Volume 5, Issue 3, 2015, 949-953 ISSN 2069-5837
Biointerface Research in Applied Chemistry
www.BiointerfaceResearch.com
Original Research Article Open Access Journal
Received: 10.05.2015 / Revised: 12.06.2015 / Accepted: 14.06.2015 / Published on-line: 15.06.2015

Refine and characterization of diatomite for the excipients of food and medicine

Xiaomeng Guan [1], Shaojun Lei [1], Jean Felix Mukerabigwi [1], Yingjie Zhang [1], Yu Cao [1,*], Shufang Wang [2]
[1]Key Laboratory of Pesticide and Chemical Biology (Ministry of Education), College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China
[2] Blood Transfusion Department, the General Hospital ofthe People's Liberation Army, Beijing 100853, China
*Corresponding author e-mail address: ***caoyu@mail.ccnu.edu.cn***

ABSTRACT
Diatomite is a kind of biogenic siliceous sedimentary rock, and amorphous gel. Due to the porous structure, low density, high specific surface area and low price, diatomite is widely used in many areas, such as food, medicine, ecological building materials, pesticide carriers, and environmental protection as a super adsorbent. Some research investigated that removing of impurities from diatomite can enhance the high specific surface area effectively, and increase the adsorption capacities of diatomite. In our study, we carried out a series of experiments about diatomite purification through calcination and acid leaching (*i.e.* at low temperature drying, high temperature roasting, drying, acidification, drying), to get the modified diatomite. Thus, every modified method on the removal-iron rate was explored to show the degree of purification.
Key words: *Diatomite,modified, purification,removal-iron rate,specific surface area.*

1. INTRODUCTION

The diatomite is a fossil diatom accumulation deposit. Its major chemical constituent is SiO_2, which also contains other minerals, such as Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, P_2O_5 and quite big specific area in the diatomite [1]. As a kind of valid filter aid, the diatomite was extensively used in food and medicine industry [2-4]. Due to its advantages such asrenewability and low-cost, it can be used to replace the activated carbon to become a new material for adsorbing suspension [5-9].

Moreover, diatomite cannot only be used for adsorption and degradation of organic pollutants, but also it can absorb a large amount of inorganic ions, toxic gas without secondary pollution, which has a great potential toward green environmental materials [10-13].Diatomite can control the releasing rate of the drug by improving its utilization, and it has a good biological compatibility. It was reported that diatomite could be an ideal material to replace part of silicon dioxide for the excipients of food and medicine [14]. Therefore, the purification of diatomite has become a hot issue in the research field. The removal of organic matters from the diatomite could result into the increased holes the specific surface area of the diatomite, as well as the content of the silica, which is mostly achieved through calcination method. Removing the metal oxide from the diatomite with the method of hot acid leaching is another direction of purification, which also increases the content of silica in the diatomite. The method of hot acid leaching cannot only improve the quality and purity of diatomite, but also can reduce the density by increasing the volume of holes and specific surface area of diatomite.Fortunately, the acid solution used through pickling purification method can be reused [15-17].

In order to get the high purified quality of diatomite at lowest cost, this paper takes two methods in the purification of diatomite. The first method combines calcination and hot acid leaching, the other uses the way of carbon-white (SiO_2•nH_2O) to treat diatomite, which includes alkali fusion and neutralization.

2. EXPERIMENTAL SECTION

2.1.Materials.

Raw diatomite and filter aid were obtained from LinjiangTianyuan catalyst Co. Ltd.Hydrochloric acid (AR),Hydrofluoric acid (AR),gracial acetic acid 99.5%, Ammonium ferric sulfate (AR)and sulfuric acid (AR) were purchased from Sinopharm Chemical Regent Co.Ltd. Rhodamine(RB) (AR),sodium hydroxide (AR), nitric acid (AR) anhydrous sodium acetate,1,10-Phenanthroline anhydrous 99%,hydroxylamine hydrochloride were kindly suppliedby Tianjin Fuchen Chemical Regent Factory.

2.2. Experimental procedure.

2.2.1. Diatomite purification.

2.2.1.1. Raw diatomite acid leaching with various concentrations of hydrochloric acid.

Four 500mL beakers filled with 300 g HCl with variousconcentration *i.e.*5%HCl, 10%HCl, 15%HCl, 20%HCl were prepared, thereafter,60g raw diatomite was dispersed into each beaker. The surly was heated under oil bath at 100^{o}C for 2 h, with continuously magnetic stirring. Thereafter the mixture was cooled down at room temperature and filtrated, then washed with 100 mL of concentrated HCl(concentrated hydrochloric acid: water =1: 4), and again wash 4 times with distilled water(200ml each time). Then the product was put into muffle furnace at 500^{o}C for 2 h. The obtained product was milled to obtain a fine powder.

