Application of Bamboo Fiber on the Adsorption of Heavy Metals in Water

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Abstract

Bamboo is a biological material that has beenwidely utilized in green product design and green construction material preparation in recent years. Bamboo is a short-term growth plant, and also an easily accessible biological material with considerably strong strength, which makes bamboo suitable for developing construction materials possessing excellent performance. Physical defibrating for obtaining bamboo fiber is considered environmental friendly compared to chemical defibrating. The physical defibrating is adopted with mechanical defibrating through conditionality control to generate bamboo materials in different dimensions, and the production rate is larger than 85% with rarely damaged structures. In order to enhancethe adsorption of the bamboo fiber for the heavy metal, the materials are surface-modified with chemical reagents. In this study, an attempt is made on enhancing the Pb^{2+} and Cu^{2+} absorption capability of bamboo fibers with phosphorylation and sulfonation. The characteristics of adsorbents affecting Pb^{2+} and Cu^{2+}absorptionwere discussed, including different bamboo fiber, pH, andadsorption time. Under the optimaladsorption condition, the thorny bamboo fiber hadthe better absorption performance of Pb^{2+}(20.0 mg/g) and Cu^{2+} (12.8 mg/g). Therefore, chemically modified bamboo fiber could be used as a good bioadsorbent to remove heavy metals from waste water.

Keyword

Bamboo fiber, mechanical defiberization, heavy metal, chemical modification

Introduction

Owing to the advance in technology, the development of the society changes from the agriculture age into the industrial age. Because the industry and commerce flourish, the environment

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is heavily polluted by the heavy metals from the processing factories. Unlike organic wastes, heavy metals are non-biodegradable and can be accumulated in living tissues, causing various diseases and disorders; therefore, they must be removed before discharge. If the heavy metals in river and soil is not removed, the crops and drinking water will be polluted to harm the environment and the human health.Specially, the endangerment of lead and copper is more serious. Lead is a common contaminant in the natural environment that can enter the water column through geologic weathering and volcanic action, or by various anthropogenic practicesincluding smelting, coal burning and use of gasoline, batteries and paint (Roger and Wood 2004;World Health Organization 1995). Though waterborne lead concentration does not normally exceed 0.6 μmol/L (Demayo et al. 1982), levels as high as 4.3mmol/l have previously been reported (US Environmental Protection Agency, 1986). Contamination of water through anthropogenic practices is the primary cause of lead poisoning in fish (Sorensen 1991). Lead has long been recognized as a poison to living organisms, with negative effects on general health, reproduction, behavior, and potentially leading to death. Ingestion and inhalation are the twomost common entry routes of lead into animals. (Demayo et al. 1982; Eisler1988; Fisher et al. 2006;Pain 1995; Mateo 1998; Guitart et al. 1999). On the other hand, copper is broadly applied to cause the serious harm of the environment. It is similar with iron that copper does not have critical toxicity and generates the oxide compound under the moist condition. Even so, when people eat any food with the overdose copper, it results in stomach pain, enteritis, acute hepatitis, and kidney toxicity (Gardea-Torresdey et al. 1996). When the heavy metals enter to the human body, most contentsare stored and cannot be removed for a long time. Consequently, it is important to prevent fromexposureto the polluted environment containing these heavy metals. There are many studies on the economic and efficient methods to remove heavy metals from water and soil (Veglio et al. 1997;Gaballah et al. 1998; Volesky et al. 2001;Ng et al. 2002; Bayramoglu et al. 2002). The approachesdescribed in these literatures include chemical precipitation, physical adsorption, membrane separation, electrolysis, composite action, ion exchange, condensation, evaporation, surface micro sedimentation, and biological treatment. However, these operating processesare generally complex, additionally, couldcause second pollution after the treatments. Furthermore, it is not cost-effective to remove heavy metalsin low concentrationsdue to mass transfer limitation. Therefore, many studies focus on more creative, low-cost technology toremove not only heavy metals from waste water but also decrease the generated waste. Adsorption using activated carbon isone of the most extensive methodsfor heavy metal removal but it is not considered cost-effective (An et al., 2001).According to Bailey et al. (1999), an adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing, and is a byproduct of waste materials from waste industry. Plant wastes are inexpensive as they have very little or no economic value.

