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Removal of Lead in a Fixed-Bed Column Packed with Activated Carbon and Crab Shell

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ABSTRACT

Crab shell particles (*Protunus trituberculatus*) and activated carbon (Norit 0,8 SUPRA) were used as packing materials in a fixed-bed column. When 1 g crab shell was added in a column packed with 10 g activated carbon, breakthrough occurred at 1500 bed volumes as compared to 380 bed volumes for 10 g activated carbon only. The addition of crab shell particles into an activated carbon column resulted in an increased uptake of lead. The dramatic improvement might be attributed to an increase in CO_3^{2-} and OH^- available for binding lead. From the results of SEM, XRD, and FT-IR analyses, the major mechanism of lead removal was based on

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dissolution of $CaCO_3$ in the crab shell followed by precipitation of $Pb_3(CO_3)_2(OH)_{2(s)}$ on the surface of activated carbon. The lead uptake increased twofold when the influent lead concentration was increased from 10 to 50 mg/L.

Key Words. Activated carbon; Crab shell; Precipitation; Fixed-bed column

INTRODUCTION

Adsorption by activated carbon is a well-established treatment method for organic contaminants (1, 2). Activated carbon can also adsorb cadmium, copper, lead, mercury, and other heavy metals (3–10). Oxygen is chemisorbed during the activation process, which places a functional group on the surface of activated carbon. Oxide groups on the surface of activated carbon, such as carboxyl, phenolic hydroxyl, and quinone groups, are very important for the removal of heavy metals because they can adsorb positively charged heavy metal ions from an aqueous solution. For removing heavy metals efficiently, certain types of activated carbon that contain oxide groups should be used, otherwise the surface of activated carbon should be properly modified (11–13). In addition, earlier works indicated that activated carbon could remove lead and cadmium by precipitation (14, 15). The activated carbon acts as an OH^- reservoir in the process. However, because most metals precipitate in the form of a metal hydroxide, regenerating activated carbon by acid and alkaline rinsing still has some limitations (16). For example, regenerated activated carbon reaches the breakthrough point at a quite high effluent pH (14). Therefore, we considered the addition of crab shell particles to an activated carbon column since they contain a high proportion of $CaCO_3$ which can act as a CO_3^{2-} reservoir (17, 18). In addition, carbonate ions are even more effective in precipitating lead than are OH^- ions. Carbonate precipitation occurs at lower pH values than precipitation with hydroxide ions (19).

For the present work, crab shell was applied to enhance the removal efficiency of lead in a fixed-bed column packed with Norit activated carbon. The goal of this work was to demonstrate the effect of an alkaline material, such as crab shell, as an aid to the adsorption of metals by activated carbon.

SELECTED BACKGROUND INFORMATION

To remove any toxic heavy metal in groundwater and wastewater, chemical precipitation is preferred to other methods because it can treat high concentrations of metal ions with low cost (20–22). Hydroxide precipitation, in which lime or caustic soda is added to adjust the pH of wastewater to the alkaline region, is preferred, particularly in treatment processes, because of the lower cost of the chemicals (21, 23). This method is cost-effective and suitable for automatic control, but it has several problems such as poor filtration, large volume of sludge, and low removal efficiency in the presence of chelating agents. Moreover, hydroxide precipitation of mixed metal ions may not be effective because the minimum solubilities occur at different pH values. Soda ash or sodium carbonate is not particularly corrosive by itself, and it has superior handling characteristics—little dust, good flow, and no arching in the feeder. Carbonate precipitation occurs at lower pH values than those for optimum hydroxide precipitation (19, 24). Metal carbonate precipitates are reported to the denser than hydroxide precipitates, thereby improving solid separation and decreasing sludge volume. In addition, carbonate sludges have better filtration characteristics than those of hydroxide sludges. However, soda ash is difficult to dissolve in water (16).