2.2.1.2. Calcination and acid leaching of diatomite.

Four different samples each composed of 60 g raw diatomite were initially put into muffle furnace at 500^{o}C for 2 h. Then, the sample was dispersed into four 500mL beakers filled with 300 g HCl with various concentrations *i.e.*5%HCl, 10%HCl, 15%HCl, 20%HCl, respectively. The surly was heated under oil bath at 100^{o}C for 2 h, with continuously magnetic stirring. Thereafter the mixture was cooled down at room temperature and filtrated, then washed with 100 mL of concentrated HCl(concentrated hydrochloric acid: water =1:4), and again wash 4 times with distilled water(200ml each time). Then the product was put into muffle furnace at 500^{o}C for 2 h. The obtained product was milled to obtain a fine powder.

2.2.1.3. Calcination and acid leaching of diatomite with different solid-liquid ratio.

Five different samples each composed of 60 g raw diatomite were initially put into muffle furnace at 500^{o}C for 2 h. Then, thesample was transferred into five 500mL beakers filled with 108g,240g,300g,360g,and 420 g of 10% HCl (the solid-liquid ratio was: 1:3,1:4,1:5,1:6, and 1:7, respectively).The mixture was heated under oil bath at 100^{o}C for 2 h, with continuouslymagnetic stirring. Thereafter the mixture was cooled down at room temperature and filtrated, then washed with 100 mL of concentrated HCl(concentrated hydrochloric acid: water =1:4), and again wash 4 times with distilled water(200ml each time). Then the product was put into muffle furnace at 500^{o}C for 2 h. The obtained product was milled to obtain a fine powder.

2.2.1.4. Calcination and acid leaching of diatomiteat different reaction time.

Six different samples each composed of 60 g raw diatomite were initially put into muffle furnace at 500^{o}C for 2 h. Then the sample was added into six500mL beakers, each filled with 240g of 10%HCl (the solid-liquid ratio=1:4). The mixture was heated under oil bath at 100^{o}C for different fixed time i.e.0.5 h, 1 h, 2 h, 3 h, 4 h, and 5 h, with continuously magnetic stirring. Thereafter the mixture was cooled down at room temperature and filtrated, then washed with 100 mL of concentrated HCl(concentrated hydrochloric acid: water =1:4), and again wash 4 times with distilled water (200ml each time). Then the product was put into muffle furnace at 500^{o}C for 2 h. The obtained product was milled to obtain a fine powder.

2.2.1.5. Preparation of carbon-white (SiO_2 • nH_2O).

100 g of raw diatomite was added into 1L beaker filled with 300 mL of distilled water and 60 g of NaOH. The mixture was heated until it boil for 5 min, then cooled down at room temperature and filtrated then washed with 400 mL of distilled water. Thereafter, 800 mL of distilled water was added to the obtained product, and then the concentrated H_2SO_4acid was added with heating to boil. The product was filtrated and washed, then dried into an oven at 80^{o}C for 12 h. The obtained product was milled to get the fine powder.

2.2.2.The characterization of diatomite.

2.2.2.1.The analysis of specific surface area.

The specific surface and pore size of the diatomite purified through: (a) acid leaching, (b) calcination and (c)carbon-white (SiO_2•nH_2O) was analyzed byV-Sorb 2800P Specific Surface Area and Pore Size Analyzer.

2.2.2.2. The morphology analysis.

The surface morphology of the diatomite purified through: (a) acid leaching, (b) calcination and (c) carbon-white (SiO_2•nH_2O) was determined by using Scanning electron microscope, Quanta 450 FE G, (FEI Hong Kong Limited, China). The sample was coated with sputter-coated with a thin layer of gold and the morphology of the composite was observed at 15 kV accelerating voltage.

2.2.3.The iron content test.