In the decades, bioadsorption from plant has been considered an innovative method to remove the heavy metals in waste water. Bioadsorption uses the biomass as the adsorbent to generate the chelation with the heavy metal ion and then the combination is removed. The mechanisms of the bioadsorption contain cell metabolism, non-cell metabolism extracellular accumulation/precipitation, cell surface sorption/precipitation, and intracellular accumulation (Veglio et al. 1997). After the bioadsorbent is used to remove the heavy metal, it can be directly burned in an incinerator withfollowing suitable dust collection equipment to avoid second pollution to the environment. Therefore, bioadsorbents have huge commercial potential. Because the waste of the agriculture and forestry is easy to be obtained and its cost is lower than commercial adsorbent, these wastes, including the woody materials, bark, tea leaves, hyacinth, duckweed, rice husk, etc.can be broadly used as the bioadsorbents. These bioadsorbents have different yields to remove various heavy metals (e.g., cadmium, lead and zinc, copper and nickel) (Masri et al. 1974; Sharma and Forster 1993; Roy et al. 1993; Srivastava et al. 1994). In addition, many studieshave been conducted to search the solution to improve the yield of the bioadsorption. Through the chemical surface modification, the adsorption capacity of the bioadsorbent is improved for the heavy metals. It is due to the change of the adsorbent's surface functional group to generate the chelation with the heavy metal ions. In the literatures, sodium hydroxide can increase the carboxylic group to adsorb the heavy metalions(Tiemann et al. 1999; Gardea-Torresdey et al 2000; Min et al. 2004). The removing yield of chromium, mercury, lead and cadmium using chitin can be improved up to 5-6 times (Yang and Zall 1984). The bioadsorbent with sulfonic acid group is effectiveto remove the heavy metals in polymer film (Choi and Moon 2003).

Because bamboo grows rapidly and has superior performance, the four-years-old bamboo can be used to manufacture many types of products. Bamboo occupies an area of approximately 150,000 ha and is one of the most important forest products in Taiwan. The bamboo forest in Taiwan contains six major domestic groups: makino bamboo (*Phyllostachys makinoi*), ma bamboo (*Dendrocalamus latiflorus Munro*), green bamboo *(Bambusaoldhamii Munro)*, thorny bamboo (*Bambusa stenostachya Hackel*), moso bamboo*(Phyllostachys heterocycla*), and long-branch bamboo*(Bambusa dolichoclada Hayata*) (Lu and Zhou, 2009). Among them, Makino bamboo is the most abundant in Taiwan and thorny bamboo is now less manufactured to the commercial product. In this study, makino bamboo and thorny bamboo are physically defibrated to obtain the bamboo fiber used as the bioadsorbent to remove lead and copper ions in water.

Materials and Methods

Defibrating process

The four-years-old bamboo was gathered and cropped to the chip. The mechanical miller was used to defibrate under 10kgf/cm^2 with the vapor at 200°Cto get 500g of the bamboo fiber per batch. The whole process was completed in 3 min and the yield is more than 90%. Because the bamboo fiber is a hydrophilic material and has many functional groups, it can be used as an adsorbent to remove the heavy metals in waste water. In this study, makino bamboo (MB) and thorny bamboo (TB) were used as the raw bioadsorbents. These two bamboos were modified by phosphoric acid and sodium sulfite, which were respectivelydesignated P-MB, S-MB, P-TB, and S-TB.

Chemical Surface Modification

In this study, phosphorylation and sulfonation were adopted to modify the surface functional group of bamboo fiber. For the phosphorylation (Klimmek et al. 2001), 15g of bamboo fiber was mixed with 22.5g of urea. Then, the mixture was added into 500 mL of phosphoric acid solution (30%), homogeneously stirred and placed for 30 min at ambient temperature. The mixture was then put into the oven at 70° C to become mushy. Finally, the mixture was cleanedby pure water to remove the excess reagent and dried in the oven with 70°C. The phosphorylated bamboo fiber is a modified bioadsorbent now.

For the sulfonation (Shin and Rowell 2005), 20g of bamboo fiber was mixed with 25.2g ofsodium sulfite and the mixtureswere put into 300 mL of water. 1N of nitric acid was used to adjust pH value to reach 3.0. The mixture in the solution was stirred for 1 day. Finally, the mixture was cleaned by pure water and dried in the oven with 70°C. The sulfonated bamboo fiber was collected and stored for the subsequent bioadsorption tests.

Adsorption of the Heavy Metal

The lead and copper were chosen as the adsorbates. The lead nitrate and copper nitrate were respectively dissolved in water as the heavy metal ion solution in various concentrations. Nitric acid and sodium hydrogen were used to adjust the pH value of the heavy metal solution from 3 to 8. For the adsorption test, 0.25 g of the bamboo fiber was addedto the solution with a fixed ratio of 1/400 g/mL. For the dynamic adsorption, the same amount of bamboo fiberwas put into100 ppm ofthe heavy metal solutionand the changes in metal concentration was monitoredat various intervals.

