Selective adsorption for indium(III) from industrial wastewater using chemically modified sawdust

Taik-Nam Kwon and Choong Jeon†

Department of Biochemical Engineering, Gangneung-Wonju National University,
Gangneung, Daehangno, 120, Gangneung, Gangwon-do 210-702, Korea

Abstract−To selectively adsorb indium(III) in industrial wastewater coexisting with zinc(II), the surface of sawdust was modified into phosphate groups through chemical reaction. Among various manufacturing methods, phosphorylated sawdsust made from using non-grinding sawdust with same ratio (based on volume) of H_3PO_4 and distilled water had a very high selectivity to indium(III), which shows removal efficiency of about 90% with 1.0 g at pH 3.5. Meanwhile, in case of zinc(II), there is almost no adsorption onto phosphorylated sawdust. The surface condition and phosphorus content of phosphorylated sawdust were analyzed by scanning electron microscopy (SEM) photograph and energy dispersive x-ray (EDX) spectrum. Also, the effects of loading of adsorbent and time on selective adsorption characteristics of indium(III) were investigated.

Key words: Indium(III), Sawdust, Phosphate, Selectivity, Adsorption

INTRODUCTION

Indium is a very soft, crystalline, ductile, and malleable substance that retains its highly plastic properties at cryogenic temperatures. In general, it increases the strength, corrosion resistance, and hardness of an alloy system to which it is added [1]. The present cost of indium is about $1 to $5/g, depending on quality and purity.

Indium is widely used in various industrial applications such as manufacture of liquid crystal displays, semiconductors and infrared photodetectors [2]. Especially, indium-tin oxide (ITO) thin film is used in optoelectronic devices for transparent conducting layers and, recently, over 60% of indium production worldwide was spent in the manufacture of ITO films [3].

The rise in recycling for valuable metals is of increasing concern among many researchers. Many studies on the extraction of indium(III) have been performed by means of solvent extraction or ion exchange technology [4-7]. But, the main weakness of the solvent extraction process is the loss of extractant into aqueous solution, which may increase environmental hazards and economic limitations. Meanwhile, the ion exchange method is even simpler than solvent extraction, but selectivity to specific metal is low. Also, ion exchange has slow adsorption and desorption rates. Even though highly selective chelating ion exchange resins have been developed, they accompany a very tedious and time-consuming search for highly selective functional groups [8].

In the 2,000 s, many studies on metal removal using various wastes such as waste wool, peanut shells, soybean hulls, rice hulls, crab shells, and cotton, which are available in large quantities and may present higher potential as cheap sorbents, have been carried out [9,10]. Especially, the use of sawdust wastes discharged from the forestry industry has showed a potential for metal removal. Shukla et al. studied the removal of Pb(II), Cu(II), and Cr(VI) in aqueous solution by means of maple tree sawdust, and Dorris et al. reported high adsorption ability for Cu(II), Ni(II), and Zn(II) using oak tree sawdust [11,12]. Furthermore, the adsorption capacity of sawdust for Pb(II) could be increased by means of chemical modification of functional groups [13]. However, there is little study on valuable metals such as indium, nickel, gold, and silver using sawdust. Furthermore, there are no studies on selective adsorption to indium(III) only, from mixed wastewater using chemically modified sawdust. According to the literature survey, among functional groups, it is reported that the groups containing phosphorous such as phosphonate and/or phosphonic acid have a high selectivity to indium(III) [14].

Therefore, in this study, to selectively adsorb indium(III) only from actual wastewater, phosphoric acid was introduced to surface onto sawdust by means of chemical reaction. In addition, selective adsorption characteristics for indium(III) using chemically modified sawdust were also investigated.

MATERIALS AND METHODS

To find optimal waste adsorbent to indium(III), sawdust (oak tree), which was obtained from a local company in Gangneung in Korea, tangerine peel obtained from a laboratory of Kangwon National University, and coffee ground supplied from a company in Korea were used as a candidate, respectively. Sawdust is very cheap at $2.2/kg and others were provided without cost. All wastewater used in this study was actual wastewater obtained from Toricom company in Chunan in Korea. The wastewater was composed of indium(In), zinc(Zn), and tin(Sn). In the case of Sn, however, the concentration was very low (~0.01 mg/L). Therefore, analysis for Sn was not performed. Also, the concentration for anionic compounds was not detected. All of the chemicals used in the experiment were of analytical grade (Sigma Aldrich, U.S.A.), and distilled water was used to

†To whom correspondence should be addressed.
E-mail: metaljeon@gwnu.ac.kr

prepare all of solutions.

