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# Biosorption of Cr (III) and Ni (II) from an Aqueous Solution Using Cuttlebone and Application for Battery Manufacturing Wastewater Treatment

Pathompong Vibhatabandhu [1, 2] and Sarawut Srithongouthai [2,*]

*[1] Program in Biotechnology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
*[2] Department of Environmental Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*

* Corresponding author: sarawut.sr@chula.ac.th

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## Abstract

The contamination of heavy metals in wastewater that has extremely low pH, is over the standard limit for heavy metals (Pb and Cr), and has a high amount of total dissolved solids (TDS) is a serious problem in lead-acid battery manufacturing. Various studies have shown that biosorption is an effective and economical technology for removing heavy metals. In this study, Cr (III) and Ni (II) adsorption of cuttlebone powder (CB) was tested, and CB was applied to treat wastewater generated by lead-acid battery manufacturing. The Cr (III) adsorption of CB was optimum in an initial pH of 6.0 using CB 0.4 g/L; in addition, Ni (II) adsorption was optimum in an initial pH of 3.0 using CB 0.2 g/L. The adsorption kinetic was suitable, as it demonstrated a high correlation coefficient ($R^2$>0.9) with pseudo-second-order kinetic model. Both Cr (III) and Ni (II) adsorption were in equilibrium in 20 minutes. By Langmuir isotherm ($R^2$>0.9), the maximum adsorption capacity of CB was 555.55 mg/g in Cr (III) adsorption and 78.74 mg/g in Ni (II). CB was an effective biosorbent, pH neutralizer, and heavy metal remover. On the laboratory scale, lead-acid battery wastewater was successfully treated into the industrial effluent standard limit using a combination of $Ca(OH)_2$ pre-treatment and CB.

***Keyword:*** cuttlebone; biosorption, heavy metal removal, lead-acid battery wastewater treatment

## 1. Introduction

Lead-acid batteries are made up of $PbO_2$ and $PbSO_4$ electrodes in an $H_2SO_4$ electrolytic solution. In brief, the lead-acid manufacturing process consists of the application of PbO paste on a lead alloy grid, resulting in the formation of plates; the plates are then assembled to form a battery, which is charged by filling the plates with sulfuric acid, cooled water, and electric current. Wastewater is generated during the process due to the washing and cleaning of equipment, including the battery plate, as well as during the charging process, while discharging from the scrubber, and in the water-cooling process (Dahodwalla and Herat, 2000).

The contamination of heavy metals in lead-acid battery effluent was measured in previous studies (Arunlertaree et al., 2007; Bahadir et al., 2007; Chauhan and Sankararamakrishnan, 2008; Noeline et al., 2005; Prado et al., 2010). Low pH, high concentration of total dissolved solids (TDS), and heavy metals contamination in wastewater have been the main problems in wastewater treatment. Wastewater treatment has especially faced the issue of Pb and Cr being over the industrial effluent standard limit (Notification the Ministry of Natural Resources and Environment, B.E. 2559 (2013)).

The contamination of heavy metals in the environment impacts the ecological food web, leading to bio-toxicity, bioaccumulation, and biomagnification (Ikemoto et al., 2008; Nayar et al., 2004). The lead-acid battery effluent treatment process was designed to chemically remove heavy metals and reduce TDS. The treatment consists of oil separation, charge neutralization, precipitation, and sedimentation. The ions exchange process is used in some systems in which the TDS of the effluent is not acceptable (Uddin et al., 2013).

Due to the formation of insoluble metal complexes, chemical precipitation is ineffective for removing low concentrations of metal ions from wastewater, and large amounts of high-water-content sludge are generated by this process (Arbabi et al., 2015; Fu and Wang, 2011). To treat wastewater, a combination of different methods has been studied, such as increased removal efficiency by Fe (III) co-precipitation, enlarged precipitate size by coagulation-flocculation, and removal of precipitate sludge by sedimentation and sand filtration (Macchi et al., 1993; Uddin et al., 2013). Electro-coagulation was found to produce more condensed heavy metals sludge than chemical precipitation, to the tune of 0.084–0.091 kg/m3 (Mansoorian et al., 2014).

A more promising approach is adsorption, which is proposed as an economical and effective method for the removal of heavy metal ions from aqueous industrial wastes. As the method's efficiency depends on the types of adsorbent, many varieties of adsorbents have been developed and tested (Arbabi et al., 2015; Fu and Wang, 2011). Biosorption, in which pollutants are adsorbed by a non-living biomass, was tested for the removal of heavy metals from contaminated water. Because abundant byproduct biomasses and waste materials are inexpensive and renewable resources, they are highly interesting materials for use in biosorption (Mudhoo et al., 2012). Various effective biosorbents, including cross linked xanthated chitosan (Chauhan and Sankararamakrishnan, 2008); polymerized banana stem (Noeline et al., 2005); egg shell (Arunlertaree et al., 2007); filamentous fungus (Rhizopus arrhizus) (Bahadir et al., 2007); and Brazilian sawdust samples of Caryocar spp., Manilkara spp., and Tabebuia spp. (Prado et al., 2010), were tested for wastewater treatment of wastewater from lead-acid battery manufacturing.

Cuttlebone is a waste product from the harvesting of cuttlefish for food, and it is commonly used as a traditional medicine or, to a lesser extent, calcium-rich dietary supplement. In previous studies, cuttlebone was an effective adsorbent for removing Pb (II) (Vibhatabandhu and Srithongouthai, 2017), Cu (II) (Li et al., 2010; Vibhatabandhu and Srithongouthai, 2016), Co (II) (Sandesh et al., 2013), and F (Ben Nasr et al., 2011).