Apparatus

The raw samples and modified materials were observed usinga scanning electron microscope (SEM, FEI Quanta 400F). The functional groups of the bioadsorbent were analyzed by Fourier transform infrared spectroscopy, FTIR. The chemical composition, including the mass concentration of C, H, N, and S for beads, was measuredusing an elemental analyzer (CE Instruments Flash 1112 Series EA). The concentration of the heavy metals in water was tested by graphite and flame atomic absorption spectroscopy (GCB 932 Plus and GCB932 AA)

Results and Discussion

In order to avoid producing a significant quantity of chemical pollutants, physical and mechanical methods were adopted in defibrating process. Figure 1 shows the SEM graphs of makino bamboo fiber, thorny bamboo fiber, and modified fibers from these. It was observed that the surface of two raw bamboo fibers was smooth and had no porous structure. The diameter was about 10 μm for both, makino bamboo and thorny bamboo, fiber. With the phosphorylation and the sulfonation, SEM graphs (B, C, E and F in Figure 1) showed that more pores were formed in cylindrical and slit shapes on the surface and within the layer of the modified bamboo fibers. These poresmaybe highly accessible and provide more chances to adsorb and retain the heavy metals in water. Figure 2 showsthe FTIR curves of makino bamboo, and thorny bamboofibers, as well as modified fibers of these two bamboos. Significant differenceson the FTIR patterns between the makino and thorny bamboo fibers were not observed. The broad peak at 3200-3600cm^{-1} was resulted from –OH group. The peak at 2800-3000 cm^{-1}was observed due to the symmetric stretching vibration band of $–CH_2$ and $–CH_3$. The stretching band of carbonyl group (-CO) was shown at 1550-1750 cm^{-1}. In phosphorylation process, phosphoric acid proceededthe dehydration to form polymeric phosphoric acid and then esterified with the hydroxyl group of bamboo fiber in urea solution. Therefore, the peakof the hydroxyl groups of phosphorylated makino bamboo and thorny bamboo (curves B and E in Figure 2) became broader than that of the raw bamboo fiber. According to the literatures (Wing et al. 1997;Welch 1992), the phosphorylated material would improve the adsorbing capacityfor the heavy meatal in water. For the sulfonated makino bamboo fiber and thorny bamboo fiber (curves C and F in Figure 2), the symmetric and asymmetric vibration bands of sulfonategroup appeared at 1150-1190cm^{-1} and 1300-1390cm^{-1}, respectively. It showed a good agreement with the result of literature (Shin and Rowell 2005).

Table 1 shows the elemental analysis results of makino bamboo, thorny bamboo and the modified bamboo fibers. The carbon content of the raw bamboo fiber was about 46%, similar with those of the modified bamboo fiber by the phosphorylation and the sulfonation. After the phosphorylation, the modified bamboo fiber (P-MB and P-TB) had greater nitrogen contents (0.52 and 0.61%, respectively) than those of the raw bamboo fibers (MB and TB). It resulted from the urea solution used in the phosphorylation. By comparison, the sulfated bamboo fibers (S-MB and S-B) had a significant increase of the sulfur content. Especially, the sulfur content of the sulfated thorny bamboo was up to 0.79%. It was effective to adsorb the heavy metal in water.

Table 1.The elemental analysis of makino bamboo, thorny bamboo, and the modified bamboo fibers

Sample	Element			
	N%	C%	S%	H%
MB	0.31±0.02	45.84±0.20	0.05±0.01	6.25±0.01
P-MB	0.52±0.00	45.97±0.07	0.18±0.01	6.54±0.05
S-MB	0.39±0.01	45.51±0.03	0.39±0.05	6.26±0.01
TB	0.35±0.01	45.57±0.12	0.13±0.03	6.22±0.01
P-TB	0.61±0.01	45.55±0.11	0.20±0.03	6.30±0.17
S-TB	0.40±0.04	45.38±0.13	0.79±0.39	6.22±0.01

Because the heavy metal solution with various concentrations has the different degree of ionization, the heavy metal shows ionic state in acidic solution, generates the hydroxide precipitate in neutral solution with slight alkaline and the hydroxide complex ion,$M(OH)_n^-$ in strong alkali solution (Lange 1964). Therefore, the adsorption of the different bamboo fibers was studied for the heavy metal solution with various pH values. Figure 3 shows the removing yield of lead ion (25ppm) using makino bamboo, thorny bamboo, and their modified fibers in solution with various pH values. For makino bamboo and thorny bamboo, the removing yield of lead ionincreased with the increasing pH value. When the pH valueof the solution was lower, the functional group of the bioadsorbents to adsorb the heavy metal ion is occupied by the hydrogen ion (Villaescusa et al. 2004). Therefore, the higher pH value increased the removing yield of the heavy metal ion forthe bamboo fiber. After the phosphorylation (curves C and D in Figure 3), the Pb^{2+} removing yield using the modified bamboo fiber was significantly promoted as the pH value was lower than 6. However, when the pH value was increased to 7 and 8,the hydroxide complex ionmight be generated to affect the adsorption of the modified bamboo for lead ion (Pb^{2+}) in water. It resulted in no difference with the raw material. For the modified bamboo fiberby the sulfonating procedure (curves E and F in Figure 3), a greater increaseof the Pb^{2+}removing yield was observed and gradually reached plateau as the pH value was higher than 6.It was suggested that the sulfonating procedure more efficiently promoted the adsorption capacity of the modified bamboo fiber for lead ion. The abovementioned results suggest that sulfonation does not result in significant difference between modified makino bamboo and thorny bamboo for Pb^{2+} adsorption. The Pb^{2+} removing yield by the sulfonated thorny bamboo fiber was up to 91%. In other words, the chemical modification would reduce the difference among the various kinds of bamboo to reach a commercial application.

