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Lead and Cadmium Removal Efficiency from Aqueous Solution by NaOH Treated Pineapple Waste

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Abstract

Adsorption efficiency of lead and cadmium by pineapple waste and NaOH treated pineapple waste from aqueous solution were studied. The stem, leaf, fruit, and mixed waste of pineapple were used as raw materials. The influences of pH (2, 4, 6), contact time (15, 30, 60, 90 min), and temperature (30, 60 °C) on adsorption experiments were evaluated. The character of adsorbent's packing (tightly packed or loosely packed) and its effect on metals ions adsorption was also studied. It was found that adsorbents from different pineapple wastes treated with sodium hydroxide have higher adsorption efficiency for cadmium and lead ions (> 95%) than untreated ones by about 50-100%. The Pb^{2+} adsorption efficiency was higher than Cd^{2+} adsorption efficiency for both NaOH treated and untreated wastes. The adsorption efficiencies for Pb^{2+} and Cd^{2+} ions of untreated and treated fruit waste are lower than leaf, stem, and mixed wastes. The equilibrium times for Pb^{2+} and Cd^{2+} adsorption on treated wastes are 30 minutes and 60 minutes, respectively. It was shown that Pb^{2+} and Cd^{2+} ions adsorptions by NaOH treated pineapple wastes are endothermal processes. The Cd^{2+} and Pb^{2+} adsorption efficiencies are increased with increasing pH above pH 2. They reach maximum at pH 4 and then a slightly decreased at pH 6. Finally, the effect of packing showed that Pb^{2+} and Cd^{2+} removal efficiency of NaOH treated loosely packed mixed pineapple waste was higher than for tightly packed waste. The equilibrium adsorption times were 30 minute and 90 minute for the loosely and tightly packed wastes, respectively. .

Keywords: Pineapple waste, sodium hydroxide, lead, cadmium, adsorption

INTRODUCTION

Adsorption techniques are widely used to remove certain classes of pollutants from waters [1]. The proposed adsorption mechanisms are ion exchange, surface adsorption, chemisorption, and complexation [2]. Activated carbon has been a popular choice as an adsorbent for the removal of pollutants from wastewater but its high cost poses an economical problem. Due to this problem, there is a need for the development of low cost and easily available materials, which can be used more economically on large scale [1]. Also, attempts have been made to develop inexpensive adsorbents utilizing numerous agro-industrial and municipal waste materials. Use of waste materials as low-cost adsorbents is attractive due to their contribution in the reduction of costs for waste disposal, therefore contributing to environmental protection. Agricultural materials containing cellulose show potential sorption capacity for various pollutants. Such materials are economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature, and low cost. Therefore they are a viable option for water and wastewater remediation [3]. Recently, much attention has been focused on the utilization of plant biomass to produce engineering materials, encompassing the technological/scientific aspects as well as the economic, environmental, and social issues [4]. Therefore, conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solving environmental problems and also to reduce the preparation costs [5]. It also has the advantage of great availability and simple operational process [6]. These materials have several advantages such as high sorption capacities, good modifiability and recoverability, insensitivity to toxic substances, and simple operation in the treatment processes. The uptake capacity and stability of biomaterials can be enhanced by physical and chemical modifications with heat (drying and pyrolysis), de-glycosilation, and inorganic/organic activations. A treatment of raw lignocellulose that will remove part of organic matter such as carbohydrates (cellulose), and increase its surface area and porosity is needed before using the material for pollutant removal [3].