According to tests of battery wastewater quality, Cr was over the standard limit and Ni was detected in high concentrations that may be over limit. Thus, this study aims to evaluate the potential of cuttlebone for removing heavy metals ions (Cr (III) and Ni (II)) from an aqueous solution and the application of cuttlebone to battery wastewater treatment.

## 2. Materials and Methods

### 2.1 Cuttlebone preparation and characterization

The cuttlebones were collected from natural sea coasts in the Lamchareon and Maerumpueng in the Rayong province of Thailand. The specimens were washed and oven-dried at 80 °C for 1–2 days, then crushed and sieved to a particle size of less than 106 μm (Endecotts; England). The cuttlebone powder (CB) was rinsed with distilled water, oven dried at 60–80 °C for 1–2 days and stored in a desiccator until used.

Cuttlebone powder was demineralized using a 1 M HCl solution (40 mL of acid solution per 1 g of CB) at ambient temperature for 3 hours. Thereafter, the precipitates were washed with distilled water, dried, and weighted. The functional groups of the CB and extracted content were measured under a Fourier Transform infrared spectrometer (PerkinElmer, Spectrum One; USA).

### 2.2 Cr (III) and Ni (II) adsorption experiment

Stock Cr (III) and Ni (II) solutions were prepared by dissolving $Cr(NO_3)_3{\cdot}7H_2O$ and $NiCl_2{\cdot}6H_2O$ in 1 M $HNO_3$. All chemicals used in the experiments was analytical grade. The batch experiments were operated for 120 minutes by augmenting 50 mL of 500 mg/L of the Cr (III) or Ni (II) solution to 0.05 g of CB in a 250-mL flask. The CB and solutions were mixed at room temperature (30±2°C) and filtrated by filter paper (Whatman No.5). The Cr and Ni in solutions were analyzed by a flame atomic absorption spectrometer (Agilient, 240AA; USA), and adsorption capacity (q) was calculated using equation 1. The effect of the initial pH of solutions (pH 2.0–6.0, adjusted by $HNO_3$ and NaOH) was tested with CB 1.0 g/L, and CB doses (0.2–1.4 g/L) were studied in the optimum initial pH of each metal solution. The experiments were done with three replicates. Equation 1 is as follows:

$$q = \frac{(C_i - C_e)}{S} \tag{1}$$

where q is adsorption capacity (mg/g), $C_i$ is initial concentration (mg/L) of the Cr or Ni solution, $C_e$ is the final concentration (mg/L) of the Cr or Ni solution, and S is the concentration of adsorbent in the mixing solution (g/L).

### 2.3 Adsorption kinetic and equilibrium

The adsorption kinetic was tested in the optimum initial pH of 500 mg/L in the Cr (III) and Ni (II) solution. 0.2 g of CB was added to 500 mL of each metal solution and mixed with a magnetic stirrer bar at 150 rpm. After CB was added for 5–240 minutes, 1 mL of solution was taken and filtrated with a syringe with a filter pore size of 0.45 μm (Advantec, 25CS045AN); then, the concentration of Cr and Ni was analyzed. The adsorption kinetic was studied by using pseudo-first-order and pseudo-second-order models, as shown in equations (2) and (3) respectively:

$$\log (Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where $q_t$ is the capacity (mg/g) at time t (minute), $q_e$ is the capacity at equilibrium (mg/g), $k_1$ is the rate constant of the pseudo-first-order model (1/minute), and $k_2$ is the rate constant of the pseudo-second-order model (g/mg/minute).

The adsorption equilibrium was confirmed by a kinetic study. The final concentration and adsorption capacity of Cr and Ni adsorption were determined. The adsorption equilibrium was analyzed by the linear form of the Langmuir isotherm and Freundlich isotherm, as shown in equations (3) and (4), respectively:

$$\frac{C_e}{q_e} = \frac{1}{k_1 q_m} + \frac{C_e}{q_m} \tag{4}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where $q_e$ is the adsorption capacity at the equilibrium of adsorption (mg/g); $C_e$ is the Cr or Ni concentration at equilibrium (mg/L); $K_L$ and $K_F$ are the Langmuir isotherm constant (L/mg) and Freundlich isotherm constant ((mg/g)·(L/g)$^n$), respectively; $q_m$ is the maximum adsorption capacity (mg/g) of the Langmuir isotherm; and n is the adsorption intensity of the Freundlich isotherm.

## 2.4 Wastewater analysis

Wastewater was collected from a lead-acid manufacturer, and wastewater quality was analyzed with three replications.

The parameters, including pH and TDS, were measured by a pH meter (DENVER, pH/mV/Temp. Meter Model UB-10; USA) and a pH-Conductivity-Dissolved oxygen meter (HACH, sens ion 156; USA). The suspended solid or particulate in wastewater were separated from dissolved wastewater by a glass micro filter (Whatman GF/F) filtration.

The particulate was digested using a high-performance microwave digestion system (MILESTONE, ETHOS ONE; Italy). The amount of heavy metals (Pb, Cr, Ni, Fe, Zn, Mn, and Cu) in both the particulate and dissolve partitions were analyzed by a flame atomic absorption spectrometer with 90% recovery. The detection limit of FAAs for Pb, Cr, Ni, Fe, Zn, Mn, and Cu was 0.1–30, 0.06–15, 0.1–20, 0.06–15, 0.01–2, 0.02–5 and 0.03–10 mg/L, respectively. Other ions ($NH_4^+$, $SO_4^{2-}$, $Cl^-$ and $NO_3^-$) were investigated using the standard method (Government of India & Government of The Natherlands, 1999). Dissolved wastewater was stored and used for the wastewater treatment experiment.

