



Adsorption of Lead (II) ions by Ecofriendly Copper Oxide Nanoparticles

SREEKALA. G^{1*}, FATHIMA BEEVI. A² and BEENA. B³

^{1,2,3}Nanoscience Research Lab, Department of Chemistry, K. S. M. D. B. College,
Sasthamcotta-690521, Kollam, Kerala, India.

*Corresponding author E-mail: sreekalamohankumar@gmail.com

<http://dx.doi.org/10.13005/ojc/350615>

(Received: October 14, 2019; Accepted: November 15, 2019)

ABSTRACT

The present investigation is on the application of green synthesized CuO nanoparticles for elimination of lead (II) from wastewater. Nano CuO was prepared from aqueous copper acetate solution and aqueous leaf extract of *Simarouba glauca* plant. The prepared nano CuO was characterized by XRD, FT-IR, UV, SEM and TEM. The nano CuO synthesized by this method was spherical in shape with particle size nearly 20 nm. The adsorption of lead (II) ions on nano CuO under various parameters such as amount of catalyst, concentration of metal ion and pH were studied using Batch adsorption experiments. Experimental results indicate that the green synthesized CuO nanoparticle is a very good adsorbent for the efficient removal of lead (II) from wastewater. Optimum conditions for 95% adsorption of Pb²⁺ on CuO nanoparticle is pH 6, amount of catalyst 0.05 g and concentration of metal ion 10 mgL⁻¹.

Keywords: Green synthesis, Copper oxide nanoparticles, *Simarouba glauca*, Adsorbent, Lead (II) ion.

INTRODUCTION

Now a day's an increase in industrial globalization produces a number of pollutant into the environment. Heavy metals are the major inorganic water pollutants in the world due to the high toxicity on human¹. Heavy metal ions are dispersed into the environment from different processes like metallurgy, mining, battery making industries etc. The heavy metal in wastewater and surface water is becoming a major health hazard. Pb (II) is one of the highly toxic materials which have adverse effects on human being. Exposure of very low levels of lead to children

can cause different types disabilities like learning disabilities, reduced IQ, behavioral problems, etc. But at high levels, a child may become mentally retarded, fall into a comma stage and even die from lead poisoning. Exposure of lead in adults cause increase in blood pressure, muscle and joint pain, and several types of disorders². Because of these health problems it is very important to eliminate such a dangerous heavy metal ion in wastewater before discharging it into the environment. The permissible limit of Pb (II) on drinking water is 0.015 mg/L as per EPA³. Hence it is very urge to eliminate such a metal ion from wastewater before it can be discharged.



The different methods have been employed for the removal of metal ions from aqueous solutions are precipitation, evaporation, electrodeposition, ion exchange, membrane separation, coagulation etc⁴. The disadvantages of these methods are secondary pollution, high cost, high energy input, large quantities of chemical reagents, poor treatment efficiency at low metal ion concentration especially when the concentration of metals in wastewater is low (<100 ppm)^{5,6}. Hence it is very urge to develop an efficient and low-cost method of elimination of this metal.

Adsorption is an efficient conventional technique to remove heavy metals and organic pollutants from aqueous solutions. A number of adsorbents for wastewater treatment have been commercialized or are being developed⁷. Most of these adsorbents are highly porous and have sufficient surface area for adsorption. Thus it is very important to develop an adsorbent with large surface area and small diffusion resistance to meet the practical and environmental applications⁸.

Copper oxide nanoparticles have wide range of applications in various fields like electronics, sensors⁹, antioxidants, heterogeneous catalysts¹⁰, and in the field of biomedicine¹¹. In the common chemical method of preparing nanoparticles find opposite effects in medicinal application due to the adsorption of hazardous chemical on the surface of nanoparticles. Hence researchers are constantly tried to make synthesizing nanoparticles by green approach to reduce the toxicity. Very recently researchers used green method of synthesizing various nanoparticles by plants such as *neem*¹², *alfalfa*^{13,14}, *Cinnamomum camphora*¹⁵, *Emblica officinalis*¹⁶, Lemon grass¹⁷, Tamarind¹⁸ and *Saraca indica*¹⁹. Copper oxide nanoparticles have very interesting biological and mechanical properties²⁰. These versatile properties and applications developed by Green method make copper oxide nanoparticle a very important material for waste water treatment.