Physical modifications are usually considered as being simple and inexpensive. However, they are not widely used because of their low effectiveness. Conversely, chemical modifications are preferred, due to their simplicity and efficiency. Modifying agents can be classified as bases, mineral and organic acids, organic compounds, oxidizing agents, and others. However, the most commonly used chemicals are acids and bases [7]. Agricultural waste based biosorbents with chemical pretreatments were successfully prepared by modifying maize straw [8] and modified apple pomace [9] with succinic anhydride in xylene for the removal of Cd(II) [8]. The wasted black tea powder modified with NaOH treatment exhibited higher removal efficiency of Cu(II) ions [10]. Coir pith has also been modified by sodium hydroxide for nickel adsorption [11]. Furthermore, biowaste obtained from the fruit juice industry with phosphorous(V) oxychloride modification has been used as biosorbent for the removal of toxic heavy metals such as Hg(II), Pb(II), Cd(II), Cu(II), Zn(II), and Ni(II) with performance dependent on the initial pH of the aqueous solution [12]. The waste from pineapple agriculture is one possible source of materials for conversion to bioadsorbents. Pineapple is grown in many countries worldwide, such

as Brazil, Philippines, Costa Rica, Malaysia, Indonesia, Hawaii, and Thailand, in total on about 2.1 million acres. After harvesting, a large amount of different types of pineapple wastes remain, causing various problems for farmers [13]. Thus the use of pineapple waste as adsorbent is an attractive alternative from both economical and environmental perspective. Such use of pineapple wastes is undoubtedly beneficial, providing a natural adsorbent and decreasing the amount of agricultural wastes [14]. Pineapple stem waste has been used to remove methylene blue from aqueous solutions [5]. In addition, the dried pineapple leaves are also used for Cr(VI) adsorption [15] and decolorization of Basic Green 4 [14] from aqueous solutions.

The aim of this work was to investigate the potential of using pineapple waste derived materials as low-cost bioadsorbents for the adsorption of lead and cadmium. The effects of NaOH treatment of different waste fractions (stem, leaf, fruit, and mixed waste) on the efficiency of lead and cadmium removal were studied. The effects of initial metal concentration, contact time, temperature, pH, and packing on metal adsorption by different fractions of modified wastes are also discussed and compared to non-modified materials.

MATERIALS AND METHODS

Preparation of synthetic wastewater

The 15 mg/L lead and cadmium solutions were prepared by diluting 1000 mg/L stock solutions of lead and cadmium solution (AA grade, Sigma–Aldrich Corporation) with double distilled water. The pH of the dilute solutions was adjusted to 6.0 using 0.1 M HNO_3 (Lab-Scan) or 0.1 M NaOH (Merck). The final solutions were poured into plastic bottles and kept in refrigerator for adsorption experiments.

Preparation of Raw Materials and Adsorbents

Raw materials

Different pineapple wastes (stem, leaf, fruit, and mixed waste) were obtained from Nakhon Thai district, Phitsanulok province, Thailand. The collected wastes were washed with distilled water several times to remove dirt particles. The washed wastes were oven dried (SL 1375 SHEL LAB 1350 FX) at100 ºC for 24 h. The dried wastes were ground and screened by 60 mesh sieve and then stored in plastic bags and desiccator for further use.

The lignin, cellulose, and hemicellulose in the different waste materials were determined following a report of Inari *et al.*[16] and Zhang *et al.* [17], respectively. These results are shown in Table 1.

Adsorbent preparation

The different fractions of dried wastes were treated with 1 M NaOH (Merck) using a 1:10 ratio of weight/volume. The slurry mixtures were boiled for 2 h with stirring at 700 rpm. After that, boiled slurry mixtures were washed for several times with distilled water until pH 7. The washed slurry mixtures were oven dried at 100 ºC for 24 h. The dried wastes were ground and screened by 60 mesh sieve and then stored in plastic bags and desiccator for further use.

Table 1: Chemical composition (%wt) of various types of pineapple wastes.