Because of several limitations to the treatment of low concentrations of heavy metals by chemical precipitation in a stirred tank reactor, which is the most common process, the removal of heavy metals by activated carbon has been considered as an alternative treatment method. Reed et al. suggested that activated carbon could be used to remove heavy metals by precipitation because it has large surface area and pore volume which make it possible to retain and release OH^- ions very slowly (14, 15). The OH^- ions form metal hydroxide precipitates which attach to the surface of activated carbon when an influent to the fixed-bed column contains heavy metals. In addition, activated carbon is fully regenerated by washing with HNO_3 and rinsing with NaOH. However, regenerated activated carbon still has the same limitations as hydroxide precipitation because it also makes metal hydroxides precipitate in the pore liquid or on the surface of activated carbon. For example, although regenerated activated carbon can treat approximately 315 bed volumes of influent containing 10 mg/L lead solution at pH 5.4, breakthrough occurs at an effluent pH of 8.5 because the major removal mechanism is precipitation of lead hydroxide. The optimum pH range for the maximum removal of lead by hydroxide precipitation is 8.5–11.0 (16). Therefore, when crab shell particles are added to the activated column, the removal performance should be increased because the crab shells contain a high proportion of $CaCO_3$. The crab shell particles act as a CO_3^{2-} reservoir and release CO_3^{2-} ions continuously. The CO_3^{2-} is probably retained and released for a long time due to the large surface area and pore volume of the activated carbon. The low solubility of calcium carbonate would no longer be a problem in the column due to the low influent pH. In addition, carbonate precipitation is more effective than that of hydroxide. When 0.5 g/L of crab shell was added, the pH range expanded to 5.5–11.0 because of carbonate precipitation (17).

EXPERIMENTAL

The shell of *Protunus trituberculatus*, a crab species, was powdered and sieved to yield particles of 25–100 mesh size. Norit 0,8 SUPRA (Norit), a peat-based extruded activated carbon, was used as the column packing material. Selected characteristics of Norit 0,8 SUPRA are presented in Table 1. The activated carbon was sieved to an appropriate particle size (≈1 mm) and washed with deionized water 4 or 5 times to remove micro particles. The air in the pores of the activated carbon was removed under low vacuum by a vacuum pump (Yamato MINIVAC PD-52) before packing. Lead nitrate (Junsei Chemical) was dissolved in deionized distilled water to prepare the lead-containing solutions. Experimental solutions with different lead concentrations (10 and 50 mg Pb/L) were prepared. In order to minimize the precipitation of lead, the pH of the solution was fixed to 3.0 with HNO_3/NaOH, and the ionic strength was adjusted to 0.05 with $NaNO_3$. The activated carbon and crab shell were packed as alternate lagers in a 30-cm long, 2-cm inner diameter glass column by the slurry packing method to minimize the formation of air voids. Glass wool and sea sand were used as the column support media. The characteristics of packing materials and influent solutions to the fixed-bed columns were as follows: 1) 10 g activated carbon and 10 g activated carbon plus 1 g crab shell, 2) 10 and 50 mg Pb/L at pH 5.0. The pH values of the influent solutions were maintained in the ±0.1 pH unit range. The hydraulic flow rate of influent in each experiment was maintained by using a peristaltic pump (EYELA SMP-23) with a speed controller at 10 mL/min (3.2 $cm^3/cm^2 \cdot min$). The empty bed contact time (EBCT) was approximately 2.2 minutes for all experiments. The fixed-bed columns were operated in the down flow mode. Effluent solutions were collected either every 30 or 60 minutes, measured for pH, acidified using concentrated HNO_3, and stored in polyethylene test tubes. Lead in the effluent solution was analyzed by a flame

TABLE 1
Characteristics of Activated Carbon, Norit 0,8 SUPRA

Apparent density (g/L)	380
Total pore volume (cm^3/g)	1.0
Slurry pH	9.5–9.9
Sieved particle size (mm)	0.7–1.0
Ash content (%)	8
Molasses number	350
Iodine adsorption (mg/g)	1100
Phenol adsorption (%)	6
Ball pan hardness (%)	94
Dechlorination halving value (cm)	4

