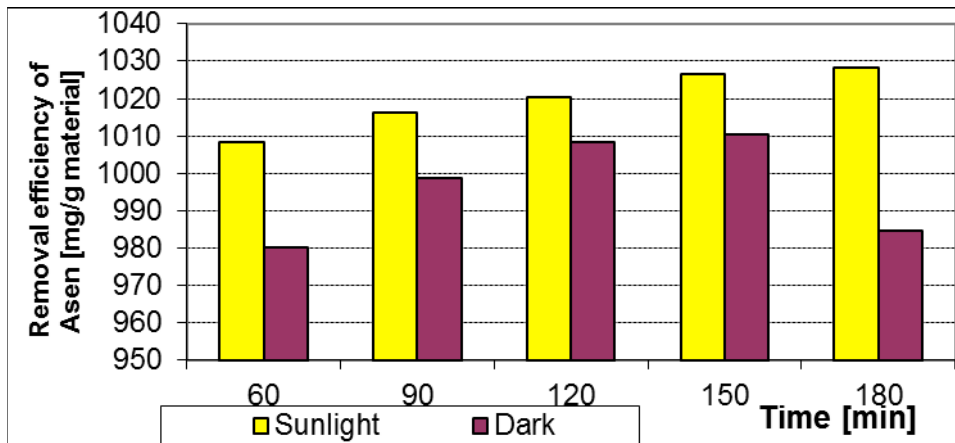


Figure 9. Arsenic removal efficiency of material with TiO₂/Fe₂O₃ ratio of 1:1 as a function of time in different light conditions. Input arsenic concentration of 1000 ppb

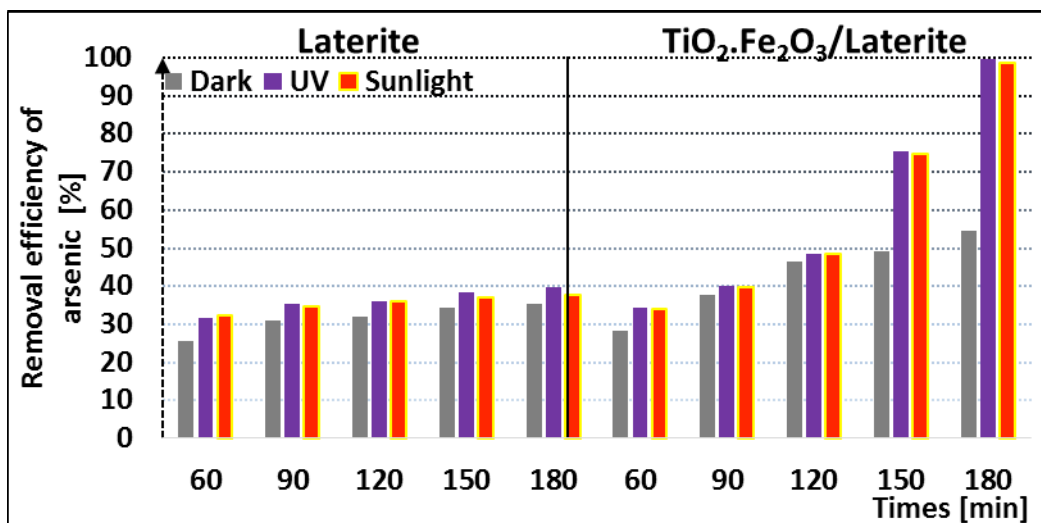
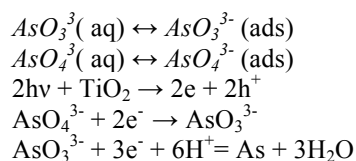


Figure 10. Arsenic removal efficiency of material with TiO₂.Fe₂O₃/laterite as a function of time in different light conditions. Inflow arsenic concentration of 10000 ppb

Figure 10 shows that in dark condition the arsenic amount removed increases as the investigation time is increased. After 60 min, 1kg of laterite can remove about 25,37 %