The phosphorylation reaction of sawdust was performed as follows: 5.0 g of sawdust and 2.24 g of urea were added to mixed solution with 1 : 1 and 3 : 1 ratio of H_3PO_4 (purity: 85%) and distilled water, respectively. The solution was mixed for 1 hr. After being filtered by means of filter paper under vacuum condition, it was then reacted at 100 °C for 2 h in a heater. After cooling, the mixture was washed thoroughly with distilled water and then filtered by filter paper. Finally, the residue was dried at room temperature for 24 h.

To confirm surface condition and component onto phosphorylated sawdust, SEM (Scanning electron microscopy, Hitachi model S-4100) photograph and EDX (Energy dispersive X-ray spectroscopy) were used.

All sorption experiments were performed by batch-type with 100 mL for real mixed wastewater, as above mentioned, in a shaking incubator (JEIO TECH, SI-600R, Korea) at room temperature for 1 day. Before shaking of solution, the initial concentration of indium (III) and zinc(II) was measured, respectively. The pH of the mixed solution was controlled as 2.0, 3.0, and 3.5 by using NH_4OH and HNO_3. To avoid precipitation in solution of metals, sorption experiment was excluded above 3.7 of pH. When the pH for mixed solution was maintained constantly, the solution was centrifuged at 4,000 rpm for 30 min to remove suspending phosphorylated sawdust by centrifuge (Gyrozen, Gyro 1236 MG), and then the concentration of indium(III) and zinc(II) in supernatant was analyzed, respectively, by means of atomic absorption spectroscopy (Perkin-Elmer A Analyst 100/A Analyst 700, U.S.A.). Each sorption experiment was carried out several times and the average value is presented. The removal efficiency and adsorption capacity of each metal ion were calculated as the following equation:

$$R.E = (C_i - C_f)/C_i$$
$$Q = (C_i \times V_i - C_f \times V_f)/m$$

Where R.E is the removal efficiency of metal ions (%), Q is the adsorption capacity of metal ions (mg/g), C_i is the initial concentration of metal ions (mg/L), V_i is the initial solution volume (L), C_f is the final concentration of metal ions (mg/L), V_f is the final solution volume (L), and m is the initial loading of adsorbent (g). To investigate the effect of loading amount on adsorption capacity and removal efficiency of metal ions, phosphorylated sawdust was loaded as 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0 g respectively. The experiment for changing of concentration for indium(III) with time was also carried out with 0.2 g of phosphorylated sawdust.

RESULTS AND DISCUSSION

1. Adsorption Characteristics for Mixed Wastewater Using Various Waste-adsorbent

The concentration of indium(III) and zinc(II) in real mixed wastewater was measured as about 19.07 and 140,600 mg/L, respectively. The pH of wastewater was also about 3.58. As mentioned above, to selectively adsorb indium(III) only from mixed wastewater, sawdust (oak tree), tangerine peel, and coffee ground were used. As shown in Fig. 1, in the case of sawdsust, removal efficiencies of indium(III) and zinc(II) were about as 15% and 9% at pH 3, respectively. When tangerine peel and coffee ground were applied, the removal efficiencies of indium(III) were lower than that of sawdust
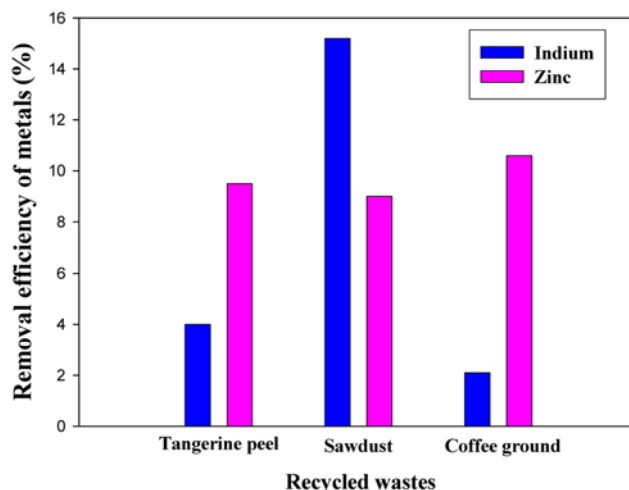

Fig. 1. Removal efficiency of metals using various recycled wastes at pH 3.0 (Loading amount of adsorbne: 1.0 g, Working volume: 100 mL).

as about 4 and 2%, respectively, while efficiencies of zinc were higher than that of sawdust. It was known that sawdust has functional groups such as phenolic -OH and carboxylic groups, while coffee grounds contain nitrogen of amino acid derived from protein and hydrolyzed protein [15,16].