atomic absorption spectrophotometer (AAS, Perkin-Elmer model 3100). The AAS was equipped with a hollow cathode lamp and was used to analyze the total concentration of lead in the effluent solutions. The wavelength and slit for lead were 283.3 nm and 0.7, respectively. If necessary, samples were diluted with deionized water prior to analysis. Following each column run, the activated carbon was regenerated by washing with 0.1 N HNO_3, rinsing with 0.1 N NaOH to an alkaline pH, and then drying for 3 hours in an oven at 200°C (14). Approximately 200 mL of 0.1 N HNO_3 was pumped through the fixed-bed column at a flow rate of 10 mL/min. Samples of the acid rinse were taken periodically and measured for pH and lead content. The above procedure was repeated with 200 mL of 0.1 N NaOH. After regeneration, new crab shell particles and regenerated activated carbon were packed alternatively and the column was restarted. Column tests were run for approximately 12 hours per day, and new influent solutions were prepared daily. All experiments were performed at room temperature.

To determine the major mechanism of lead removal, the activated carbon which was contacted with lead up to the breakthrough point in the fixed-bed column was analyzed with a scanning electron microscope (SEM, Philips 535M), an x-ray diffractometer (XRD, RIGAKU D/MAX-III), and a Fourier transform infrared spectrometer (FT-IR, Bomem MB-100). The characteristics of the column influent and packing material for the removal mechanism study were as follows: 1) 50 mg Pb/L only at initial pH 5.0, 2) 10 g activated carbon only and 10 g activated carbon plus 1 g crab shell. After the column test, samples of the packing material were collected, washed with distilled water, and then dried in an oven. The crashed packing material was observed with an SEM equipped with energy dispersive spectroscopy (EDS, EDAX International Co. PV 9900) at 15 kV of the acceleration voltage. The crashed packing material was mounted on a stainless steel stub using double-stick tape and then coated with a thin layer of gold. The solid formed on the surface of the packing material was examined by XRD using CuKα radiation at 30 kV and 40 mA. Measurement was made using the continuous scanning technique from 10 to 70 of 2θ. FT-IR for the raw activated carbon and packing material were used to identify the changes after contact with the lead solution. The infrared spectra of the raw activated carbon and packing material were recorded by serial dilution with KBr in the 4000–400 cm^{-1} range of wavenumbers.

RESULTS AND DISCUSSION

Effects of Crab Shell as an Aid to Activated Carbon Column

Experiments were conducted with Norit activated carbon and crab shell particles in the fixed-bed column to remove lead. The normalized effluent

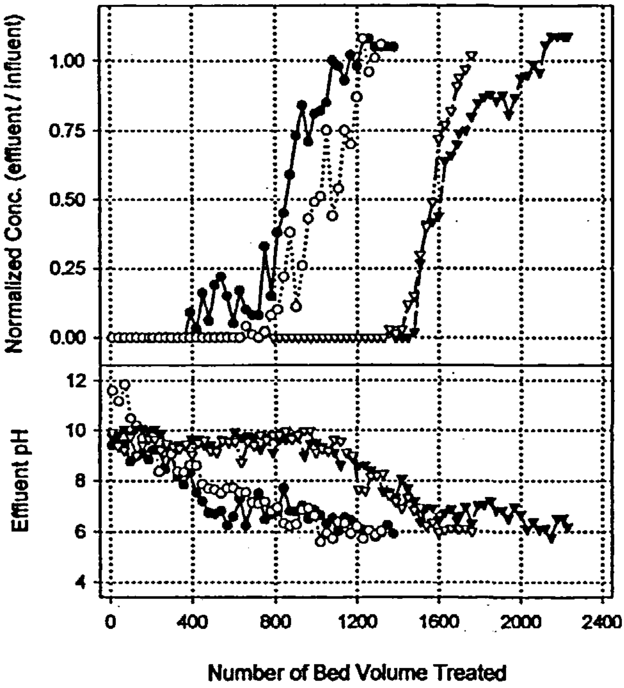

FIG. 1 Breakthrough and effluent pH curves for influent containing 10 mg Pb/L at pH 5.0: (●) 10 g activated carbon, (○) 10 g regenerated activated carbon, (▼) 1 g crab shell + 10 g activated carbon, (▽) 1 g crab shell + 10 g regenerated activated carbon.