Pineapple wastes	Lignin	Hemicellulose	Cellulose
Stem	3.54	3.26	17.36
Fruit	1.7	24.27	15.06
Leaf	3.1	21.38	20.25
Mixed waste	2.8	15.39	20.40

Table 2: Pb^{2+} and Cd^{2+} removal efficiency of each part of pineapple waste for both untreated and NaOH treated absorbents

Absorbents	Pb^{2+} removal efficiency (%)		Cd^{2+} removal efficiency (%)	
	untreated	treated	untreated	treated
Stem	64.50 ± 0.61^{bA}	97.08 ± 0.62^{bB}	42.72 ± 1.92^{dX}	94.62 ± 0.09^{aY}
Fruit	59.08 ± 3.18^{cA}	78.50 ± 0.55^{cB}	47.93 ± 1.68^{cX}	83.75 ± 0.68^{cY}
Leaf	63.39 ± 1.13^{bA}	100.00^{aB}	80.59 ± 2.12^{aX}	91.06 ± 0.38^{bY}
Mixed waste	77.16 ± 0.72^{aA}	98.60 ± 0.93^{abB}	64.34 ± 1.09^{bX}	91.51 ± 0.35^{bY}

-Values followed by the same lowercase letter within the same column are not significantly different ($p > 0.05$)

-Values followed by the same capital letter within the same row are not significantly different ($p > 0.05$)

(a) (b)

Figure 1: Two types of packaging in cloth bag (a) tight packing (BB1) and (b) loose packing (BB2)

Batch adsorption experiments

Batch adsorption studies were carried out using 250 ml conical flasks containing 100 mL of a 15 mg/L solution of metals ions with 1 g of dry NaOH treated adsorbents. The slurry mixtures were agitated at 200 rpm in rotary shaker at room temperature for 1 h. The supernatants were separated by filtration with filter paper Whatman no. 42. The heavy metals in the supernatant were measured using an atomic absorption spectrophotometer (Varian SpectrAA 220, Australia). All experiments were carried out in triplicate. The NaOH untreated adsorbents were also studied in a same manner

as NaOH treated adsorbents. The metal adsorption efficiencies were calculated for comparison of NaOH treated adsorbents and the untreated ones.

The metal removal efficiency was calculated as [18]:

metal ions removal efficiency (%) = $[(C_i - C_f)/C_i]$x100

where C_i and C_f are the initial and final Pb^{2+} or Cd^{2+} concentrations, respectively.

The effect of contact time, pH, and temperature

The dilute 15 mg/L solutions of lead or cadmium (100 mL) were added to a series of 200 mL volumetric flasks containing adsorbents 1 g. The pH values of the solutions were adjusted to 2, 4, or 6 using 0.1 M HNO_3 or 0.1 M NaOH. The slurry mixtures were shaken at 200 rpm for 15, 30, 60, or 90 minutes at 30 or 60 ºC. The supernatants were separated by filtration with filter paper (Whatman no. 42). The heavy metals in the supernatant were measured using an atomic absorption spectrophotometer.

Effect of packing of adsorbents

The tight packing (Figure 1 (a)) and loose packing (Figure 1 (b)) of adsorbents were used to study the effect of the form of adsorbent used for metal adsorption. Solutions of the metals (500 mL) at the concentration of 5000 ppb were added to beakers containing adsorbents (25 g) in different forms. The beakers were shaken at 200 rpm at room temperature. The supernatants were corrected at 15, 30, 60, 90, and 120 minutes. The heavy metals in the supernatant were also measured using an atomic absorption spectrophotometer.

Statistical analysis

Analysis of Variance (CRD) and Duncan, s New Multipe Range Test (DMRT) were used for evaluation of statistical variance, statistical differences and coefficient of variation for all data of metal removal efficiency, respectively. The data was considered statistically different from control at $P< 0.05$.

RESULTS AND DISCUSSION

The effects of untreated and NaOH treated adsorbents

As can be seen from Table 2, the Pb^{2+} and Cd^{2+} adsorptions on NaOH treated waste materials of all types were significantly higher than adsorption on untreated ones ($P<0.05$). This can be explained by the fact that the treatment with NaOH can remove surface impurities present on the adsorbents and expose the active sites for metal adsorption. This improvement was also attributed to the solubilization of hemicellulose and pectin embedded in the cell walls of wastes, leaving behind a material with exposed active binding sites for sorption of metals. Furthermore a deprotonation of the waste materials should have taken place and the Na cation from NaOH could act as the counter ion to negatively charged functional groups in the modified sorbents. These Na ions will be exchanged with the heavy metals ion during the sorption process. Finally, the result might also be attributed to ion exchange associated with carboxylate and hydroxylate anions as acidic groups, carboxyl and