Figure 4 showsthe results for the removing yield of copper ion (25ppm) using makino bamboo, thorny bamboo, and their modified fiber in solution with various pH values, respectively. In comparison with the results of Figure 3, raw bamboo fiber had lesser removing yield of copper ion than that of lead ion. For the chemical surface modification, the sulfonated bamboo fibers (curves E and F in Figure 4) had the higher removing yield of copper ion (Cu^{2+}) at various pH value than that of the phosphorylated bamboo fibers (curves C and D in Figure 4).

In order to study the dynamic adsorption of the various bamboo fibers, the initial concentration of the heavy metal solution was increased to 100 ppm. Figure 5 showed various dynamic Pb^{2+}adsorption of makino bamboo, thorny bamboo, and their modified fibers for lead ion in solution with pH=6.5 at 30°C.A great decrease in the concentration of lead ionwas observed at the initial 10 min, which was resulted from the adsorption of bamboo fiber. After 30 min, the curves of all the samples appeared a flat trend. For the sulfonated thorny bamboo fiber with the greatest adsorption capacity, the lead ion concentration was reduced to 55ppm (av. 18.0 mg Pb^{2+}/g adsorbent) in 10 min and 50ppm in 30 min (av. 20.0 mg Pb^{2+}/g adsorbent). This result indicated that the dynamic adsorption of various bamboo fibers reached a balance in a short timefor lead ion. Figure 6 shows the various dynamic Cu^{2+} adsorption of makino bamboo, thorny bamboo, and their modified fiber for copper ion in solution with pH=6 at 30°C. Similarly, the concentration of the copper ion was decreased by the adsorption of the bamboo fiber. The thorny bamboo fiber could reduce the copper ion more than the makino bamboo fiber. In addition, the sulfated bamboo fiber adsorbed more the copper ion in water than the phosphorylated bamboo fiber. Specially, for the sulfated bamboo fiber (S-TB), the copper ion concentration was reduced to 68 ppm (av. 12.8 mg Cu^{2+}/g adsorbent). In other words, the sequential adsorbing ability of various bamboo fibers were the sulfonated thorny bamboo fiber (S-TB), the sulfated makino bamboo fiber (S-MB), the phosphorylated thorny bamboo fiber (P-TB), the phosphorylated makino bamboo fiber (P-MB), the thorny bamboo fiber (TB) and the makino bamboo fiber (MB). Therefore, the simply chemical modification could greatly promote the adsorption capacity of the modified bamboo fiber.

Conclusion

Bamboo was physically defibrated at high pressure with the vapor. By the chemical modification, the adsorption capacity of the bamboo fiber could be promoted for the heavy metals in water. The sulfonated thorny bamboo fiber would more effectively reduce the heavy metals in the waste water and could prevent from the second pollution after the processing program. In addition, the application of bamboo fiber on a bioadsorbent to remove the heavy metals would promote the innovative development of a bamboo industry and the income of the bamboo farmers in Taiwan.

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Figure caption

Figure 1. SEM graphs for makino bamboo, thorny bamboo and their modified fiber:(A) MB, (B) P-MB, (C)S-MB, (D) TB, (E)P-TB and (F)S-TB

Figure 2. . FT-IR curves for makino bamboo, thorny bamboo and their modified fiber:(A) MB, (B) P-MB, (C)S-MB, (D) TB, (E)P-TB and (F)S-TB

Figure 3. Removing yield oflead ion (25ppm) usingmakino bamboo, thorny bamboo and their modified fiber in solution with various pH values

Figure 4. Removing yield of copper ion (25ppm) using makino bamboo, thorny bamboo and their modified fiberin solution with various pH values

Figure 5. Dynamic Pb^{2+} adsorption of makino bamboo, thorny bamboo and their modified fiber for lead ion in solution with pH=6.5 at 30℃

Figure 6. Dynamic Cu^{2+} adsorption of makino bamboo, thorny bamboo and their modified fiber for copper ion in solution with pH=6 at 30℃