Simarouba glauca is an evergreen tree and has a long history of herbal medicine²¹ metabolites which include alkaloids, steroids, flavonoids, terpenoids, glycoside, saponia, tannins, phenolic compounds and so on²². These metabolites can act as reducing agent as well as capping agent. *Simarouba glauca* was reported with medicinal applications such as haemostatic, anthelmintic, antiparasitic, antidysentric, antipyretic and anticancerous.²³

Reports on biosynthesis of CuO nanoparticles are very few. Green method for the synthesis of CuO nanoparticles is simple, low cost, not time consuming, single step and eco-friendly. Therefore, this present work was planned to investigate the adsorption of lead (II) ions in solutions with nano copper oxide catalyst prepared from aqueous leaves extract of *Simarouba Glauca* plant.

MATERIALS AND METHODS

Materials

The only chemical used in this present study was analytical grade copper (II) acetate monohydrate [(CH₃COO)₂Cu.H₂O].

Methods of Synthesis of CuO nanoparticles

Preparation of Leaf Extract

Simarouba glauca leaves were collected, washed, dried in shade and pulverized. 20 g of the pulverized leaves were treated with 300 ml deionised water and heated in a microwave oven at 100W for 30 minutes. Thereafter the solution was filtered using Whatman 1 filter paper the filtrate obtained was collected. This freshly prepared leaf extract was used for synthesizing copper oxide nanoparticles.

Preparation of CuO nanoparticles with *Simarouba glauca* leaf extract

120 ml of freshly prepared *Simarouba glauca* leaf extract solution was added to aqueous Copper acetate (50 ml, 0.1 M) solution drop wise with stirring using a magnetic stirrer for 1 hour. The blue colour of the solution first change to green and then dark brown on the addition of plant extract. The brownish black coloured precipitate indicates the formation of CuO nanoparticles. Then this mixture was sonicated for 30 min allowed to settle overnight, filtered, washed with distilled water, dried and annealed using a muffle furnace at 500°C for 2 h to obtain the product.

Characterization of Nano CuO

The phase purity and crystallinity of the prepared material were verified by powder X-ray diffraction technique (XRD) of Bruker AXS D8 Advance model with Cu K α radiation. The functional groups were identified with Fourier transform infrared (FT-IR) spectrometer of Thermo Nicolet, Avatar 370 model by converting the product into pellet using KBr. The absorption spectra of the powder sample

were recorded at room temperature using UV-Visible spectrophotometer of model Cary 5000. Surface morphology of the sample was analyzed by SEM of JEOL Model JSM - 6390LV, and particle size and shape by TEM of JEOL/JEM 2100.

Adsorption study of Nano CuO

Adsorption studies on the surface were performed by batch process. In this process, taking 0.1 g of synthesized CuO and 100 ml 10 mg L⁻¹ Pb²⁺ solution in a stoppered conical flask and placed on a mechanical shaker at 160 rpm. The rate of adsorption of lead on CuO nanoparticles after desired time intervals [30, 60, 90, 120, 150 minutes. etc], was determined by measuring absorbance using atomic absorption spectroscopy. The experiments were repeated for different concentration, adsorbent dosage and pH for heavy metal ion solutions. The adsorption efficiency (q) and removal percentage are determined as follows:

$$q = \frac{[C_0 - C_e]V}{W} \quad (1)$$

$$\text{Removal percentage} = \frac{(C_0 - C_e)100}{C_0} \quad (2)$$

Where q is adsorption efficiency of the adsorbent [mg.g⁻¹], W is weight of adsorbent [g], V is volume of solution [L], C₀ [mgL⁻¹] and C_e [mgL⁻¹] are initial and equilibrium concentration of adsorbate in the solution respectively.

RESULTS AND DISCUSSION

The nano CuO prepared in the present study was obtained as black fine powder.

XRD Analysis

The powder XRD pattern of the nano CuO obtained is shown in Fig.1. The XRD pattern of CuO nano structures (Fig.1) is well matched with single phase monoclinic structure and well consistent with the standard data reported by JCPDS card no. [80-1916]. XRD pattern of nano CuO have no impurity peaks indicating the high phase purity of the product obtained. The small crystal size is indicated by broadening of the peaks in XRD spectrum. The average particle size of the prepared CuO nanoparticles were determined by Debye-Scherrer's formula,

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

Where, D is size of the particle (nm), k is a constant (0.94), λ is the wave length of X-rays used (1.5406 Å), β is full-width at half maximum (FWHM) of the peak (in radians) and θ is Bragg angle (degree). The average particle size was found to be nearly 18–24 nm.