From the result, sawdust, which has the highest removal efficiency for indium(III) and the lowest removal efficiency for zinc(II), simultaneously, was selected as optimum adsorbent to treat actual mixed wastewater supplied from the Toricom company.

2. Selective Sorption Characteristics for Indium(III) Using Phosphorylated Sawdust

To increase selectivity and adsorption capacity for indium(III) into wastewater, chemically modified sawdust containing phosphate groups was synthesized. To investigate surface condition and phosphorous content for phosphorylated sawdust, SEM photograph and EDX spectrum were used. As shown in Fig. 2(a), (b), and (c), the surface condition of adsorbent was not greatly different, which means that chemical modification of sawdust was not affecting the physical change of sawdust. However, as shown in EDX spectrum, the phosphorous content of phosphorylated sawdust with 1 : 1 ratio (H_3PO_4 : distilled water, volume) was 3.05 wt% and the value was much lower than 9.05 wt% of phosphorylated sawdust with 3 : 1 ratio (H_3PO_4 : distilled water, volume). According to the literature survey, after adsorption of metals phosphoric acid was not leaching [17].

Effect of pH on removal efficiency of indium(III) and zinc(II) using phosphorylated sawdust is shown in Fig. 3 (H_3PO_4 : distilled water=1 : 1) and 4 (H_3PO_4 : distilled water=3 : 1). As pH increased, removal efficiencies of indium(III) increased, while those of zinc(II) decreased regardless of H_3PO_4 content. Especially, removal efficiency of indium(III) was about 90% and zinc(II) was almost not removed at pH 3.5. Decreasing of removal efficiency for indium(III) at low pH can be explained by strong competition adsorption between indium (III) and protons (H^+) for same adsorption sites in acidic conditions [18]. Why phosphorylated sawdust has high selectivity to indium(III) could be due to the effect of phosphate groups. According to the HSAB (Hard and Soft Acids and Bases) theory, hard acid strong
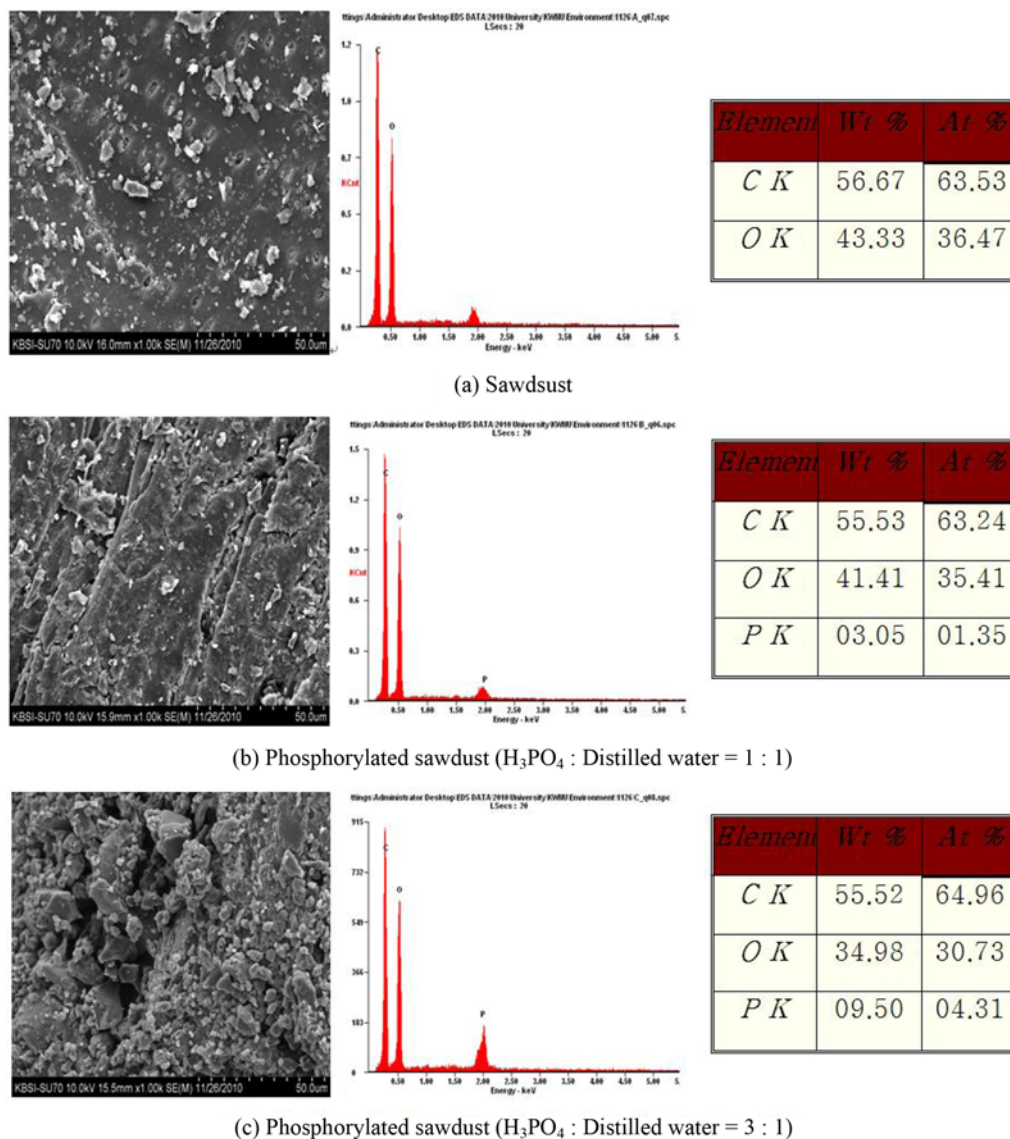
(a) Sawdsust