lead concentration versus the number of bed volume treated for influent containing 10 mg Pb/L at pH 5.0 are presented in Fig. 1. A normalized effluent concentration of 0.05 was selected as the breakthrough concentration. When the fixed-bed column was packed with 10 g activated carbon + 1 g crab shell, the volume of bed and EBCT were approximately 22 cm^3 and 2.2 minutes, respectively. Breakthrough occurred at about 1500 bed volumes (31.4 mg Pb/g) when 1 g crab shell particles was added to 10 g activated carbon, and at 380 bed volumes (8.4 mg Pb/g) with 10 g activated carbon only. For the fixed-bed column packed with 10 g activated carbon only, the Norit activated carbon produced an alkaline pH, which might cause precipitation of lead on the surface of activated carbon. When 1 g crab shell was added, the lead uptake increased approximately fourfold due to the alkalinity of the calcium carbonate in the crab shell. The effluent pH for 10 g activated carbon only decreased from 10 at the beginning of column operation to 5.5

at the end, but the effluent pH for regenerated activated carbon increased a little at the beginning of the column work. The effluent pH was about 8 at the breakthrough point. However, when 1 g crab shell was supplemented, the effluent pH decreased more slowly due to the dissolution of calcium carbonate in the crab shell, which enhanced the efficiency of lead removal in the fixed-bed column. In addition, breakthrough occurred at pH 6.7. The dramatic improvement in column performance by the addition of 1 g crab shell may be attributed to an increase in CO_3^{2-} and OH^- available for lead precipitation on the surface of the activated carbon. The optimum pH of precipitation for lead carbonate occurred at 5.5–11.0 and for lead hydroxide at 8.5–11.0 (17). When 1 g crab shell (= 0.58 g $CaCO_3$) was added, 1.2 g Pb will be removed by precipitation, theoretically. However, 0.26 g Pb was removed by the crab shell particles in the column work. This was presumably because some of $CaCO_3$ changed to the H_2CO_3 form at the low influent pH, and also some portions of CO_3^{2-} and OH^- ions did not combine with lead. The solubility of calcium carbonate in the crab shell varied with the pH value. The speciations of carbonate ions are defined in three pH ranges, the dividing points of which are the two dissociation constants for carbonic acid, $pK_1 = 6.3$ and $pK_2 = 10.3$, theoretically (16). Therefore, H_2CO_3, HCO_3^-, and CO_3^{2-} predominate for $pH < pK_1$, $pK_1 < pH < pK_2$, and $pH > pK_2$, respectively. The calcium carbonate in the crab shell started to dissolve at pH 11.0, and most of it was dissolved at pH 5.0 (17). According to Reed et al., the regenerated activated carbon could treat approximately 240 (≈5.4 mg Pb/g carbon) and 315 (≈7.2 mg Pb/g carbon) bed volumes of influent containing 10 mg/L lead solution at pH 4.0 and 5.4, respectively. The activated carbon was successfully regenerated by a relatively simple procedure consisting of 200 mL (≈9 bed volume) rinses with 0.1 N HNO_3 and 0.1 N NaOH. The HNO_3 dissolved/desorbed the carbon-bound Pb, and the NaOH neutralized the carbon for the next carbon run. The column performance was not adversely affected by either three or four regenerations (Table 2).

Effects of Influent Lead Concentration

Breakthrough of the fixed-bed column occurred sooner at a high influent concentration of lead, but the surface concentration of lead was increased because OH^- ions were used more efficiently for lead precipitation (14). Similarly, the surface concentration increases as the influent concentration of lead is increased because more CO_3^{2-} and OH^- ions are used for lead removal. Breakthrough curves for influent containing 50 mg/L Pb at pH 5.0 are shown in Fig. 2. The breakthrough occurred at about 600 bed volumes (62.7 mg Pb/g) for a column packed with 1 g crab shell + 10 g activated carbon, whereas break through was at 130 bed volumes (14.3 mg Pb/g) for 10 g activated carbon only. The surface concentration of lead was greater in the "with crab shell" column than in the "without crab shell" column. The