## 2.5 Wastewater treatment experiment

The procedures for each of the four treatments that comprised the experiments are shown in Table 1. Analytical grade chemical reagents, including NaOH and $Ca(OH)_2$, were used to adjust wastewater pH to 4.0 (the optimum initial pH of Cr (III) adsorption and minimum TDS of wastewater). CB was augmented to wastewater then shaken for 240 minutes and filtrated. Wastewater quality parameters (pH, TDS, Pb, Cr, Ni, and Zn) in the filtrated solution after CB was added were measured and compared to the industrial effluent standard.

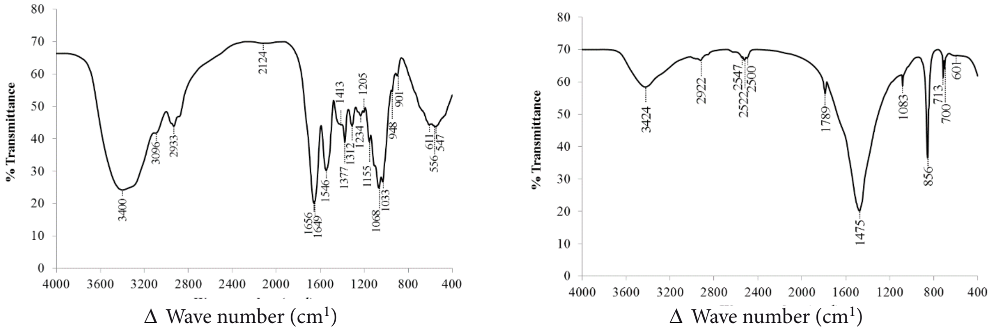
**Table 1.** Battery wastewater treatment procedures

| Treatment | Waste water | Adjusted pH | CB dose (g/L) |
|---|---|---|---|
| I | filtrated | - | 0.2–10.0 |
| II | filtrated | NaOH (17.8 g/L) | 0.2–1.0 |
| III | filtrated | $Ca(OH)_2$ (16.5 g/L) | 0.2–1.0 |
| IV | Non-filtrated | $Ca(OH)_2$ (16.5 g/L) | 0.8–1.6 |

## 3. Results and discussion

### *3.1 Adsorbent functional groups*

The proportion of minerals and extracted content in CB is 97.23±0.10 % of mineral content and 2.77±0.10 % of extracted content. The functional groups of CB and extracted content were analyzed; their FTIR spectra are presented in Figure 1. More than 90 % of the adsorbent's composition was mineral content. Besides the band characteristic (Figure 1 (a)), major peaks of 1475, 856, and 713 cm$^{-1}$ of $CO_3^{2-}$ vibration were found (Huang, 1960). There were minor peaks of 2522, 1789, and 1083 cm$^{-1}$ for $CaCO_3$ (aragonite) and 3424 cm$^{-1}$ for water molecules of crystallization (Huang, 1960)



(a) (b)

**Figure 1.** FTIR spectra of (a) CB and (b) CB extracted content

While $CaCO_3$ is its main component, cuttlebone also has some organic content, including β-chitin and proteins (Florek et al., 2009; Klungsuwan et al., 2012). The absorption peaks of the extracted content of CB (Figure 1 (b)) show a broad peak of O-H stretching to 3400 $cm^{-1}$, C-O stretching to 1033 $cm^{-1}$ and 1068 $cm^{-1}$, and C-O-C stretching to 1155 $cm^{-1}$. The functional groups of chitin and protein were presented in C = O bonded amide stretching at 1656 $cm^{-1}$ and 1650 $cm^{-1}$, N-H bending of amine at 3096 $cm^{-1}$ and 1546 $cm^{-1}$, C-N stretching at 1312 $cm^{-1}$, and amide III stretching at 1233 $cm^{-1}$ and 1205 $cm^{-1}$ (Florek et al., 2009; Klungsuwan et al., 2012).

## *3.2 Cr (III) and Ni (II) adsorption*

### *3.2.1 Effect of initial pH*

The Cr (III) and Ni (II) adsorption in solutions whose initial pH of was 2.0–6.0 were tested. The results (Figure 2) found that capacity increased depending on initial pH, and the highest capacity was found at an initial pH of 6.0 in Cr (III) adsorption. With Ni (II) adsorption, the capacity seems to be constant at an initial pH 3.0–6.0.

Because of the $CaCO_3$ component in cuttlebone, $CO_3^{2-}$ precipitation on the adsorbent surface was effective in soluble divalent cation adsorption (Vibhatabandhu and Srithongouthai, 2016, 2017). For this reason, dissolution of $CaCO_3$ to $HCO_{3-}$ and $H_2CO_3$ in acidic solution results in less capacity at an initial pH of 2.0 in the Cr and Ni solutions.

Additionally, the pH of the solution mainly affects the oxidation state and complexation of heavy metals. In the environment, speciation of Cr (III) and Cr (VI) is related to pH and redox potential. Various forms of Cr compounds such as $CrOH^{2+}$ and $Cr_2O_7^{2-}$ can demonstrate in solutions with different pH levels. By speciation diagrams (Chen et al., 2015; Kotas and Stasicka, 2000), $Cr^{3+}$ is presented in the solution with a pH of less than 3, and Cr is presented as $CrOH^{2+}$ and $Cr(OH)_2^+$ in the solution with a pH of 4–6.5; equally, $Cr(OH)_3$ is presented in the solution with a pH that is higher than 7. As the result of forming $Cr(OH)^{2+}$ in a solution with a high initial pH (4.0–6.0) and because the adsorbent's $CaCO_3$ is effective in divalent cations precipitation, high Cr removing capacity was found in the solution with an initial pH of 4.0–6.0. Besides decreasing the acidity of the solution, the precipitated form of $Cr(OH)_3$ can occur as particle solids and induce the removal of Cr from the solution by filtration after the experiments (Chen et al., 2015; Gupta et al., 2013; Kotas and Stasicka, 2000). Conversely, without theprecipitation of $Ni(OH)_2$ and $NiCO_3$ in a solution with a pH of 2.0–6.0, the Ni adsorption capacity was lower than the Cr adsorption capacity, and the Ni adsorption capacity was constant in the solution with an initial pH of 2.0–6.0. According to the results, the optimum initial pH was 6.0 and 3.0 for Cr (III) and Ni (II) adsorption, respectively.