(b) Phosphorylated sawdust (H₃PO₄ : Distilled water = 1 : 1)

(c) Phosphorylated sawdust (H₃PO₄ : Distilled water = 3 : 1)

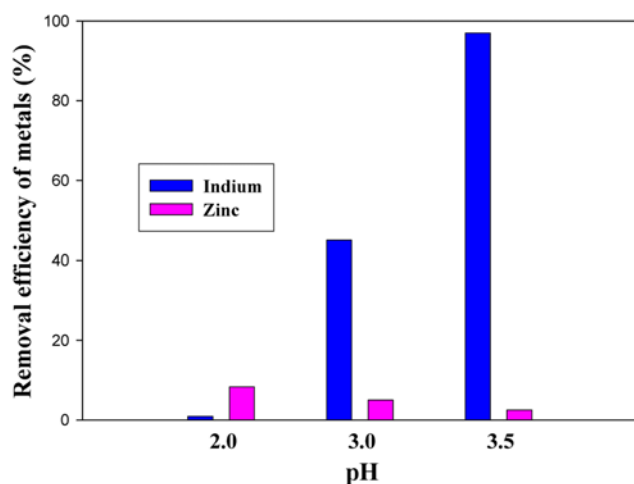**Fig. 2. SEM photograph and EDX spectrum.**

Fig. 3. Removal efficiency of metals using phosphorylated sawdust (H₃PO₄ : Distilled water=1 : 1) (Loading amount: 1.0 g, Working volume: 100 mL).

bonds with hard base and soft acid strong bonds with soft base, respectively. Indium(III) and zinc(II) are classified as a hard acid and intermediate which depend on oxidation state of acid, respectively. Also, phosphate groups into phosphorylated sawdust are classified as a hard base. Therefore, indium(III) as hard acid very strongly bonds; however, zinc(II) cannot be bond with phosphate groups, which are hard base [19].

Also, as shown in Fig. 4, although removal efficiency of indium (III) for phosphorylated sawdust with 3 : 1 of ratio was higher than that of phosphorylated sawdust with 1 : 1 of ratio, the former was not chosen as optimum adsorbent as removal efficiency of zinc(II) was higher compared to the latter. When the phosphorylated sawdust produced after reducing size of particle through grinding of raw sawdust was used, as shown in Fig. 5, indium(III) could be almost removed at pH 3.5 regardless of mixing ratio; however, zinc(II) could be also removed as about 5-10%. It means that the adsorbent was poor in selectivity to indium(III).