TABLE 2
Summary of Column Performance for Regeneration[a]

Influent						
pH	Pb (mg/L)	Packing materials	Run number	BV treated	Pb removed (mg)	mg Pb/g packing materials
5.0	10	10 g AC	1	380	83.5	8.4
			2	610	121.4	12.1
			3	580	125.6	12.6
			4	560	127.2	12.7
5.0	10	1 g CS + 10 g AC	1	1500	344.9	31.4
			2	1470	342.0	31.1
			3	1470	346.4	31.5
			4	1460	350.1	31.8

[a] CS = crab shell, AC = activated carbon, and BV = bed volume

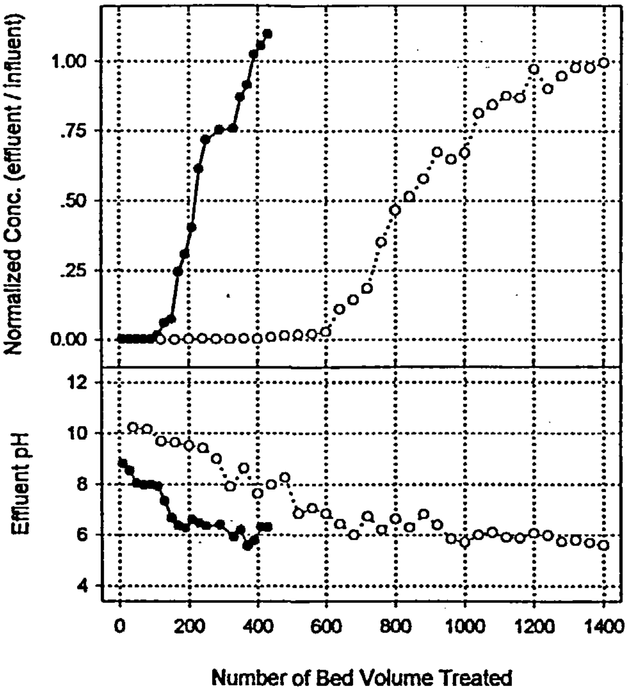

FIG. 2 Breakthrough curves for influent containing 50 mg Pb/L at pH 5.0: (●) 10 g activated carbon, (○) 1 g crab shell + 10 g activated carbon.

efficiency of lead removal was increased about four times due to the carbonate in the crab shell. When the concentration of lead was increased from 10 to 50 mg Pb/L, much more lead was removed and the shape of the breakthrough curves was similar to that of Fig. 1. In addition, the effluent pH decreased more rapidly at higher concentrations of lead because more CO_3^{2-} and OH^- ions were combined with the high concentration of lead. Therefore, when the influent concentration was 50 mg Pb/L, the amount of lead removed by crab shell increased to 0.55 g Pb in the column compared to 0.26 g Pb at 10 mg Pb/L. Reed at al. also found out that regenerated activated carbon could treat approximately 110 and 120 bed volumes of 50 mg/L lead solution at pH 4.0 and 5.4, respectively.