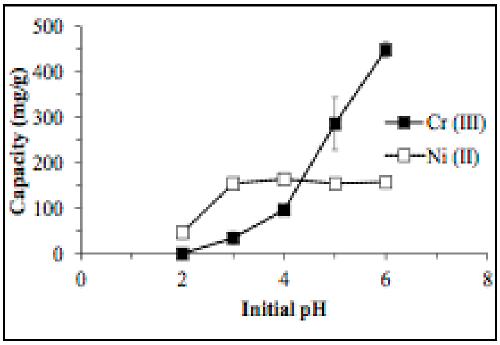


**Figure 2.** Effect of initial pH on Cr (III) and Ni (II) adsorption capacity using a CB dose of 1.0 g/L with an initial concentration of 500 mg/L of Cr (III) and Ni (II) solution for 120 minutes.

### *3.2.2 Effect of CB dose*

The effect of CB dose is shown in Figure 3. The capacity of Cr (III) adsorption was peak when using 0.4 g/L of CB. Ni (II) adsorption capacity slightly decreased when more CB was used. In term of the quantity of removed heavy metals, more heavy metal was removed in higher dose of adsorbent due to increased surface area and available sites (Gupta et al., 2013; Vibhatabandhu and Srithongouthai, 2016, 2017). While amounts of adsorbent were increased, some surface area was not used to adsorb heavy metals; for this reason, the adsorption capacity was decreased when using a higher dose. (Vibhatabandhu and Srithongouthai, 2016; 2017).

### *3.2.3 Adsorption kinetic*

The adsorption capacity at 5–240 minutes (Figure 4) shows rapid reaction with strongly increased capacity. After 20 minutes, the constant of capacity represents the equilibrium of Cr (III) and Ni (II) adsorption. Shown in Table 2, the adsorption kinetic of both heavy metals was fixed with a pseudo-second-order model ($R^2 > 0.9$). The reaction rate constant ($k_2$) was inferred to the reaction rate ($1.59x10^{-3}$ g/mg/min) of Ni (II) adsorption, which was more rapid than that $3.18x10^{-5}$ g/mg/min of Cr (III) (Table 2).

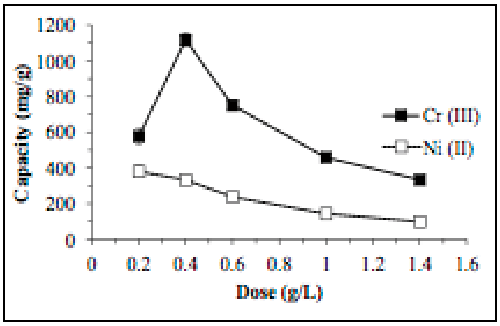


**Figure 3.** Effect of CB-P dose on Cr (III) and Ni (II) adsorption capacity with an initial concentration of 500 mg/L of the Cr (III) solution with an initial pH of 6.0 and the Ni (II) solution with an initial pH of 3.0 for 120 minutes.

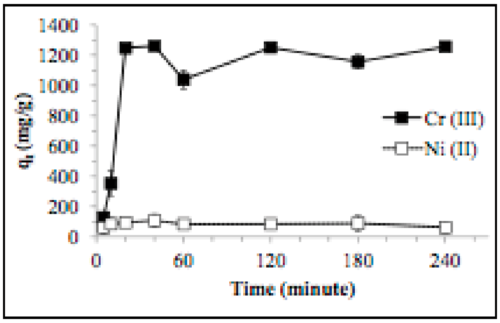


**Figure 4.** Cr (III) and Ni (II) adsorption capacity from 5–240 minutes using a CB dose of 0.4 g/L with an initial concentration of 500 mg/L of the Cr (III) solution with an initial pH of 6.0 and the Ni (II) solution with an initial pH of 3.0.

### *3.2.4 Adsorption equilibrium*

The isotherm parameters (Table 2) were that Cr (III) and Ni (II) adsorption were fixed to the Langmuir isotherm with correlation coefficients ($R^2$) of 0.9940 and 0.9626. The maximum capacity of the Langmuir isotherm was calculated. Compared with other adsor bents' capacities (Table 3), CB was effective in Cr (III) adsorption.

The Langmuir isotherm assumption (Foo and Hameed, 2010), which suggests that chemical adsorption or monolayer adsorption will occur at a fixed number of active sites, was suitable in this study.The metal adsorption mechanism of cuttlebone adsorbent relates to ion exchange, mainly between Ca and metal ions, in terms of even surface complexation, electrostatic adsorption, and micro-deposition (Li et al., 2010). The Langmuir isotherm ensures that chemical reaction of Cr (III) and Ni (II) removal in CB is the effect of metal precipitation and adsorption on the surface.

### 3.3 Application for battery manufacturing wastewater treatment

The parameters of lead-acid battery manufacturing wastewater quality and industrial effluent standard limit are shown in Table 4. The TDS, pH, Pb, and Cr of the wastewater were over the industrial effluent standard limit; Ni, Mn, and Zn were lower than the standard limit; and Fe was at a high concentration without a standard limit.