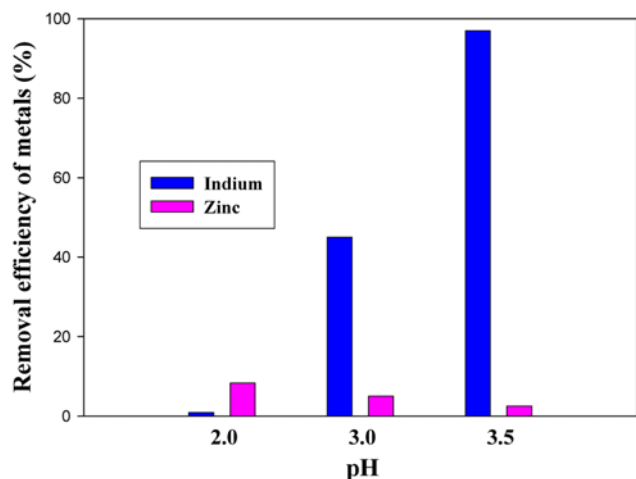From the result, it could be concluded that the optimal adsorbent

Fig. 4. Removal efficiency of metals using phosphorylated sawdust (H_3PO_4 : Distilled water=3 : 1) (Loading amount: 1.0 g, Working volume: 100 mL).
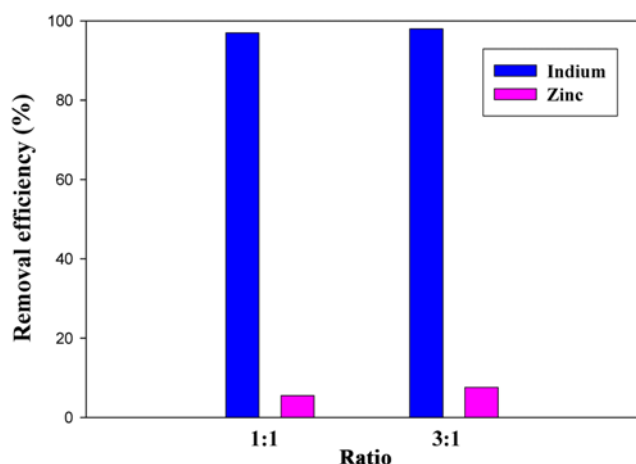

Fig. 5. Removal efficiency on ratio of H_3PO_4 and distilled water at pH 3.5 using grounded phosphorylated sawdust (Loading amount: 1.0 g, Working volume: 100 mL).
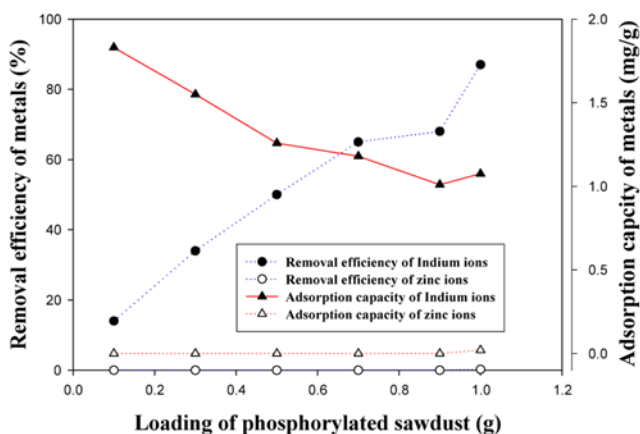

Fig. 6. Effect of doses of phosphorylated sawdust on adsorption capacities and removal efficiencies of indium and zinc ions (Initial concentration of indium ions: 14 mg/L, Initial concentration of zinc ions: 160,000 mg/L, Final pH: 3.5, Working volume: 100 mL).
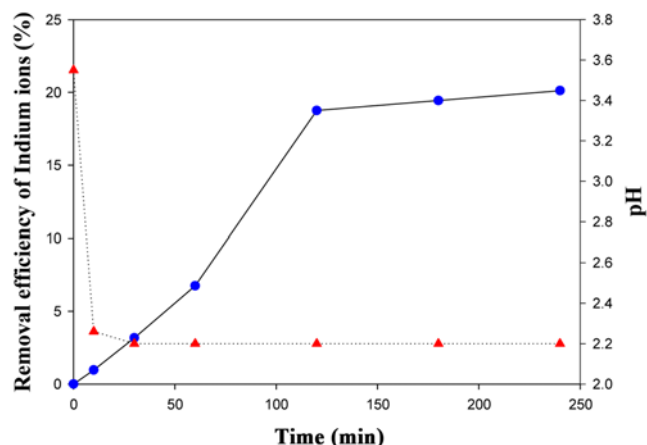

Fig. 7. Removal efficiency of indium ions and pH change with time (Initial concentration of indium ions: 7.25 mg/L, Initial pH of metal solution: 3.55, Loading amount: 0.2 g, Working volume: 100 mL).

for selective removal of indium(III) only, from actual mixed wastewater containing indium(III) and zinc(II), was phosphorylated sawdust made from non-grinding sawdust with 1 : 1 of ratio (H_3PO_4 : distilled water).