Prior to determine the iron content of the raw and purified diatomite, the sample was pretreated through digestion as follow: 0.2 g of well dried diatomite micro powder was transferred into 250 mL beaker and 5 mL concentrated $HNO_3$and cover the container with watch glass then heat the solution under hot plate at 120^{o}C for 20 min.The solution was cooled down and after, the5mL concentrated HF was added to the mixture and heated at 120^{o}C to evaporate HF. The solution was cooled down until the strong white smoketo appear. Then 5mL concentrated HF and 5mL concentrated $HClO_4$were transferred into the solution and heated at 270^{o}C and allowed to evaporate to nearly dryness and then cooled down. Finally,4mL of 1:1 HCland 2mL of distilled H_2O were added to the solution and then slightly heated to dissolve the residues. The obtained solutionwas transferred into 50 mL volumetric flask ready to measure the iron content.

The iron content was determined with 1,10phenanthroline by UV visible spectrophotometer. The calibration curve for iron +II was constructed and then content of the Fe (+II) in the samples was determined. Briefly, 0.1 g/L iron standard solution was prepared as by weighing accurately 0.2153g $NH_4Fe(SO4)_2$•$12H_2O$ and dissolve it in a small amount of distilled water into a 250 mL beaker, then 20 mL of (1:1) H_2SO_4 was added to the beaker. The mixture was transferred into 250 mL volumetric flask and then 100 mL of distilled water was added.The other chemicals such as: 100 g/L (10 %） Aqueous hydroxylamine hydrochloride solution(configuration in time),1.5 g/L1,10-Phenanthroline monohydrate solution(depositing without light), and Acetic acid-acetate buffer solution(PH=5) were separately prepared for the next steps.

The standard curve was constructed by preparing six 50 mL volumetric flasks filled with 0.0mL, 0.10mL, 0.20mL, 0.30mL, 0.40mL, 0.50mL iron standard solution, respectively. Then, 1mL of 100 g/L hydroxylamine hydrochloride was added in each volumetric flask. The solution was deposited 2 min after shaking-up. Thereafter2 mL of 1.5 g/L1,10-Phenanthroline monohydrate solution,5 mL of acetic acid-acetate buffer solution (pH=5) were added to the mixture and diluted with distilled water up to the scale of the volumetric flask. The iron standard curve was plotted by measuring the absorbance of the above solutions through Hitachi U-3310 (Japan) UV vis spectrophotometer at the wavelength of 510 nm. The sample absorption measurements were determined by transferring 2 mL of the digested solution into 50 mL volumetric flask and then follow the above procedure.

3. RESULTS AND DISCUSSION

3.1. SEM observation.

SEM micrograph pictures of raw diatomite, diatomite purified through hot acid leaching and carbon white are depicted in Figure 1a-c, respectively. As it can be seen from Figure 1 b, the diatomite treated with hot acid leaching presented a reduced number of impurity materials and an increased number and size of the holes on the spherical shaped diatoms compared to raw diatomite (Figure 1a). From Figure 1c, the diatomite treated with carbon white showed rough surface without any pore.

3.2. Surface area analysis.

The results for surface area analysis of diatomite purified through calcination, hot acid leaching and carbon white are summarized in Table 1. It is easy to find that the pore size samples were increased as follow: acid leached diatomite>diatomite treated through calcination>diatomite treated with carbon white.This shows that the pore size in the purified diatomite through calcination was greatly improved.The diatomite treated with carbon-white shows the small pore size

3.3. The iron content in samples.

3.3.1. Effect of leaching raw diatomite with various HCl concentration on removal-iron rate.

The effect of HCl concentration on removal-iron rate was investigated and the results are presented in Figure 2. It was revealed that the removal-iron rate was linearly increasing with the HCl concentration increase. However, when 15% HCl and 20% HClacid concentrationswere used to treat the diatomite, there was no significant difference between these HCl concentrations.

3.3.2. The effect of various HCl concentrations on the removal-iron rate in the diatomite treated through calcination and acid leaching.

As it can be seen from Figure 3, the removal-iron rate increased with the increase of the acid concentration up to 10% HCl, beyond that concentration a decreased and increased removal-iron rate was remarked. This may suggest that, the 10% HCl concentration should be the most suitable to get a good product with less iron content. Additionally, there was no significant difference in the removal-iron rate between the sample treated with 10% HCl and 20% HCl acid concentration.

3.3.3. Effect of various solid-liquid ratios on the removal-iron rate in the diatomite treated through calcination and acid leaching.