The wastewater pH indicates an acid condition caused by $H_2SO_4$, which leads to high total dissolved solid (TDS) from concentrated $HSO_4^-$ and $SO_4^{2-}$ ions. Due to the production process, the use of PbO, $PbSO_4$, and $H_2SO_4$ are the chief causes of Pb impurity in wastewater. Other contaminant ions may be deposited in wastewater by battery-plating paste composition and production unit corrosion (Dahodwalla and Herat, 2000). Stability constants, solubility products, and the pH of the solution affect the species of heavy metal complexes and dissolve them (Benjamin, 2002; Snoeyink and Jenkins, 1980). Concerning wastewater composition, most ions in wastewater occur as dissolved ions, except for Pb and Zn ions, which are more often found in suspended solids. This is because the complexation of Pb (II) and $SO_4^{2-}$ in low pH forms less soluble solids of $PbSO_4$, which is also the case for particulates of Zn. However, soluble complexes of heavy metal ions that bind to $NH_3$ and $Cl^-$ ligand may also possibly occur.

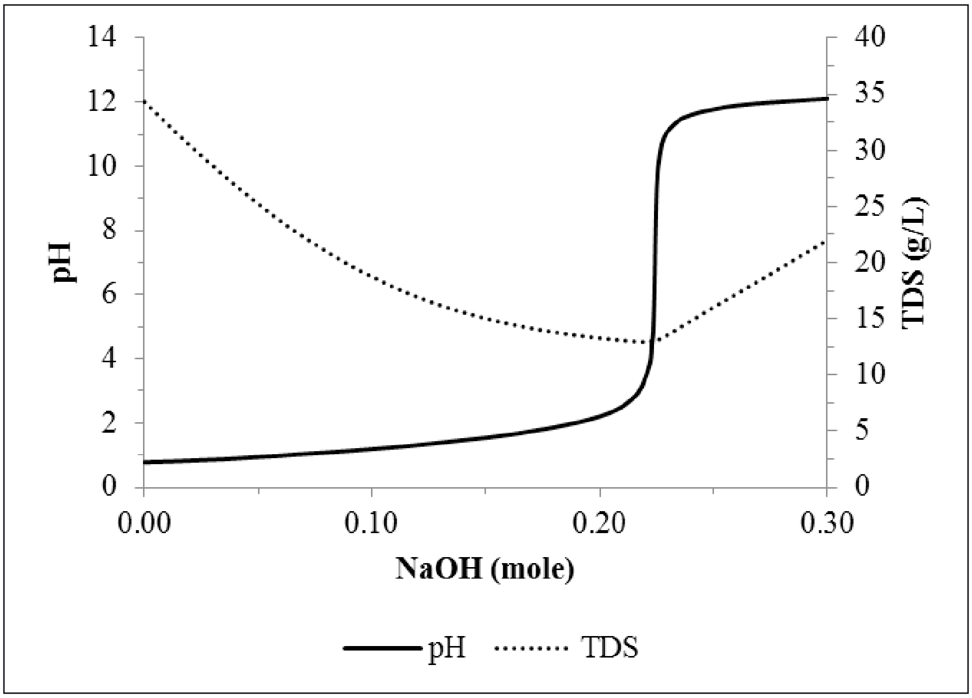


**Figure 5.** TDS of battery manufacturing wastewater in varied pH with NaOH.

According to titration of wastewater with a NaOH solution (Figure 5), the TDS of wastewater was measured in different pH levels. The results showed that TDS had a minimum value (about 13 g/L) in wastewater with a pH of 4.0, but the value was still over the standard limit. Moreover, TDS was increased, while the pH was adjusted to higher than 4.0. Thus, adjusted pH and heavy metals precipitation by NaOH was an ineffective method in this wastewater treatment, and TDS must be considered a parameter in the treatment experiment.

The treatment experiment was designed to investigate the combination of adsorbent and widely used basic reagents (NaOH and $Ca(OH)_2$). In the treatment II, the pH of the wastewater was adjusted to 4.0 by using NaOH, which minimized TDS and optimized pH for Cr (III) adsorption. Accordingly, $Ca(OH)_2$ was used to replace NaOH as an equivalent weight. The parameters of treated wastewater in the experiment were illustrated in Figure 6.

Adding CB neutralized wastewater pH and decreased the concentration of heavy metals (Pb, Cr, Ni, and Zn). The over-standard limit of wastewater quality parameters (pH, TDS, Pb, and Cr) tend to be lower than the limit with using treatments III and IV. In treatment I, the pH of wastewater was slightly increased, whereas TDS and Pb were clearly decreased in higher CB doses, and other metals seemed to be stable. While adding strong base reagents in treatments II and III, the pH of the wastewater was neutralized, and most of the TDS and some metals were removed. The pH of the wastewater and the removal of heavy metals more increased after CB was added, but TDS was not clearly decreased. The results of filtrated wastewater in treatment III were similar to those of non-filtrated wastewater in treatment IV, although treatment IV had a bit less efficiency in removing Pb. However, the efficiency of pH neutralization and the removal of some metals (Ni and Zn) was increased. The dissolution of $CaCO_3$ content in adsorbents affects the $CO_3^{2-}$ equilibrium and the discharge of $Ca^{2+}$ ions and causes a slight increase in pH of solution (Vibhatabandhu and Srithongouthai, 2017). The $H_2SO_4$, $HSO_4^-$, and $SO_4^{2-}$ equilibrium in wastewater shifts to more $SO_4^{2-}$ ions when the pH increases, and the precipitation of metals-$SO_4^{2-}$ was enhanced (Macchi et al., 1993; Marani et al., 1995). By adding CB to wastewater, the formation of $PbSO_{4(s)}$, $FeSO_{4(s)}$, and $CaSO_{4(s)}$ reduces TDS, mainly from $H_2SO_4$, $HSO_4^-$, and $SO_4^{2-}$.