Fig. 6 shows the effect of loading of phosphorylated sawdust on the adsorption capacities and removal efficiencies at pH 3.5. For indium(III), removal efficiencies increased while adsorption capacity decreased as loading of adsorbent increased. In general, unsaturated sorption sites for metal ions increased as loading of adsorbent increased [20]. In case of zinc(II), there is almost no adsorption regardless of loading.

Another important parameter in the adsorption process is time. Fig. 7 shows the change of concentration of indium(III) and pH of the suspension solution including indium(III) and phosphorylated sawdust with time. In this study, the concentration of zinc(II) was not considered because of very low adsorption capacity (~0). As time increased, the concentration of indium(III) decreased until 120 min, which means that the adsorption process to indium(III) using phosphorylated sawdust was almost completed within 120 min. Generally, most of adsorption of metals occurs very rapidly and is completed within 2 h [21]. The decrease of pH can be explained as ion exchange mechanism between indium(III) and proton (H^+) ions which occurred from dissociation of carboxyl and phosphate groups in aqueous solution.

CONCLUSION

Phosphorylated sawdsust, which is made from non-grinding sawdust with 1 : 1 of ratio (H_3PO_4 : distilled water), had a very high selectivity to indium(III) in actual mixed wastewater coexisting with zinc(II). It could selectively remove indium(III) of about 90% with 1.0 g at pH 3.5 while there was almost no adsorption to zinc(II). Also, most of the adsorption process for indium(III) was completed within 120 min. From these selective adsorption characteristics and in terms of resource recycling of waste, it could therefore be concluded that conventional treatment methods such as solvent extraction and commercial ion exchange resin can be sufficiently replaced

with an economical process using phosphorylated sawdust.

REFERENCES

1. M. C. B. Fortes, A. H. Martins and J. S. Benedetto, *Miner. Eng.*, **16**, 659 (2003).
2. P. Bermejo-Barrera, N. Martinez-Alsonso and A. Bermejo-Barrera, *Fresen. J. Anal.*, **369**, 191 (2001).
3. A. M. Alfantatazi and R. R. Moskalyk, *Miner. Eng.*, **16**, 687 (2003).
4. B. Gupta, N. Mudhar and I. Singh, *Sep. Purif. Technol.*, **57**, 294 (2007).
5. X. Y. Zhang, C. Y. Yin and Z. G. Hu, *Talanta.*, **59**, 905 (2003).
6. A. W. Trochimczuk and S. Czerwinska, *React. Funct. Polym.*, **63**, 215 (2005).
7. C. H. Xiong and C. P. Yao, *Rare Met.*, **27**, 153 (2008).
8. I.-K. Sung, J.-Y. Song and B.-S. Kim, *Korean Chem. Eng. Res.*, **49**(4), 475 (2011).
9. C. Jeon, *Korean J. Chem. Eng.*, **28**(3), 813 (2011).
10. C. R. T. Tarley and M. A. Z. Arruda, *Chemosphere.*, **54**, 987 (2004).
11. S. S. Shukla, Y. H. Zhang, P. Dubey and J. L. Margrave, *J. Hazard. Mater.*, **B95**, 137 (2002).
12. K. L. Dorris, B. Yu, Y. Zhang and A. Shukla., *J. Hazard. Mater.*, **B80**, 33 (2000).
13. C. Jeon and J.-H. Kim, *J. Ind. Eng. Chem.*, **15**, 910 (2009).
14. J. S. Liu, H. Chen, X. Y. Chen, Y. C. Hu, C. P. Liu and Y. Z. Sun, *Hydromet.*, **82**, 137 (2006).
15. C. Jeon and J.-H. Kim, *J. Korean Org. Res. Rec. Assoc.*, **15**(2), 81 (2007).
16. H. D. Utomo and K. A. Hunter, *Bioresour. Technol.*, **101**, 1482 (2010).
17. C. Jeon, Y.-D. Kwon and K.-H. Park, *J. Ind. Eng. Chem.*, **11**(5), 643 (2005).
18. R. S. Juang and H. J. Shao, *Water Res.*, **36**, 2999 (2002).
19. B. Volesky, Boca Raton, FL: CRC Press, 253-275 (1990).
20. B. D. Honeyman and A. H. Santcchi, *Environ. Sci. Technol.*, **22**, 862 (1988).
21. S. S. Shukla, A. Shukla, Y. H. Zhang and P. Dubey, *J. Hazard. Mater.*, **B95**, 137 (2002).