Figure 1

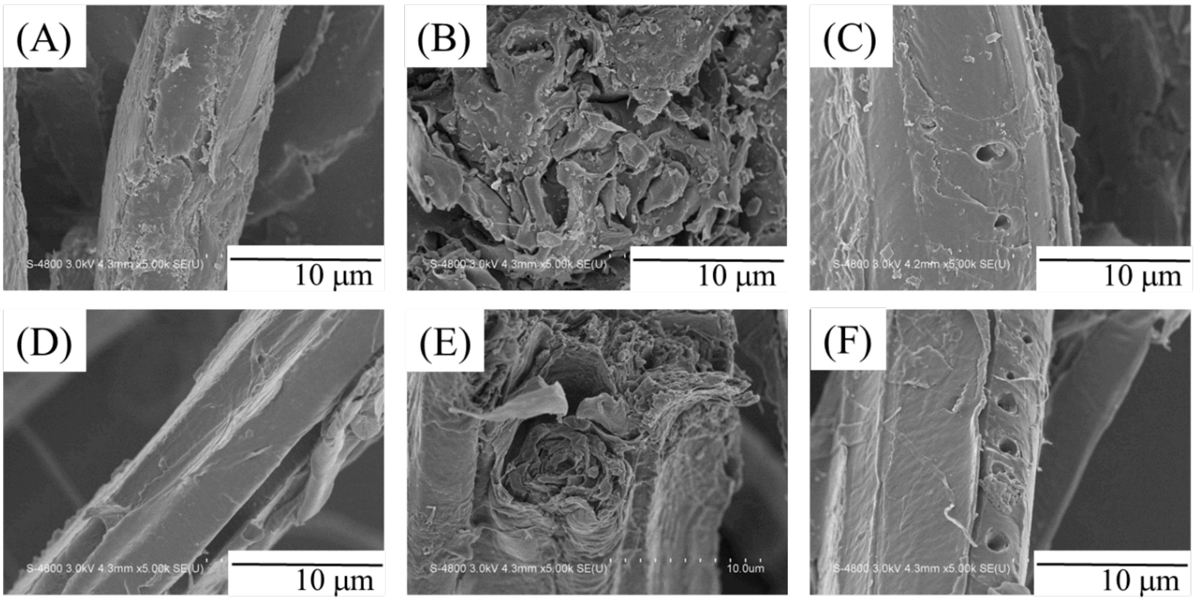


Figure 2

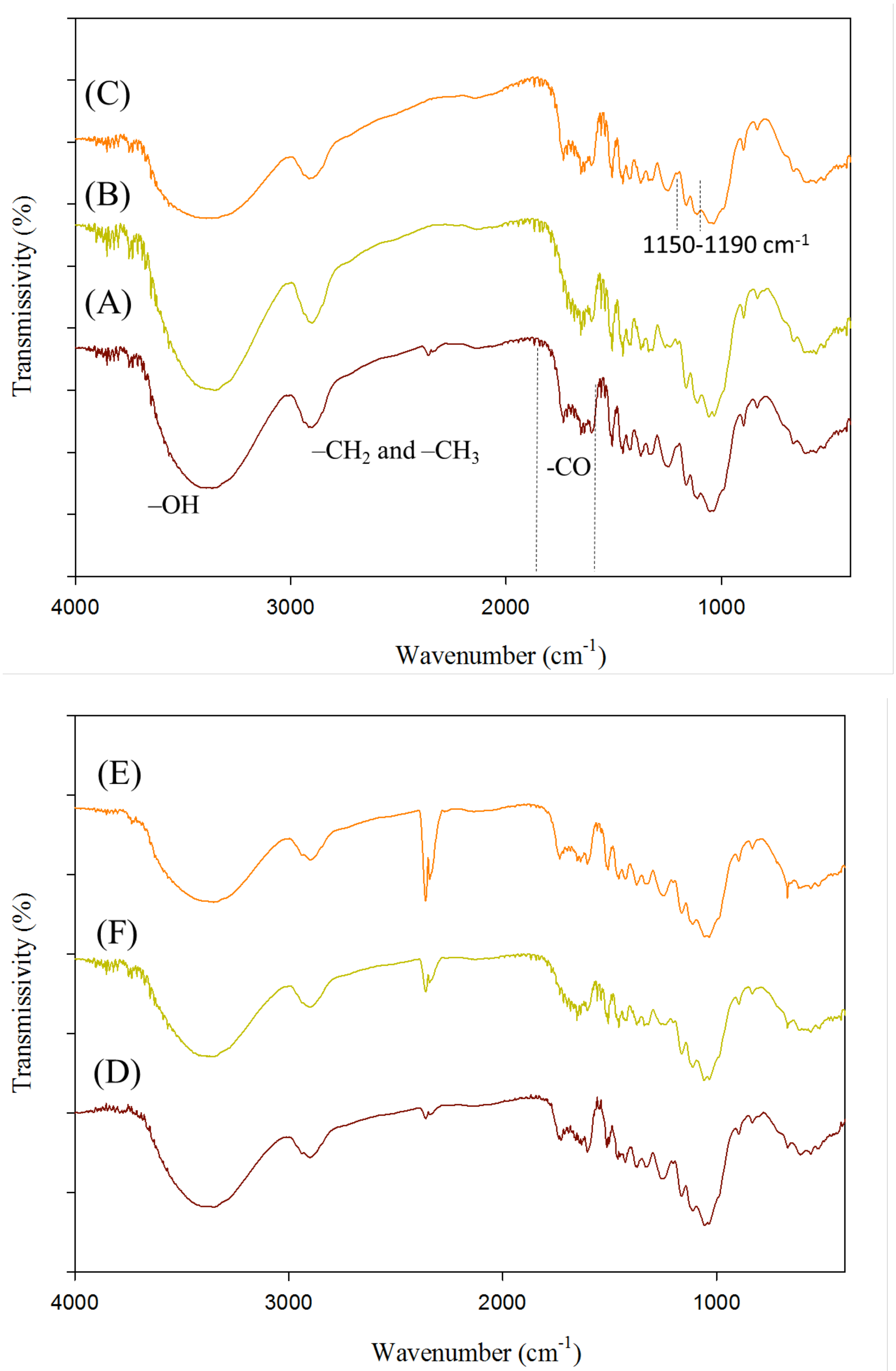
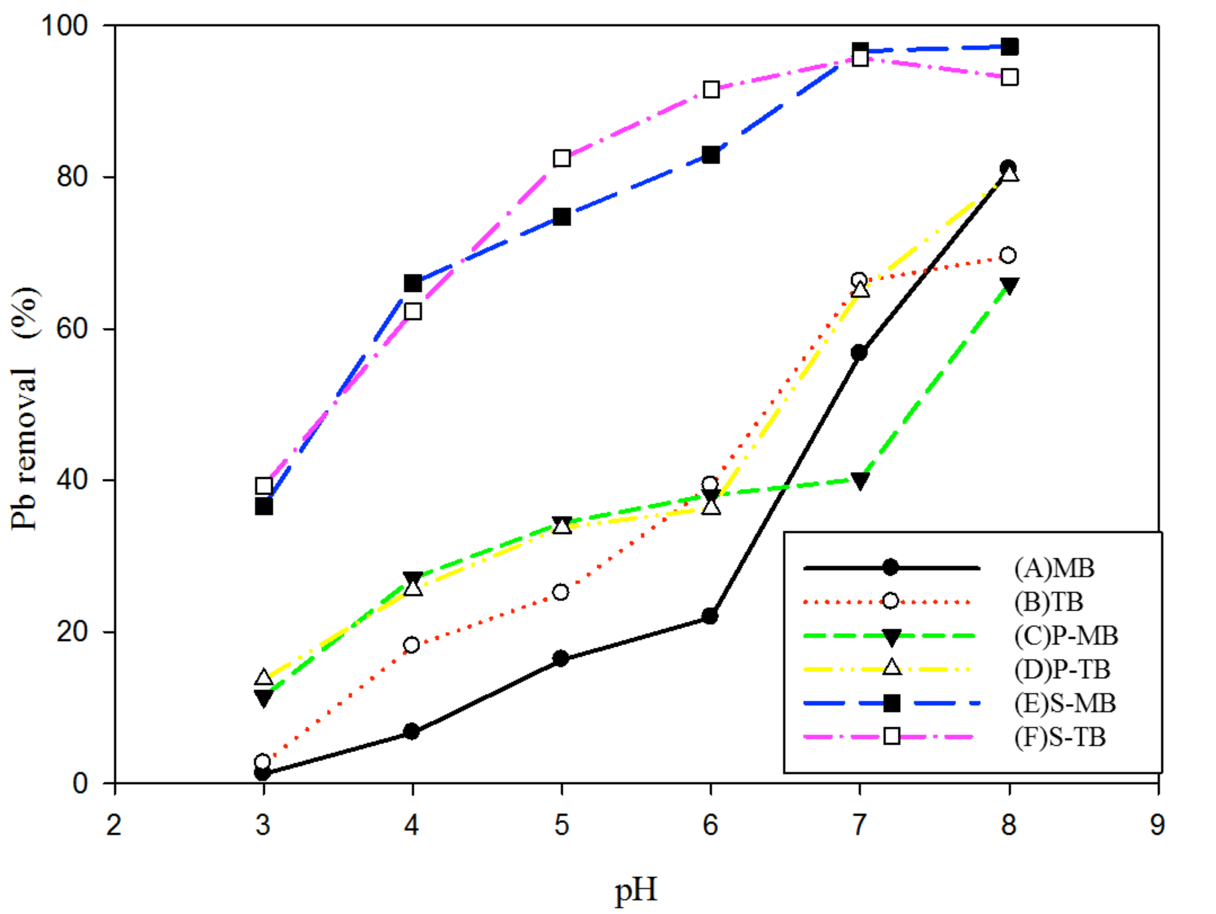

(C)
(B)
(A)
1150-1190 cm-1
–CH2 and –CH3
-CO
–OH
Transmissivity (%)
4000
3000
2000
1000
Wavenumber (cm-1)
(E)
(F)
(D)
Transmissivity (%)
4000
3000
2000
1000
Wavenumber (cm-1)