In line with previous studies, this study found that when the pH of the solution is adjusted so that it is more alkaline, heavy metal hydroxide precipitation occurs (Gupta et al., 2013; Kotas and Stasicka, 2000; Vibhatabandhu and Srithongouthai, 2016 and 2017; Zafar et al., 2015). Regarding TDS and the pH of wastewater, TDS is at its minimum in wastewater with a pH of 4.0 because some heavy metals form into solid complexes with $SO_4^2{}_-$ and OH-. Increasing the pH to 4.0 by NaOH in treatment II causes the clear decrease in the concentration of TDS (33.36 g/L to 13.58 g/L), Fe (88.57 mg/L to 5.06 mg/L) Cr (1.78 mg/L to 0.56 mg/L), and Pb (2.83 mg/L to 1.38 mg/L). By augmenting CB, contaminated heavy metals were removed. The $Ca^{2+}$ from dissolved $CaCO_3$ content induced a slight increase in the TDS. To be specific, TDS went over the standard TDS in the baseline of added soluble $Na^+$ ions, which were not removed by adsorbents.

**Table 2.** Cr (III) and Ni (II) adsorption kinetic and adsorption isotherm parameters of CB

| Heavy metals | Adsorption kinetic | | | | | | Adsorption isotherm | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pseudo-first-order | | | Pseudo-second-order | | | Langmuir isotherm | | | Freundlich isotherm | | |
| | $k_1$ (1/min) | $q_e$ (mg/g) | $R^2$ | $k_2$ (g/mg/min) | $q_e$ (mg/g) | $R^2$ | $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | n | $K_F$ (mg/g)·(L/g)n | $R^2$ |
| Cr (III) | -0.0002 | 11825.34 | 0.2995 | $3.18x10^{-5}$ | 1428.57 | 0.9653 | 555.55 | -3.60 | 0.9940 | -5.34 | 2.18 | 0.0006 |
| Ni (II) | -0.0012 | 23.16 | 0.0687 | $1.59x10^{-3}$ | 69.93 | 0.9611 | 78.74 | 0.12 | 0.9626 | 0.68 | 0.22 | 0.0495 |

**Table 3.** Comparison of maximum capacity (qm) in Cr (III) and Ni (II) adsorption by the Langmuir isotherm

| Adsorbent | Cr (III) | | Ni (II) | | Reference |
|---|---|---|---|---|---|
| | pH | $q_m$ (mg/g) | pH | $q_m$ (mg/g) | |
| CB | 6.0 | 555.55 | 3.0 | 78.74 | This study |
| Rubber tire-derived carbon | 6.0 | 12.08 | - | - | Gupta et al. (2013) |
| Extracted alginate | 3.0 | 33.02 | - | - | Bertagnolli et al. (2014) |
| NaOH treated rice bran | - | - | 6.0 | 400.00 | Zafar et al. (2015) |
| Living Arthrospira platensis | - | - | 6.0 | 90.91 | Markou et al. (2015) |