hydroxyl, are predominant on the material surface after NaOH treated [18], for example due to the transformation of methyl esters into carboxylate ligands. Especially, the -OH group form NaOH is the key functional group responsible for metal ion adsorption [10]. Consequently, the metal binding capability was substantially improved [7]. Therefore, metals ions adsorption on NaOH treated wastes is much higher than on the untreated ones. For untreated wastes, the lower metal ions adsorption levels suggest that adsorption occurs mainly on unsaturated alkenes(CH_2–) of untreated wastes, which react weakly with metals ions [15].

It can be seen that the efficiency of Pb^{2+} adsorption was higher than that of Cd^{2+} for both NaOH treated and untreated waste materials. It can be concluded that the adsorbents were able to selectively adsorb Pb^{2+} more than Cd^{2+} from aqueous solution. This is likely due to the different ionic radii of the Pb^{2+} and Cd^{2+} cations. A larger ionic radius reduces the electrostatic nature of a metal ion and favors interactions of a covalent nature between metals ions and the surface functional groups of an adsorbent. Therefore, the adsorption of $Pb^{2+}$with larger ionic radius is relatively unaffected and the adsorption of Pb^{2+} is more favorable than that of Cd^{2+} [19].

The efficiency of Pb^{2+} adsorption on untreated leaf and stem waste materials are not significantly different. The efficiency Pb^{2+} adsorption of fruit waste is lowest. The low metal adsorption capacity of fruit waste may be due to decreased diffusivity of the metal ions across the liquid film formed on the fruit with high content of glucose and carbohydrates [20]. Another reason might be the fact that fruit waste has high content of hemicellulose (Table 1), which is water-soluble matter [21]. So, the complex form of metals ions and hemicellulose is also water-soluble. On the other hand, the efficiency of Pb^{2+} adsorption of mixed waste is the highest. However, the NaOH treated leaf waste has 100% Pb^{2+} adsorption efficiency, which is not significantly different from the adsorption efficiency of the treated stem and mixed wastes. The adsorption efficiencies are dependent on the cellulose and lignin content of different wastes. However, these are similar for various waste types (Table 1). Most importantly, lignocellulose materials in the form of fibers contain functional groups such as hydroxyl (–OH), carboxyl (–COOH), and silanol (Si-OH), which are responsible for sorption of metal ions from the aqueous environment [3]. Therefore, the leaf, stem, and mixed waste with high cellulose content (Table 1) possess high capacity for metals ions adsorption. For the same reasons, the Pb^{2+} adsorption efficiency of NaOH treated fruit waste is lowest. The Cd^{2+} adsorption efficiency of all untreated wastes are significantly different with the adsorption efficiency decreasing in the order leaf, mixed, fruit, and stem waste. But after NaOH treatment, the treated stem waste has the highest Cd^{2+} adsorption efficiency. This is followed by treated leaf and treated mixed waste, which are not significantly different. The treated fruit waste has once again the lowest adsorption efficiency. These results are similar to sugar beet pulp, which shows adsorption efficiency for Cd^{2+} and $Pb^{2+}$of about 57% at pH about 5 [22]. It was seen that the Pb^{2+} and Cd^{2+} adsorption efficiencies of treated stem, treated leaf, and treated mixed waste are not significantly different ($p > 0.05$). Therefore, in further experiments we focused on treated mixed pineapple waste, as the

waste is present in this form in the field after harvest. This makes it more cost and time efficient by eliminating separation.