The results for this experiment were collected in Figure 4. The removal-iron rate was changing with changing the solid-liquid ratio. The removal-iron rate reached to 71.55% when the solid to liquid ratio was 1:4, then the decreased and increased removal-iron rate was remarked. The highest removal-iron rate was obtained when the solid to liquid ratio was 1:6. According to this observation, the 1:4 solid to liquid should be considered as the best proportion to be applied to get a purified diatomite with low iron content and by using low amount of liquid.

3.3.4. Effect of reaction timeon the removal-iron rate in the diatomite treated through calcination and acid leaching.

As it can be seen in Figure 5, the short and high time could decrease the removal-iron rate. According to this study, the removal-iron rate was increased to 72.31 when the diatomite sample was baked for 1 h. Then a slight decrease of removal-iron rate was observed. The highest removal-iron rate was obtained when the sample was treated for. 5 h. Therefore, to obtain a purified diatomite with low iron content by using short time and littleenergy, the reaction time of 1 h is highly suggested.

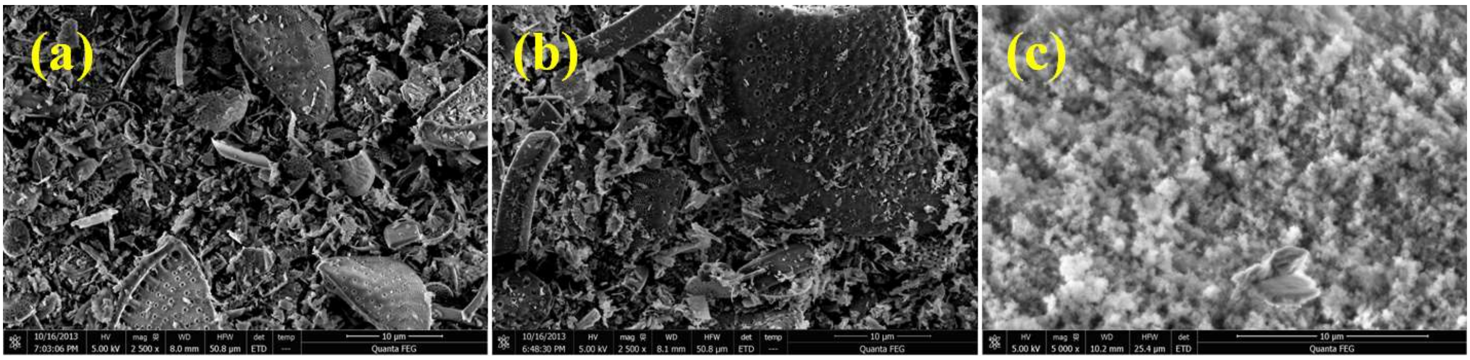

Figure 1. SEM micrographs of (a) raw diatomite at 2,500X, (b) diatomite purified through acid leaching at 2,500X, and (c) diatomite treated with carbon white at 5,000X

Table 1. Analysis of specific surface area

Sample	specific area（m^2/g）	
	single-point BET Specific area	Langmuir Specific area
Calcined diatomite	19.163371	27.292371
Acid leached diatomite*	25.272359	34.906405
Diatomite treated with Carbon-white	4.083311	5.981865

*The condition of acid leaching: Acid concentration:10% HCl; solid-liquid ratio: 1: 4;reaction time: 1 h.

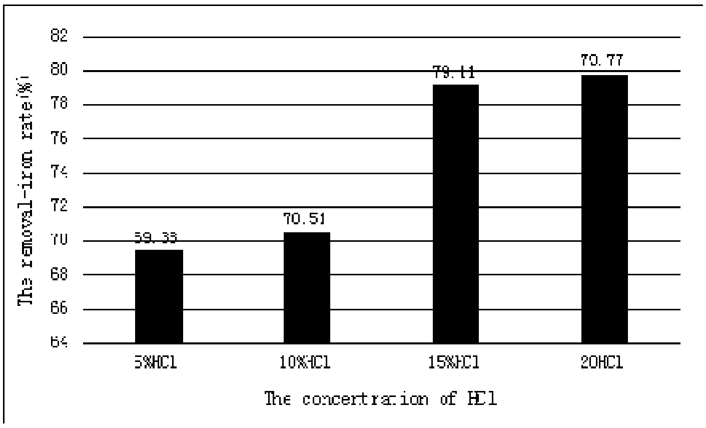

Figure 2. Removal-iron rate for raw diatomite purified through acid leaching at various HCl concentrations (5%, 10%, 15%, and 20% HCl)