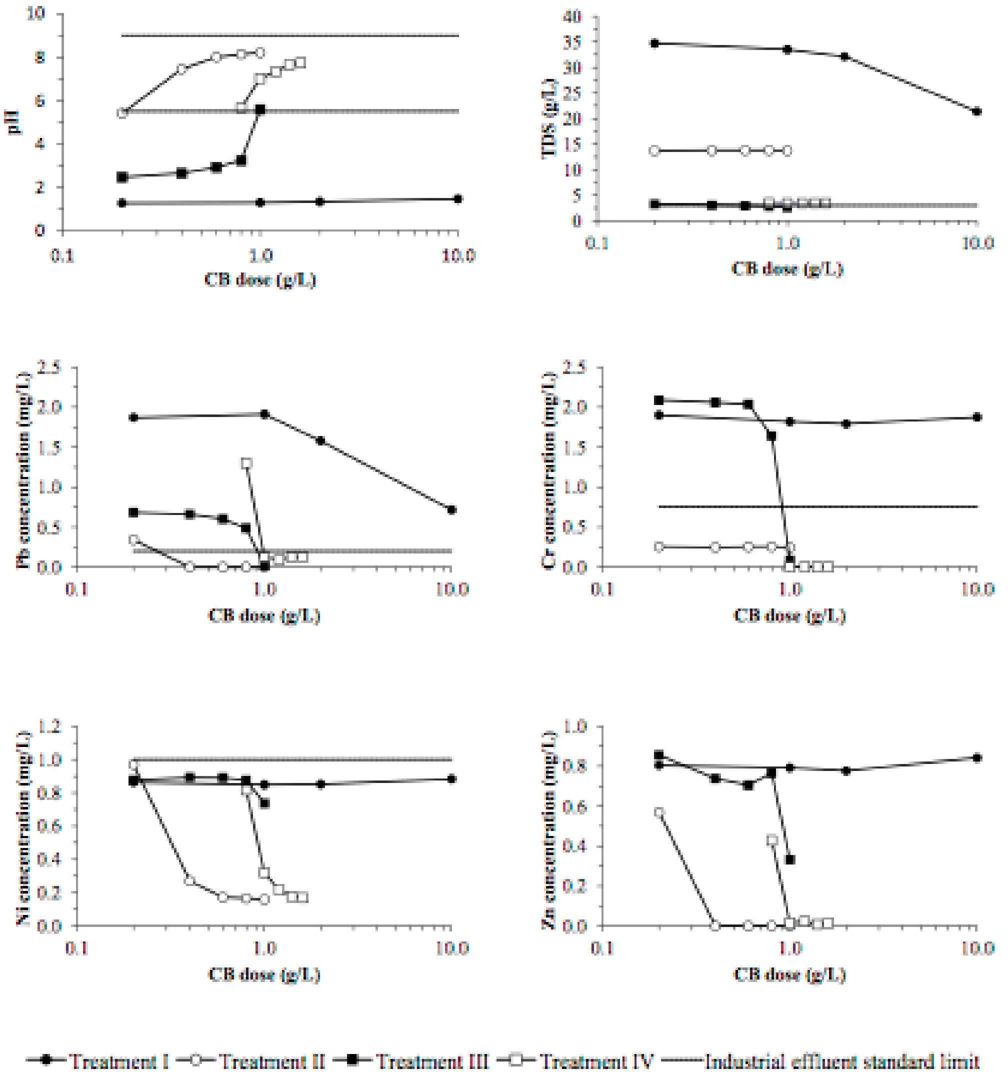


**Figure 6.** Quality of battery wastewater treated by CB with the industrial effluent standard limit

In treatment III, $Ca(OH)_2$ was used in pre-treatment to increase the pH of wastewater. In general, the solubility of $Ca(OH)_2$ depends on the pH of the solution and it does not dissolve in water at all. However, $Ca^{2+}$ from dissolution of $Ca(OH)_2$ was removed $SO_4^{2-}$ due to $CaSO_4$ precipitation. Because of interference from $CaSO_4$ precipitate in wastewater after $Ca(OH)_2$ pre-treatment, the low concentration of CB was ineffective at removing heavy metals. Furthermore, the effect of particulate in wastewater was considered in treatment IV. $CaSO_4$ was also generated by $Ca(OH)_2$ pre-treatment of non-filtrated wastewater; therefore, the concentration of dissolved $SO_4^{2-}$ was reduced. Because most of the particulate in the wastewater was $PbSO_4$, the dissolution equilibrium of $PbSO_4$ particle was shifted to be more dissolved, while dissolved $SO_4^{2-}$ was removed. Because this equilibrium changed, the concentration of dissolved Pb after pre-treatment was increased and caused less efficiency in the removal of Pb.

Regarding the effluent standard value of pH, which ranges between 5.5–9.0 (Environment Notification the Ministry of Natural Resources and Environment, B.E. 2559 (2013)), due to the behavior of strong base and solubility of $Ca(OH)_2$, not all soluble $Ca(OH)_2$ was a barrier to the control of the wastewater's pH. The pH of wastewater could be rapidly increased to 9.0 and posed a risk of exceeding the standard value if a slightly higher dose of $Ca(OH)_2$ was used. Meanwhile, a higher dose of CB or $CaCO_3$ produced a slow increase in the pH, contributing to the pH resistance of the $HCO_3^-$ and $CO_3^{2-}$ buffer.

Discharged heavy metals from sludge, which depend on the stability of the heavy metals complex, are one of the key points in sludge management. Stability of Pb-ligand after wastewater precipitation was tested during 30 days leaching (Matlock et al., 2002). For the heavy metal removal of CB, a metals-$CO_3^{2-}$ complex was founded. The special consistency of $CaCO_3$, chitin, and protein content along with the adsorption of small-sized particulates may increase the stability of heavy metals precipitate by ions. Because they can be used in a broad range of doses, heavy metals in leachate from sludge could be adsorbed by excess CB.

To respond to the demands of resource and waste management strategies, the use of renewable biological materials has been investigated to assess their performance in battery wastewater treatment (Arunlertaree et al., 2007; Bahadir et al., 2007; Chauhan and Sankararamakrishnan, 2008; Noeline et al., 2005; Prado et al., 2010). As presented in this study, CB, derived from cuttlebone, is an attractive alternative adsorbent for heavy metals removal and wastewater treatment.

## 4. Conclusion

With Cr (III) and Ni (II) solutions, high efficiency in heavy metals removal was found in 20 minutes. The maximum adsorption capacity was 555.55 mg/g of Cr (III) adsorption in the initial pH of 6.0 when using CB 0.4 g/L and 78.74 mg/g of Ni (II) adsorption in the initial pH of 3.0 when using CB 0.2 g/L. Besides treating wastewater generated by lead-acid battery manufacturing, CB has other potential applications in wastewater treatment, in the same way as NaOH, $CaCO_3$, and $Ca(OH)_2$. The combination of CB and $Ca(OH)_2$ pre-treatment was an effective method for balancing pH, removing TDS, and treating heavy metals in wastewater. Moreover, using CB and adjusting pH by NaOH to remove heavy metals from wastewater is also an acceptable treatment if the TDS in the wastewater is low or the TDS treatment unit was operated. According to the results, cuttlebone can be modified as an alternative option for wastewater treatment, and the use of cuttlebone in wastewater treatment can produce guidelines for the utilization of cuttlefish waste products.

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## References

Arbabi M, Hemati S, Amiri M. Removal of lead ions from industrial wastewater: a review of removal methods. International Journal of Epidemiologic Research 2015; 2: 105-109.

Arunlertaree C, Kaewsomboon W, Kumsopa A, Pokethitiyook P, Panyawathanakit P. Removal of lead from battery manufacturing wastewater by egg shell. Songklanakarin Journal of Science and Technology 2007; 29: 858-868.

Bahadir T, Bakan G, Altas L, Buyukgungor H. The investigation of lead removal by biosorption: An application at storage battery industry wastewaters. Enzyme and Microbial Technology 2007; 41: 98-102.

Ben Nasr A, Walha K, Charcosset C, BenAmar R. Removal of fluoride ions using cuttlefish bones. Journal of Fluorine Chemistry 2011; 132: 57-62.

Benjamin MM. 2002. Water chemistry. 1 ed. Singapore:McGraw-Hill.

Bertagnolli C, da Silva MGC, Guibal E. Chromum biosorption using the residue of alginate extraction from Sargassum filipendula. Chemical Engineering Journal 2014; 237: 362-371.

Chauhan D, Sankararamakrishnan N. Highly enhanced adsorption for decontamination of lead ions from battery wastewaters using chitosan functionalized with xanthate. Bioresource technology 2008; 99: 9021-9024.