Effects of contact time and pH

The effect of contact time on adsorption of Pb^{2+} and Cd^{2+}using NaOH treated mixed pineapple waste at30°C and 60°C at pH 6 is shown in Figure 2. It was found that the Pb^{2+} and Cd^{2+} adsorption reach equilibrium at 30 and 60 minutes of extraction, respectively. Adsorption efficiency over 95% is observed for both metals ions. This is a relatively fast adsorption process. The fast adsorption in the initial stage of adsorption was attributed to the large amount of active sites available [18]. Therefore, further adsorption experiments were carried out with 1 h contact time to ensure that the equilibrium was achieved. Furthermore, it was found that the adsorption of efficiency of the Cd^{2+}cation was higher at 60ºC than at 30ºC using NaOH treated mixed pineapple waste. This was true for all pH values tested. It could be seen that the adsorption rate at 60°C is higher than at 30°C with only 15 minutes needed to reach equilibrium. This could be assisted by the structure of the wastes, which was quite spongy at high temperature facilitating the diffusion of the metal ions from solution into the surface of the adsorbent [23]. It was also shown that the Cd^{2+} adsorption on NaOH treated mixed pineapple waste is endothermal adsorption. For Pb^{2+} adsorption equilibrium time on NaOH treated mixed pineapple waste is 15 minutes for both 30°C and 60°C indicating a higher rate than for Cd^{2+} adsorption. This was different at pH 2, where Pb^{2+} and Cd^{2+} adsorption time on NaOH treated mixed pineapple waste needed to reach equilibrium was 30 minutes and 60 minutes (Table 3 and 4), respectively. This shows that the adsorption rate at pH 2 is slower than at pH >4. At lower pH values the H_3O^+ ions compete with the metal ions for the exchange sites in the adsorbents. The H_3O^+ ions occupy the sites and cover the surface of waste based adsorbents. On the other hand, there are more metal ions than H_3O^+ ions and the competition from H_3O^+ ions was weak at higher pH values, resulting in more exchange sites being available for metal ions at higher pH values [24].

The Cd^{2+} and Pb^{2+} adsorption efficiency increases above pH 2 and reaches maximum at pH 4. This is then followed by a slight decrease at pH 6. It expected that the pH_{PZC} of NaOH treated wastes is lower than 4. The report of Yang and Cui [18] shows that the pH_{PZC} of NaOH treated tea residue is 2.8±0.1.Therefore, these observations can be explained by the surface charge of the adsorbent and the concentration of H_3O^+ ions present in the solution. At pH 2, the treated adsorbents become positively charged due to the adsorption of H_3O^+ ions. Thus there is significant electrostatic repulsion between the adsorbent surface and Cd^{2+} or Pb^{2+} cations. In addition, the concentration of H_3O^+ ions is high at low pH and they compete with metal ions in the solution for the active sites on the adsorbent material. Therefore, adsorption capacities of the materials are low. At pH 4 the treated adsorbents become deprotonated and negatively charged due to the adsorption of OH^- ions and the electrostatic attractive force between treated adsorbents and metal ions. Moreover, as pH increases, the competition of H_3O^+ with Cd^{2+} or Pb^{2+} decreases as these surface active sites become more negatively charged [18]. However, at pH $\geq$6, a slight decrease in the Cd^{2+} and Pb^{2+} adsorption is due to the formation of soluble hydroxyl complexes [25].

Furthermore, metal precipitation is observed at higher pH values and the adsorbent deteriorates with the accumulation of metals ions [18].

The effect of temperature

The data showing the effect of temperature on Pb^{2+} and Cd^{2+} adsorption efficiency are shown in Table 3 and 4. It can be seen that the percentage of adsorption efficiency increases along with increasing the temperature from 30°C to 60°C. It was suggested that the adsorption process for Pb^{2+} and Cd^{2+} is endothermic in nature [26]. These results are similar to those obtained with alkali modified lignin [27] and meranti sawdust [25]. It was suggested that the higher temperature improves the trend by either increasing the number of available active sites or decreasing the thickness of the boundary layer surrounding the adsorbents [7].