Major Mechanism of Lead Removal

Because the pH in the column was quite high, surface precipitation is suggested as the major mechanism of lead removal. If the lead ions are precipitated on the surface of the activated carbon, the lead precipitates can be analyzed by SEM and XRD. Otherwise the lead ions are just adsorbed on the surface of the activated carbon, for it was impossible to find out any lead precipitates and crystal structures. SEM micrographs equipped with EDS showed that lead precipitates were formed on the surface of activated carbon (Fig. 3). In the column packed with only 10 g activated carbon, small flake-shaped particles were noted on the surface of activated carbon, whereas needle-shaped particles were formed in the column packed with 1 g crab shell + 10 g activated carbon. According to EDS analysis, both types of white particles indicate lead precipitates. However, it was impossible to detect lead precipitates in the pores of activated carbon, even for the crashed activated carbon. This may be because the lead precipitates are too small to detect by using SEM or that precipitation occurred only on the surface of activated carbon. The most common forms of precipitated lead in aqueous solutions are $PbCO_3$, $Pb_3(OH)_2(CO_3)_2$, and $Pb(OH)_2$, whose structures are easily determined by XRD. XRD was used to determine the metal structure on the surface of activated carbon. In spite of the base line increase, the XRD pattern of the precipitates was matched to that of lead hydroxycarbonate, $Pb_3(CO_3)_2(OH)_{2(s)}$ (Fig. 4). The XRD pattern showed that $Pb_3(CO_3)_2(OH)_{2(s)}$ was formed on the surface of activated carbon. The peaks were somewhat different with $PbCO_3$. Reed et al. also recommended $Pb(OH)_2$ precipitates for regenerated activated carbon. In addition, FT-IR was used to determine the functional group on the surface of the activated carbon and whether CO_3^{2-} diffuses through the carbon pores and is retained in the pores. If the CO_3^{2-} diffuses and is retained in activated carbon, precipitation of lead may occur in the pore solution. The FT-IR spectrum for the column packed with crab shell and activated carbon after the breakthrough point did not reveal any significant differences compared with that of raw activated carbon (Fig. 5). However, the adsorption band at 2330

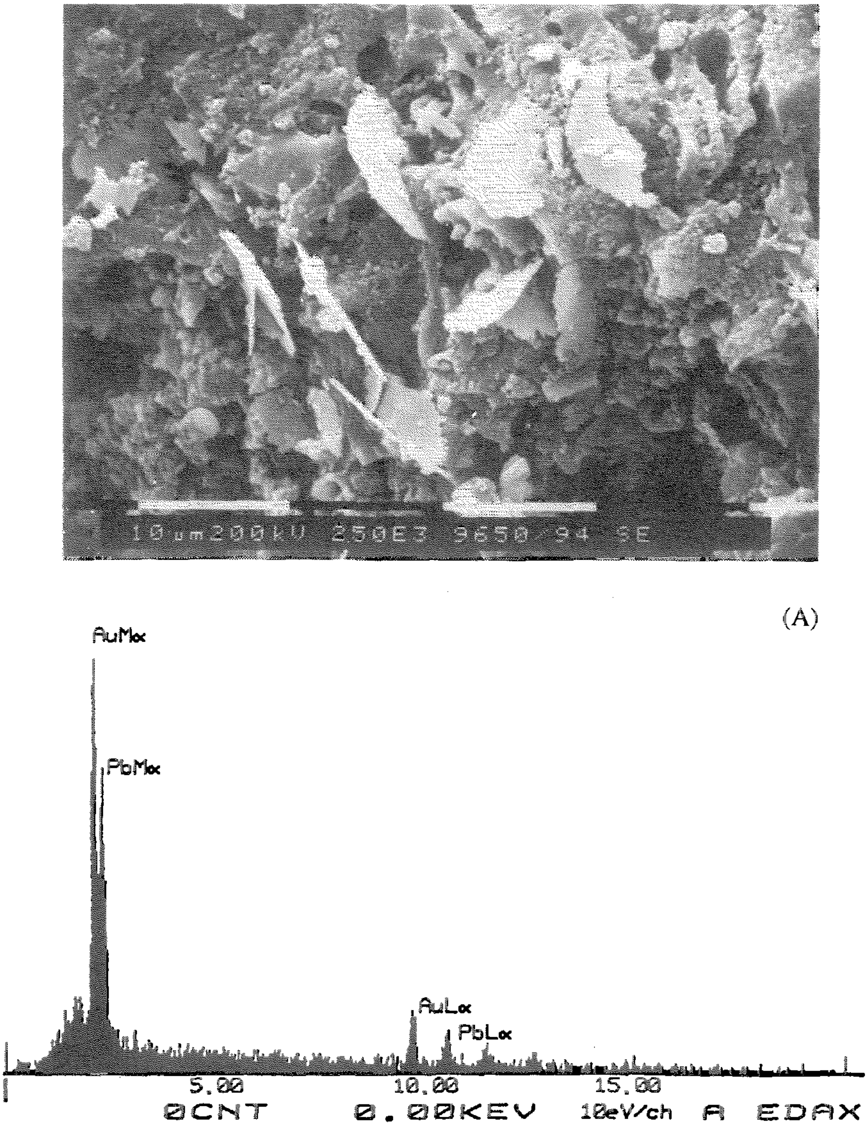

FIG. 3 SEM micrographs of activated carbon and EDS spectrograms of precipitates on the surface of activated carbon after contact up to breakthrough point with influent containing 50 mg Pb/L at pH 5.0 in the fixed-bed column: (A) packed with 10 g activated carbon only (× 2500), (B) packed with 1 g crab shell + 10 g activated carbon (× 5000).