Chen T, Zhou Z, Xu S, Wang H, Lu W. Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge. Bioresource Technology 2015; 190: 388-394.

Dahodwalla H, Herat S. Cleaner production options for lead-acid battery manufacturing industry. Journal of Cleaner Production 2000; 8: 133-142.

Florek M, Fornal E, Gómez-Romero P, Zieba E, Paszkowicz W, Lekki J, Nowak J, Kuczumow A. Complementary microstructural and chemical analyses of Sepia officinalis endoskeleton. Materials Science and Engineering: C 2009; 29: 1220-1226.

Foo KY, Hameed BH. Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal 2010; 156: 2-10.

Fu F, Wang Q. Removal of heavy metal ion from wastewater: A review. Journal of Environmental Management 2011; 92: 407-418.

Government of India & Government of The Natherlands 1999. Standard Analytical Procedures for Water Analysis.

Gupta VK, Ali I, Saleh TA, Siddiqui MN, Agarwal S. Chromium removal from water by activated carbon developed from waste rubber tires. Environmental Science Pollution Research 2013; 20: 1261-1268.

Huang CKaK, P.F. Infrared study of the carbonate minerals. The American Mineralogist 1960; 45: 311-324.

Ikemoto T, Tu NP, Okuda N, Iwata A, Omori K, Tanabe S, Tuyen BC, Takeuchi I. Biomag nification of trace elements in the aquatic food web in the Mekong Delta, South Vietnam using stable carbon and nitrogen isotope analysis. Archives of Environmental Contamination and Toxicology 2008; 54: 504-515.

Klungsuwan P, Jarerat A, Poompradub S. Mechanical Properties and Biodegradability of Cuttlebone/NR Composites. Journal of Polymers and the Environment 2012; 21: 766-779.

Kotas J, Stasicka Z. Chromium occurrence in the environment and methods of its speciation. Environmental Pollution 2000; 107: 263-283.

Li YZ, Pan H, Xu J, Fan XW, Song XC, Zhang Q, Xu J, Liu Y. Characterization of metal removal by os sepiae of Sepiella maindroni Rochebrune from aqueous solutions. Journal of hazardous materials 2010; 179: 266-275.

Macchi G, Pagand M, Santor M, Tiravanti G. Battery industry wastewater: Pb removal and produced sludge. Water Research 1993; 27: 1511-1518.

Mansoorian HJ, Mahvi AH, Jafari AJ. Removal of lead and zinc from battery industry wastewater using electrocoagulation process: Influence of direct and alternating current by using iron and stainless steel rod electrodes. Separation and Purification Technology 2014; 135: 165-175.

Marani D, Macchi G, Pagand M. Lead precipitation in the presence of sulphate and carbonate: Testing of thermodynamic predictions. Water Research 1995; 24: 1085-1092.

Markou G, Mitrogiannis D, Çelekli A, Bozkurt H, Georgakakis D, Chrysikopoulos CV. Biosorption of Cu2+ and Ni2+ by Arthrospira platensis with different biochemical compositions. Chemical Engineering Journal 2015; 259: 806-813.

Matlock MM, Howerton BS, Atwood DA. Chemical precipitation of lead from lead battery recycling plant wastewater. Industrial & Engineering Chemistry Research 2002; 41: 1579-1582.

Mudhoo A, Garg VK, Wang S. Removal of heavy metals by biosorption. Environmental Chemistry Letters 2012; 10: 109-117.

Nayar S, Goh BP, Chou LM. Environmental impact of heavy metals from dredged and resuspended sediments on phytoplankton and bacteria assessed in in situ mesocosms. Ecotoxicology and Environmet Safety 2004; 59: 349-369.

Noeline BF, Manohar DM, Anirudhan TS. Kinetic and equilibrium modelling of lead (II) sorption from water and wastewater by polymerized banana stem in a batch reactor. Separation and Purification Technology 2005; 45: 131-140.

Notification the Ministry of Natural Resources and Environment. B.E. 2559 (2013). Standard limit for controllingwastewater discharge from industrial, industrial estate and industrial zones [in Thai]. the Royal Government Gazette. Fed Reg 133.

Prado AGS, Moura AO, Holanda MS, Carvalho TO, Andrade RDA, Pescara IC, de Oliveira AHA, Okino EYA, Pastore TCM, Silva DJ, Zara LF. Thermodynamic aspects of the Pb adsorption using Brazilian sawdust samples: Removal of metal ions from battery industry wastewater. Chemical Engineering Journal 2010; 160:549-555.

Sandesh K, Suresh Kumar R, JagadeeshBabu PE. Rapid removal of cobalt (II) from aqueous solution using cuttlefish bones; equilibrium, kinetics, and thermodynamic study. Asia-Pacific Journal of Chemical Engineering 2013; 8: 144-153.

Snoeyink VL, Jenkins D. 1980. Water chemistry. New York:John Willy & sons.

Uddin J, Mondal PK, Rahman A, Lemon HR. An approach to reduce waste in lead acid battery industries. Global Journal of Researches in Engineering 2013; 13: 16-22.

Vibhatabandhu P, Srithongouthai S. Removal of Copper (II) from Aqueous Solutions. Applied Environmental Research 2016; 38: 39-47.

Vibhatabandhu P, Srithongouthai S. Removal of Pb (II) from an Aqueous Solution Using Modified Cuttlebone as a Biosorbent. EnvironmentAsia 2017; 10: 34-43.

Zafar MN, Aslam I, Nadeem R, Munir S, Rana UA, Khan SU-D. Characterization of chemically modified biosorbents from rice bran for biosorption of Ni(II). Journal of the Taiwan Institute of Chemical Engineers 2015; 46: 82-8