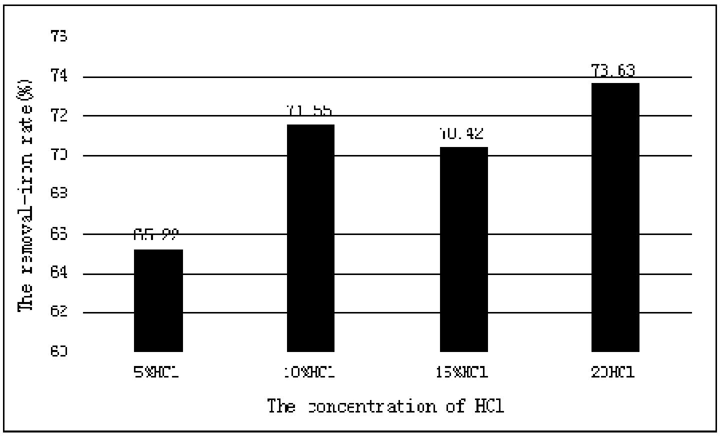

Figure 3. Removal-iron rate for diatomite purified through calcination with various HCl concentrations (5%, 10%, 15%, and 20% HCl)

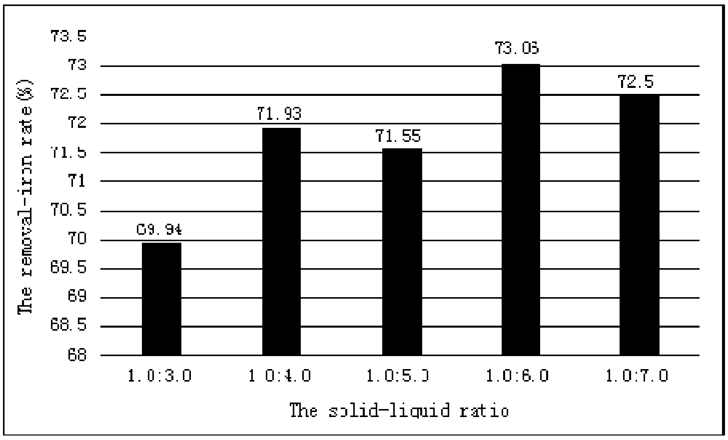

Figure 4. Removal-iron rate for diatomite treated through calcination with different solid-to-liquid ratio

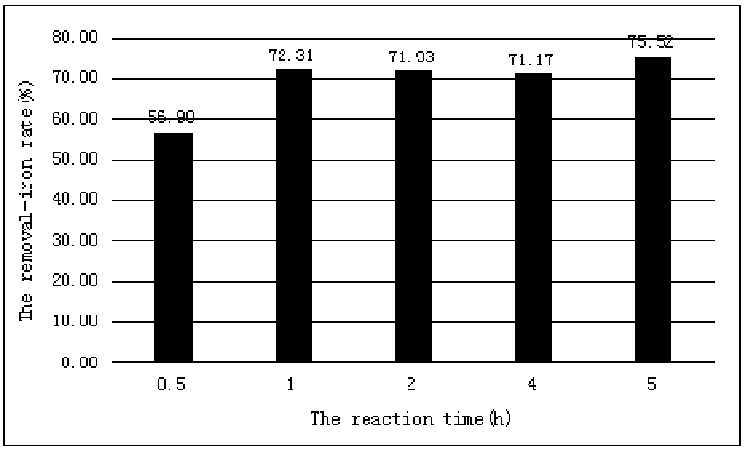

Figure 5. Removal-iron rate of calcination for diatomite treated through calcination at different reaction time

4. CONCLUSION

Through above analysis, we have developed the optimized conditions for diatomite purification calcination and acid leaching as follow: baking diatomite, acid concentration: 10% HCl, solid-liquid ratio: 1:4, and the leaching reaction time: 1 h. At these conditions,the content of impurities and iron are low, which means that product should be pure enough to replace part of silicon dioxide used in food and medical applications.According to SEM analysis, the determined iron content and the specific surface area analysis of the purified diatomite, the results suggested that the combination of two purification methods i.e. calcination and acid leaching could greatly enhance the properties of diatomite by increasing the porous number and size as well as reduced amount of various impurities. Therefore, it should be pointed out that the methods presented above require simple process at low cost to get high purified product, they are believed to provide large in industrial production.