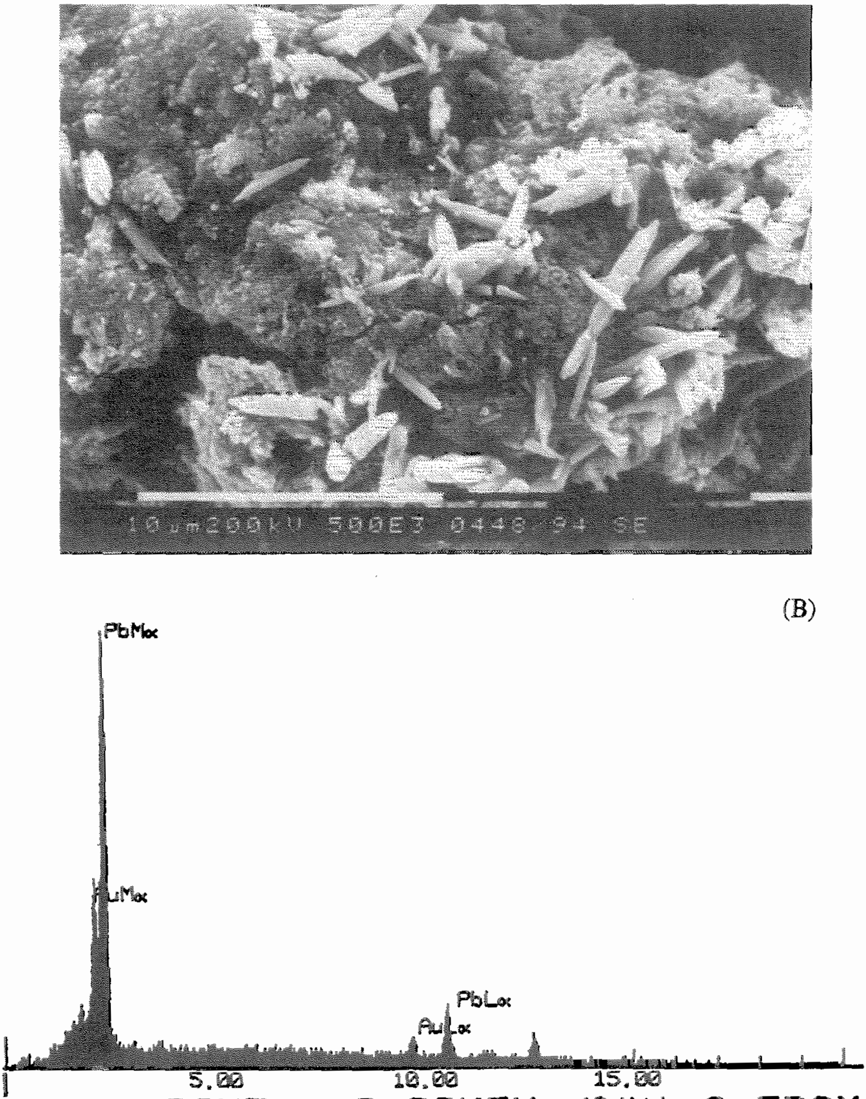

FIG. 3 Continued.