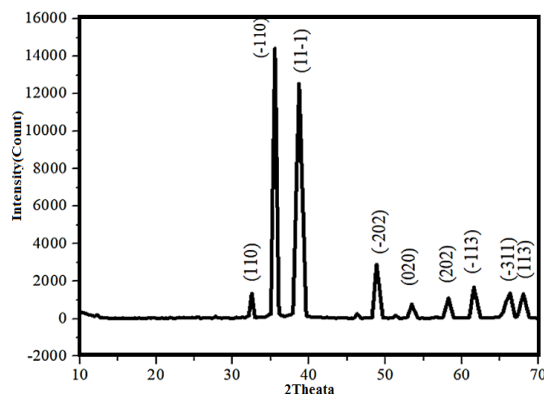


Fig. 1. XRD Spectrum of Nano CuO

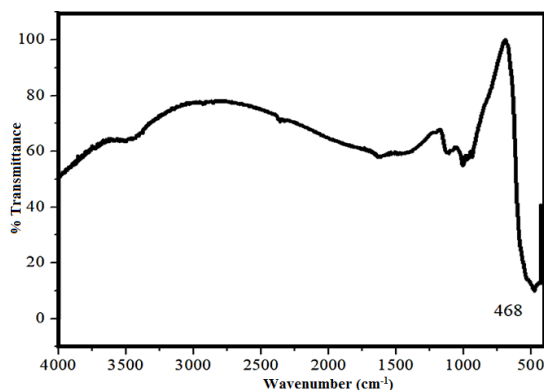


Fig. 2. FT-IR Spectrum of Nano CuO

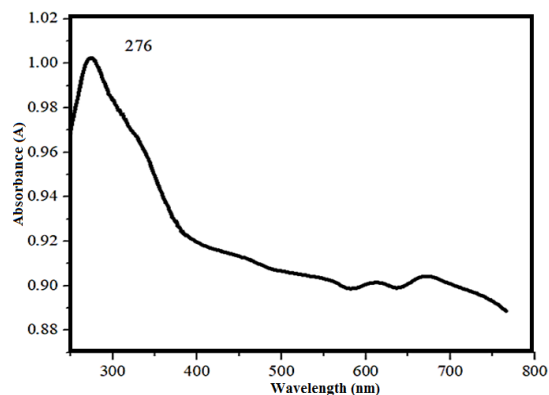


Fig. 3. UV-Visible Spectrum of Nano CuO

FT-IR Spectral Study

Figure 2 shows the FT-IR spectrum of the obtained CuO nano particles. The narrow absorption peak at 468 cm⁻¹ is assigned for Cu-O bond vibration.

No other functional groups are present in IR spectrum indicates the purity of the prepared CuO nanoparticle.

UV-Visible spectrum

A strong absorption peak at 276 nm in the UV-Visible spectrum (Fig. 3) indicates the formation of nano copper oxide²⁴.

SEM-EDX Investigation

Figure 4 shows the EDX Spectrum of the prepared nano CuO. The elemental composition is given in Table 1. EDX spectrum shows only peaks corresponding to Cu and O which also verifies the formation of nano CuO in accordance with previous report⁹. The SEM image (Fig.5) shows nearly spherical morphology for CuO nanoparticles.