5. REFERENCE

[1]Zhang Z., Wang Z., .Diatomite-Supported Pd Nanoparticles: An Efficient Catalyst for Heck and Suzuki Reactions, *The Journal of organic chemistry,* 71, 19, 7485-7487, **2006**.

[2]Zheng S., Sun Z., Hu Z., et al., The processing and utilization of China resource and its development trend, *Earth Science Frontiers,* 21, 5, 274-280,**2007.**

[3]Zheng SL., Shu F., Wang LJ., Study on the preparation and application of compound materials of nano-TiO_2 supported on diatomite, *Proceedings of XXIV International Mineral Processing Congress.Beijing*, 2151-2156, **2008.**

[4]Serdar A., Bulent B., Mechanical and microstructural properties of heat cured alkali-activated slag mortars, *Materials and Design,* 35, 374-38, **2012.**

[5]LiuY., Zheng SL., Du GX., et al., Photocatalytic degradation property of nano-TiO2/diatomite for Rodamine B dye wastewater, *International Journal of Modern Physics B,* 23, 6/7, 1683-1688, **2009**.

[6]Qu XP., Yang YX., Wang ZL., Zhang JB., Chen YR., Nie LX., A study on the decoloring mechanism of diatomite and its treatment on waste water, *Silicates Industriels,*71, 9- 14, **2006**.

[7]Yeoman S., Stephenson T., Lester J N., et al., Biotechnology for phosphorus removal during wastewater treatment, *Biotechnology Advances,* 4, 1, 13-26, **1986**.

[5]Al-Ghouti MA., Khraisheh MAM., Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite, *Journal of Colloid and Interface Science*, 287, 6- 13, **2005.**

[6]Zohuriaan-Mehr MJ., Kabiri K., Superabsorbent polymer materials: A review, *Iranian Polymer Journal,* 17, 451- 477, **2008**.

[7] Parvathy PC., Jyothi AN., John KS.,Sreekumar J., Cassava Starch Based Superabsorbent Polymer as Soil Conditioner: Impact on Soil Physico- Chemical and Biological Properties and Plant Growth, *Clean-Soil Air Water*, 42, 1610- 1617, **2014**.

[8] Wang D., Song Z., Shang S., Synthesis of amphoteric superabsorbent polymers modified by carboxymethyl cellulose, *Nanjing Forestry University,* 31, 27- 31, **2007.**

[9]Wang Y., Zhang X., Wei H., Zhang B., Xiang X., Chen R., Synthesis of Poly(AA-co-AM) Superabsorbent Composites by Reinforcement of Halloysite Nanotubes, *Polymer Composites*, 36, 229- 236, **2015**.

[10]Youngran J., Maohong F., ShilpiS., et al., Evaluation of iron oxide and aluminum oxide as potential arsenic(V) adsorbents, *Chemical Engineering and Processing,* 46, 10, 1030-1039, **2007**.

[11]Shawabkeh RA., Tutunji MF., Experimental study and modeling of basic dye sorption by diatomaceous clay, *Applied Clay Science*, 24, 1, 111-120, **2003**.

[12]Kominek EG., Industrial Applications of Diatomite Filters, *Industrial & Engineering Chemistry*, 39, 11, 1413-1419, **1947.**

[13]Jie L., Dongfeng Z., The Present Situation and Development of Diatomite, *Environmental Science and Management*, 5, 027, **2009.**

[14]Zhang F., Process and Application of diatomaceous earth, *Beijing:Chemical Industry press*, 87-89, **2001.**

[15]Karaca S., Gürses A., Ejder, M., Açıkyıldız M., Adsorptive removal of phosphate from aqueous solutions using raw and calcinated dolomite, *Journal of Hazardous Materials,* 128, 2, 273-279, **2006.**

[16]Cestari AR.,Vieira E., Tavares AMG., et al., The removal of the indigo carmine dye from aqueous solutions using cross-liked chitosan-Evalution of adsorption thermodynamics using a full factorial design, *Journal of Hazardous Materials,*153, 1/2, 566-567, **2008**.

[17]Dai RC., Zhang T., Guo Q., et al., Summary of printing-dyeing waste water treatment technology, *Water & Waste Water Engineering,(in Chinese),*26, 10, 33-37, **2000**.

6. ACKNOWLEDGEMENTS

This work was supported by the Central China Normal University Innovation and Entrepreneurship Training Program for College Students - Innovation training program.