(about 2,537 mg) of arsenic, when HRT extended to 180 minutes, the amount of removed arsenic is increasing, it achieve about 35.35%. Whereas, TiO₂.Fe₂O₃/laterite ma-

terials can remove better arsenic (see figure 10). This can be explained that, the nano materials ability to adsorb arsenic very good. So, it can be seen that the removal of arsenic in the dark condition is just because of the adsorption process (Savinaa et al., 2011; Sylvester et al., 2007). When sunlight or UV conditions are used, arsenic removal ability of the materials increases. The results obtained in the sunlight condition are always higher than that in the dark condition. Laterite can remove arsenic highest achieve about 40% used UV conditions after 180 minutes. Meanwhile, TiO₂.Fe₂O₃/laterite materials can removed better. Arsenic removal efficiency can reach 99% in the UV conditions and of 98% sunlight condition. Almost 99% arsenic amount were removed after 180 min. In this research condition, the material nano TiO₂.Fe₂O₃/laterite has higher adsorption ability than casual laterite material. Simultaneously, in illuminated condition, its arsenic removal efficiency increase from 25% to 45%. This means that the light condition plays an important role in the arsenic removal using the synthesized materials. Based on the results obtained, it can be found that the arsenic removal by using the nano composite TiO₂.Fe₂O₃/laterite materials may undergo through two processes. The first process is the adsorption of ions on the surface of materials. The second process is the receiving proton in the light condition and leaving electrons to arsenic ions forming As⁰, which then is separated out of water. The mechanisms are described as follow:



The combination of adsorption and oxidation-reduction processes gives very high efficiency of the arsenic treatment. The results also show that that this material remove arsenic in sunlight condition achieve the result equivalent to UV.

4. Conclusions

Nano composite nitrogen-modified F₂O₃.TiO₂ materials with Fe₂O₃/TiO₂ ratio of 1:1 and TiO₂.Fe₂O₃/laterite were successfully prepared. The obtained materials have very high efficiency of arsenic removal. The materials use their photoactivity to form the electrons source for arsenic ions being converted to As⁰ which then was removed out of water. The results of this research bring the promised method for treating As contaminated ground water.

5. Acknowledgements

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6. References

- [1] Clifford, D.A., Ghurye, G.L. 2002. Metal-oxide adsorption, ion exchange and coagulation-microfiltration for arsenic removal from water. New York: Marcel Dekker, Environmental chemistry of Arsenic
- [2] Driehaus, W., Jekal, M., Hildebrand, U. 1998. Granular ferric hydroxide: a novel adsorbent for the removal of arsenic from natural water. *Water SRT*, 47, 30-35
- [3] Ghurye, G.L., Clifford, D.L., Tripp, A.R. 1999. Combined nitrate and arsenic removal by ion exchange. *Am Water Works Assoc*, 91, 85-96
- [4] Hering, J.G., Elimelech, M. 1996. Arsenic removal by enhanced coagulation and membrane processes. Report 90706. Denver, CO: American Water Works Association and Research Foundation.
- [5] Hongqi Sun, Y.B., Wanqin, J., Nanping, X. 2008. Visible-light-driven TiO₂ catalysts doped with low-concentration nitrogen species. *Journal of Photochemistry and Photobiology A: Chemistry*, 92, 76-83.
- [6] Hug, S.J., Canonica, L., Wegelin, M., Gechter, D., von-Gunten, U. 2001. Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. *Environ. Sci. Technol.*, 35(10), 2114–2121.
- [7] Qin, H.-L., Gu, G.-B., Liu, S. 2008a. Preparation of nitrogen-doped titania using sol-gel technique and its photocatalytic activity. *Materials Chemistry and Physics*, 112(2), 346-352.
- [8] Qin, H.-L., Gu, G.-B., Liu, S. 2008b. Preparation of nitrogen-doped titania with visible-light activity and its application. *Comptes Rendus Chimie*, 11(1-2), 95-100.
- [9] Savinaa, I.N., Englisha, C.J., Whitbya, R.L.D., Zheng, Y., Leistner, A., Mikhalovsky, S.V., Cundya, A.B. 2011. High efficiency removal of dissolved As(III) using iron nanoparticle-embedded macroporous polymer composites. *Journal of Hazardous Materials* 192, 1002–1008.
- [10] Sorg, T.J., Logsdon, G.S. 1978. Treatment technology to meet the interim primary drinking water regulation for inorganics. Part 2. *J. Am Water Works Assoc*, 70, 379-392.
- [11] Stumm, W., Morgan, J.J. 1996. Aquatic chemistry: chemical equilibria and rates in natural waters, New York: Wiley.
- [12] Sylvester, P., Westerhoff, P., Möller, T., Badruzaman, M., Boyd, O. 2007. A hybridsorbent utilizing nanoparticles of hydrous iron oxide for arsenic removal from drinking water. *Environ. Eng. Sci.*, 24, 104–112.
- [13] Wu, D., Long, M., Cai, W., Chen, C., Low, Y.W. 2010. Temperature hydrothermal synthesis of N-doped TiO₂ photocatalyst with high visible-light activity. *Journal of Alloys and Compounds*, 502(2), 289- 294.