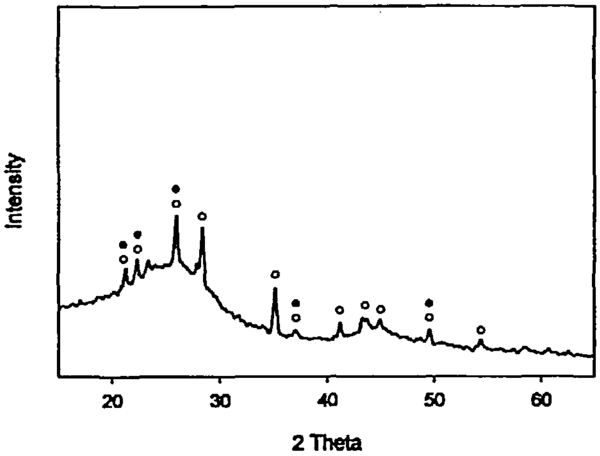

FIG. 4 XRD pattern of activated carbon after contact up to breakthrough point with influent containing 50 mg Pb/L at pH 5.0 in the fixed-bed column packed with 1 g crab shell + 10 g activated carbn: (●) $PbCO_3$, (○) $Pb_3(CO_3)_2(OH)_2$.

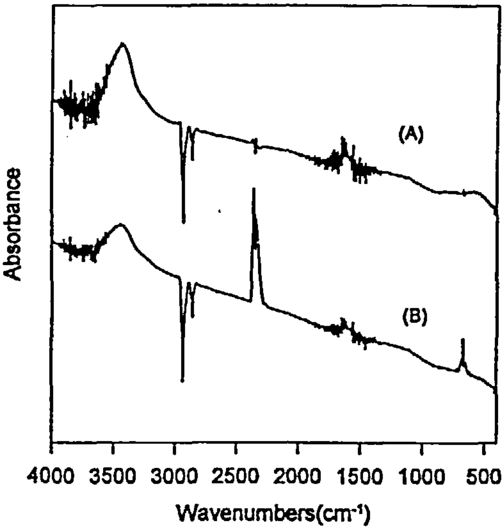

FIG. 5 FT-IR spectra of activated carbon, Norit 0,8 SUPRA: (A) raw activated carbon, (B) after contact up to breakthrough point with influent containing 50 mg Pb/L at pH 5.0 in the fixed-bed column packed with 1 g crab shell + 10 g activated carbon. The peak at 3650 and 1627 cm^{-1} is attributable to the H_2O band; 3448 cm^{-1} to the —OH band; 2892 cm^{-1} to the —CH band; 2330 cm^{-1} to the CO_2 band.

cm^{-1} was much stronger than that of raw activated carbon. The band showed that CO_2 groups in the activated carbons tend to increase because of CO_3^{2-} that formed H_2CO_3 in acidic conditions. This means that CO_3^{2-} diffuses and is retained in the pores, and then some CO_3^{2-} reacts with H^+. Based on the results from SEM micrographs, FT-IR spectra, and XRD patterns, we conclude that the removal of lead in the influent solution was mainly through the dissolution of $CaCO_3$ in the crab shell followed by precipitation of $Pb_3(CO_3)_2(OH)_{2(s)}$ on the surface or in the pore solution of activated carbon in the fixed-bed column. However, the amount of lead removed by surface and pore precipitation was very difficult to separate. In addition, it is also difficult to determine what portion is contributed by adsorption.

CONCLUSIONS

Significant quantities of synthetic lead-bearing wastewater were treated in a fixed-bed column packed with activated carbon and crab shell particles. When 1 g crab shell was added to a column packed with 10 g activated carbon, breakthrough occurred at 1500 bed volumes (31.4 mg Pb/g), whereas breakthrough occurred at 380 bed volumes (8.4 mg Pb/g) with 10 g activated carbon only. The dramatic improvement might be attributed to an increase in the CO_3^{2-} and OH^- available for precipitation of lead. The results of SEM, XRD, and FT-IR showed that the fixed-bed column could remove soluble forms of lead by precipitation on the surface or in the pore solution of the activated carbon. The major mechanism of lead removal was through dissolution of $CaCO_3$ in the crab shell followed by precipitation of lead in the form of $Pb_3(CO_3)_2(OH)_{2(s)}$. The surface concentration of lead increased from 31.4 to 62.7 mg Pb/g packing material as the concentration of lead was increased from 10 to 50 mg/L.

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