Figure 3


Pb removal (%)
pH
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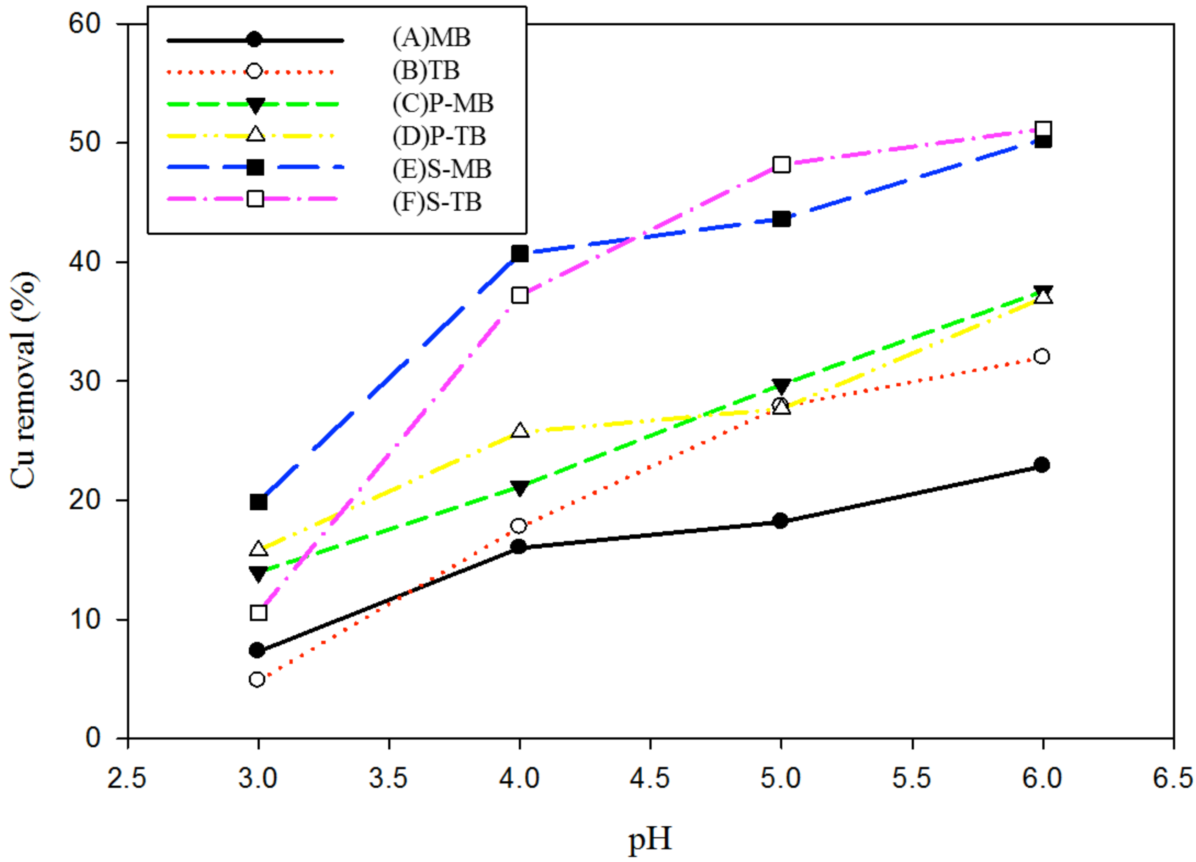
20
40
60
80
100
2
3
4
5
6
7
8
9
(A)MB
(B)TB
(C)P-MB
(D)P-TB
(E)S-MB
(F)S-TB

Figure 4


60
50
40
30
20
10
0
Cu removal (%)
2.5
3.0
3.5
4.0
4.5
5.0
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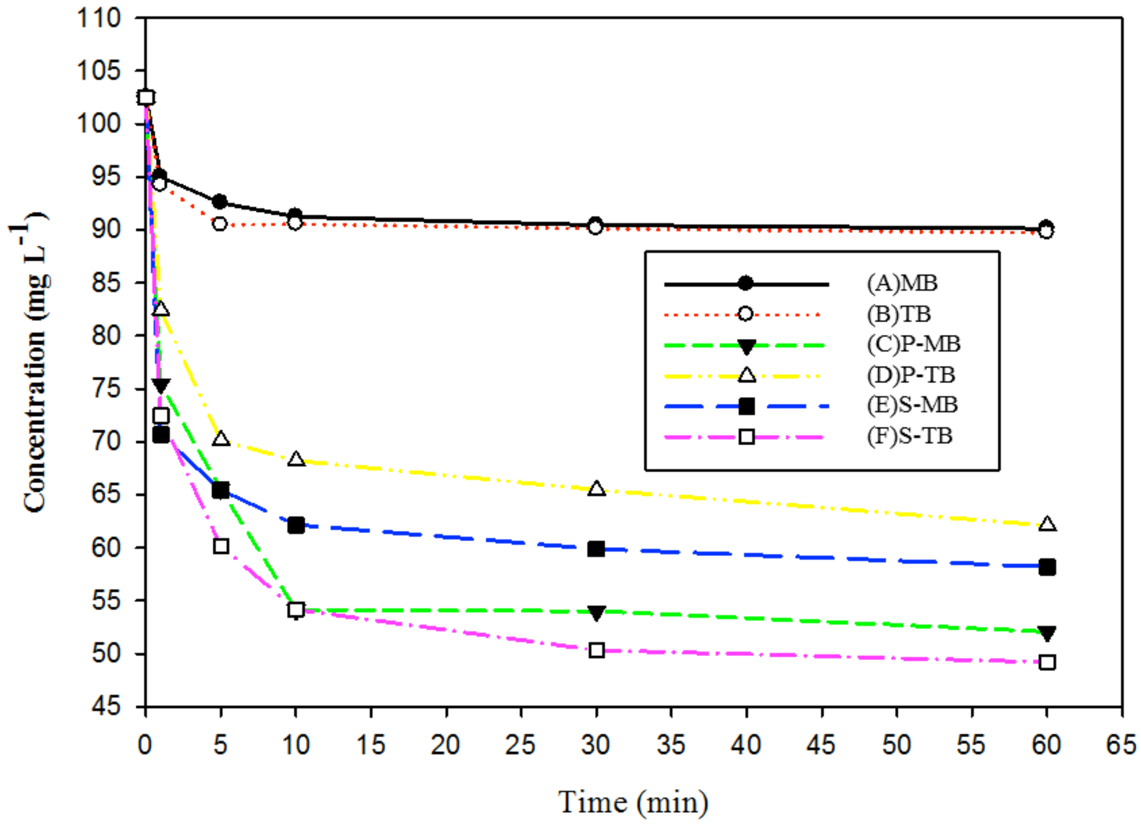
(E)S-MB
(F)S-TB