Table 1: Percentage composition of elements from EDX spectrum

Element	Weight %	Atomic %
O	15.79	42.69
Cu	84.21	57.31
Total	100	100

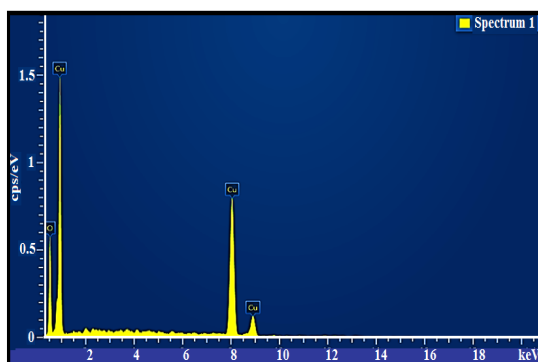


Fig. 4. EDX Spectrum of the synthesized Nano CuO

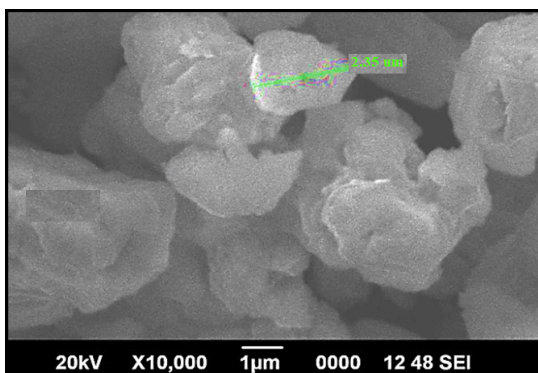


Fig. 5. SEM image of obtained Nano CuO

TEM Investigation

TEM image in Fig. 6 reveals the presence of spherical particles of CuO with uniform morphology having particle size nearly 20 nm. Selected area

electron diffraction (SAED) in Fig. 7 shows the crystalline nature for nano CuO. The diffraction rings in SAED pattern match well with the peaks in XRD spectrum. This also confirms the monoclinic nature of the prepared nano copper oxide.

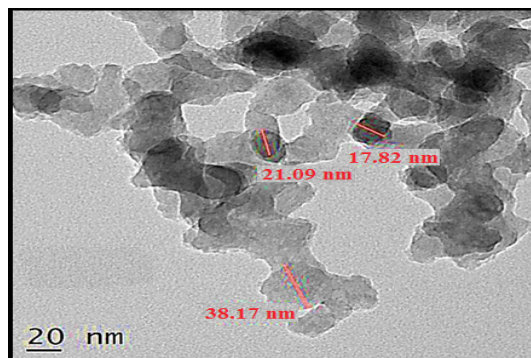


Fig. 6. TEM Image of obtained Nano CuO

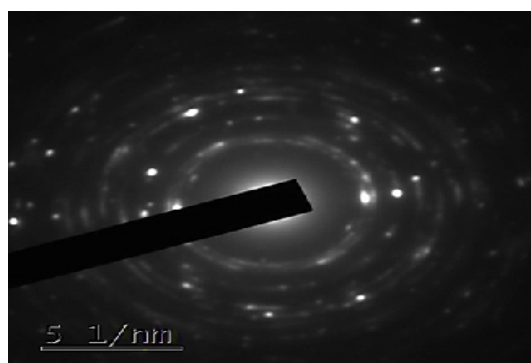


Fig. 7. SAED pattern of as prepared Nano CuO

Adsorption of lead (II) from solution

Small portion of the Pb (II) solution was withdrawn at regular intervals and absorbance was measured by Atomic absorption spectrometer. It was observed that the absorbance of the solution decreases with increasing time intervals.

Effect of Concentration of Pb²⁺ ions

Effect of adsorbate concentration in the rate of adsorption was determined by varying the concentration of Pb²⁺ ions from 10 to 40 mgL⁻¹ (Fig. 8). It can be seen that rate of adsorption is maximum for 10 mgL⁻¹ and then decreases. At low concentration the ratio between surface active sites and the total metal ions in solution was very high. Then all the ions of metal interacted with nano CuO and are carried away from solution. On increasing the concentration, the mass of metal ion adsorbed per unit mass of adsorbent was low due to high concentration gradient²⁵.

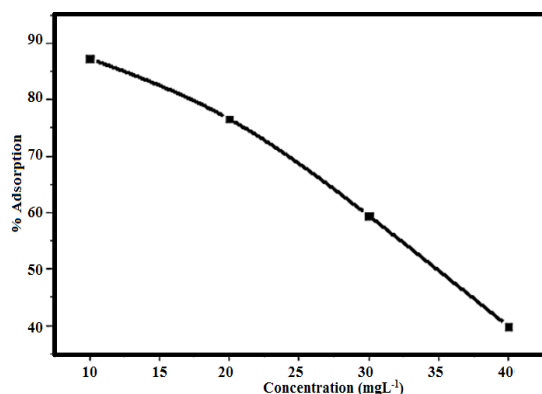
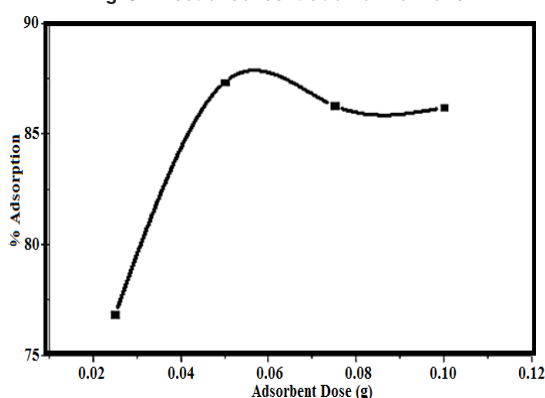
Fig. 8. Effect of concentration of Pb²⁺ ions