Figure 5


Concentration (mg L^{-1})
Time (min)
(A)MB
(B)TB
(C)P-MB
(D)P-TB
(E)S-MB
(F)S-TB
110
105
100
95
90
85
80
75
70
65
60
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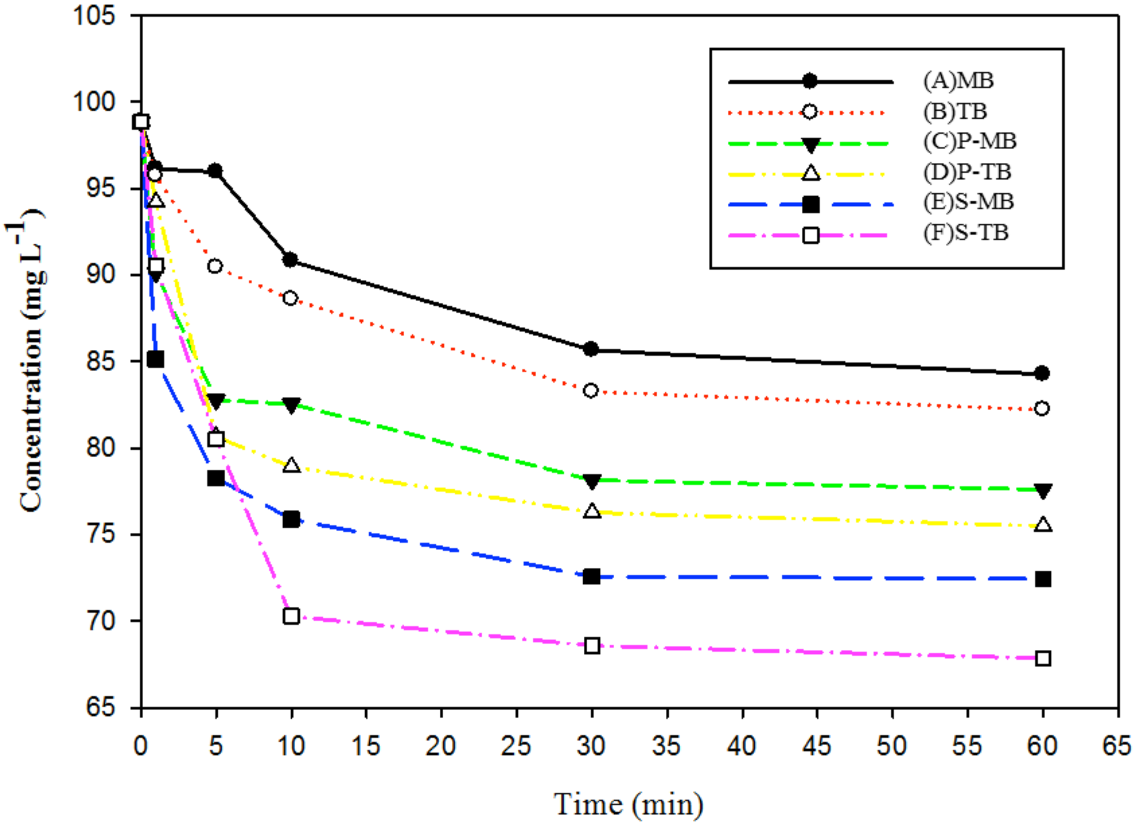
65

Figure 6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60
65
Concentration (mg L^{-1})
Time (min)
(A)MB
(B)TB
(C)P-MB
(D)P-TB
(E)S-MB
(F)S-TB

Theme: Ecology and Environmental Concerns