Fig. 9. Effect of amount of adsorbent

Effect of Amount of nano CuO

Effect of amount of nano CuO on the rate of adsorption was examined by varying from 0.025 to 0.1g/100 ml of 10ppm Lead solution (Fig. 9). It was observed that the maximum extent of adsorption takes place at 0.05 g of nano CuO. But at higher dose (0.075 to 0.1 g), no further increase of adsorption takes place due to the fact that the amount of Pb²⁺ held to the nano CuO and the amount of free Pb²⁺ in solution remains constant^{26,27}.

Effect of pH

The removal ability of adsorbent depends on pH of solution. Dependence of pH on metal adsorption is related to both metal chemistry and ionization state of the sorbent there by affecting the number of binding sites^{28,29}. The surface of metal oxide in aqueous phase consists of hydroxyl groups which depend on pH of solution²⁸. Variation of adsorptivity with pH is explained by the behavior of hydrogen ion and counter ion activity in aqueous solution. The hydrogen ion activity decreases up to

pH 6 and percentage adsorptivity increases. Above pH 6, adsorptivity decreases since concentration of hydrogen ion is too low and precipitation occurred in strong basic pH^{29,30}.

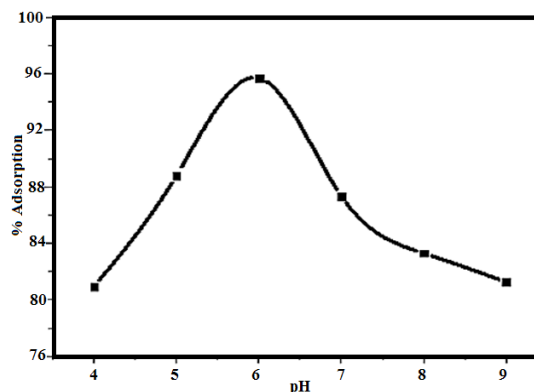


Fig. 10. Effect of pH on adsorption

CONCLUSION

Synthesis of pure nano CuO by green route is a simple, environment friendly, non-toxic and low cost using aqueous leaf extract of *Simarouba glauca*. Metabolites present in the leaf extract of *Simarouba glauca* can act as bio-reducing agent and also as a capping agent in the synthesis nano CuO. CuO nanoparticles with monoclinic structure and spherical shape with approximately 20 nm size is reported. In the present work, nano copper oxide is used for the adsorption of Pb²⁺ from solution. Optimum reaction conditions for the 95% removal of Pb²⁺ on nano copper oxide were experimentally determined and found that lead (II) ion concentration of 10 mgL⁻¹, adsorbent dose 0.05 g and pH 6. The synthesized nano CuO may be used for the elimination of other inorganic pollutant from industrial waste water.

ACKNOWLEDGEMENT

One of the authors (G. Sreekala) is grateful to UGC, New Delhi for providing the financial assistance in the form of FDP. STIC-CUSAT is also acknowledged for instrumental facilities.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

1. Zhou, Y. M.; Hu, X. C.; Zhang, M.; Zhuo, X. F.; Niu, J. Y. *Ind. Eng. Chem. Res.*, **2013**, *52*, 876-884.
2. NSC. Lead poisoning available at, <http://www.nsc.org/library/facts/lead.htm>; 1. 9. **2007**.
3. Naiya, T.K.; Bhattacharya, A.K.; Das, S. K. *J Colloid Interface Sci.*, **2009**, *333*, 14-26.
4. Rao, R. A. K.; Ikram, S. *Desalination.*, **2011**, *277*, 3908.
5. Ding, Y.; Jing, D.; Gong, H.; Zhou, L.; Yang, X. *Bioresour Technol.*, **2012**, *114*, 20-25.
6. Witek-Krowiak, A.; Szafran, R.G.; Modelski, S. *Desalination.*, **2011**, *265*, 12634.
7. Kannan, N.; Sundaram, M. M. *Dyes Pigm.*, **2001**, *51*, 25-40.
8. Hu, J.; Chen, G.; I.M.C.L. *Journal of Environmental Engineering.*, **2006**, *132*, 709-715.
9. Ren, G.; Hu, D.; Cheng, E.W.; Vargas-Reus, M. A.; Reip, P.; Allaker, R. P. *Int J Antimicrob Agents.*, **2009**, *33*, 587- 590.
10. Iravani, S. *Green Chem.*, **2011**, *13*, 2638-2650.
11. Sankar, R.; Manikandan, P.; Malarvizhi, V.; Fathima, T.; Shivashangari, K. S.; Ravikumar, V. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.*, **2014**, *121*, 746-750.
12. Shankar, S. S.; Rai, A.; Ahmad, A.; Sastry, M. *Journal of Colloid and Interface Science.*, **2004**, *275*, 496-502.
13. Gardea-Torresdey, J. L.; Parsons, J. G.; Gomez, E. *Nano Letters.*, **2002**, *2*, 397-401.
14. Gardea-Torresdey, J. L.; Gomez, E.; Peralta-Videa, J. R., Parsons, J. G.; Troiani, H.; Jose-Yacaman, M. *Langmuir.*, **2003**, *19*, 1357-1361.
15. Huang, J.; Li, Q.; Sun, D. *Nanotechnology.*, **2007**, *18*, 105104-105115.
16. Ankamwar, B.; Damle, C.; Ahmad, A.; Sastry, M. *Journal of Nanoscience and Nanotechnology.*, **2005**, *5*, 1665-1671.
17. Shankar, S. S.; Rai, A.; Ankamwar, B.; Singh, A. Ahmad, A.; Sastry, M. *Nature Materials.*, **2004**, *3*, 482-488,
18. Ankamwar, B.; Chaudhary, M.; Sastry, M. *Synthesis and Reactivity in Inorganic, Metal- Organic and Nano-Metal Chemistry.*, **2005**, *35*, 19-26.
19. Shiva Prasad, K.; Patra, A.; Shruthi, G.; Chandan, S. *Journal of Nanotechnology.*, **2017**, *2017*, 6.
20. Sivaraj, R.; Rahman, P. K. S. M.; Rajiv, P.; Narendhran, S.; Venkatesh, R. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.*, **2014**, *129*, 255.
21. Sharanya, V. K.; Gayathiri, K.; Sangeetha, M.; Shyam, P. G.; Gopi, S. K.; Vimalavathini, R.; Kavimani, S. A. *Int. J. Pharma Res. and Rev.*, **2016**, *5*, 32-36.
22. Ghahi, A. *Introduction to pharmacognosy*, Ahmadu Bello University press, Ltd. Zaria, Nigeria., **1990**, 45-47.
23. Patil, M. S.; Gaikwad, D. K. *J. Pharm. Sci. & Res.*, **2011**, *3*, 1195-1213.
24. Wang, H.; Zhang, J. J.; Zhu, H. Y. Chen, J. *Cryst. Growth.*, **2002**, *244*, 88.
25. Fu, F. L., Wang, Q., *J. Environ. Manage.*, **2011**, *92*, 407-418.
26. Yogesh Kumar, K.; Muralidhara, H. B.; Arthoba, Y. *Powder Technol.*, **2013**, *239*, 208-216.
27. Heidari, A; Younesi, H; Mehraban, Z. *Chem Eng J.*, **2009**, *153*, 709.
28. Mendez, J. R. R; Zepeda, R. M; Ramos, E. L; Flores, P. E. D; Shirai, K. *J Hazard Mater.*, **2009**, *162*, 503-11.
29. Ngomsik, A. F; Bee; Siaugue, J. M.; Talbot, D.; Cabuil, V.; Cote, G. *J Hazard Mater.*, **2009**, *166*, 1043-9.
30. Hu, J. Chen, G.; Lo, I. M. C. *Water Research.*, **2005**, *39*, 4528-4536.
31. Kim, M. S.; Hong, S. C.; Chung, J. G. *Environ. Eng. Res.*, **2005**, *10*, 45-53.
32. Kosa, S. A.; Zhrani, G. A.; Salam, M. A. *Chem. Eng. J.*, **2012**, *181-182*, 159-168.