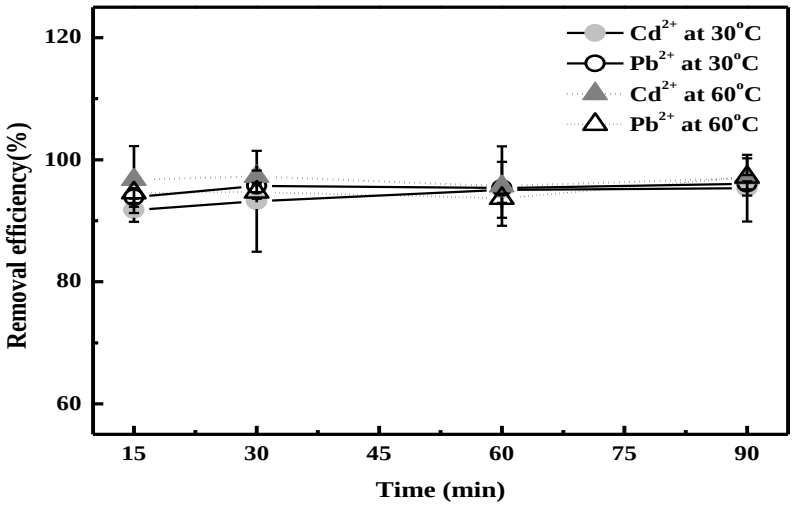

Figure 2: Pb^{2+} and Cd^{2+} removal efficiencies of treated mixed pineapple waste at various absorption time points at 30 °C and 60 °C, and pH 6.

Table 3: Pb^{2+} removal efficiency of treated mixed pineapple waste with various absorption times at 30 °C and 60 °C, and pH 2, 4, 6.

Pb^{2+}removal efficiency (%)				
Temperature(°C)	Time (min)	pH		
		2	4	6
30	15	84.95 ± 0.81^{a}	97.47 ± 0.20^{b}	93.83 ± 1.55^{c}
	30	91.26 ± 0.61^{a}	97.84 ± 0.28^{b}	95.74 ± 1.05^{c}
	60	94.29 ± 0.34^{a}	97.82 ± 0.12^{b}	95.37 ± 0.77^{c}
	90	94.86 ± 0.41^{a}	97.74 ± 0.36^{b}	96.04 ± 0.90^{c}
60	15	85.27 ± 0.83^{a}	97.10 ± 0.13^{b}	94.59 ± 1.70^{c}
	30	93.16 ± 0.29^{a}	96.87 ± 1.26^{b}	94.71 ± 1.11^{c}
	60	93.41 ± 0.17^{a}	96.86 ± 1.23^{b}	93.67 ± 0.74^{c}
	90	95.36 ± 0.78^{a}	97.00 ± 0.29^{b}	97.18 ± 3.05^{c}

- Values followed by the same lowercase letter within the same row are not significantly different ($p > 0.05$)

Table 4: Cd^{2+} removal efficiency of treated mixed pineapple waste with various absorption times at 30 °C and 60 °C, and pH 2, 4, 6.

Cd^{2+} removal efficiency(%)				
Temperature(°C)	Time (min)	pH		
		2	4	6
30	15	3.63 ± 0.76 [a]	92.30 ± 3.05 [b]	91.74 ± 1.92 [b]
	30	9.23 ± 1.10 [a]	93.90 ± 0.25 [b]	93.20 ± 8.26 [b]
	60	10.79 ± 1.91 [a]	94.79 ± 1.78 [b]	95.07 ± 4.59 [b]
	90	15.86 ± 3.70 [a]	96.34 ± 0.84 [b]	95.33 ± 5.46 [b]
60	15	2.00 ± 1.47 [a]	95.64 ± 3.09 [b]	96.76 ± 5.48 [b]
	30	3.05 ± 2.20 [a]	96.19 ± 0.89 [b]	97.23 ± 1.00 [b]
	60	10.24 ± 3.10 [a]	96.59 ± 2.73 [b]	95.69 ± 6.50 [b]
	90	10.63 ± 3.52 [a]	96.70 ± 0.83 [b]	96.99 ± 0.52 [b]

- Values followed by the same lowercase letter within the same row are not significantly different ($p > 0.05$)

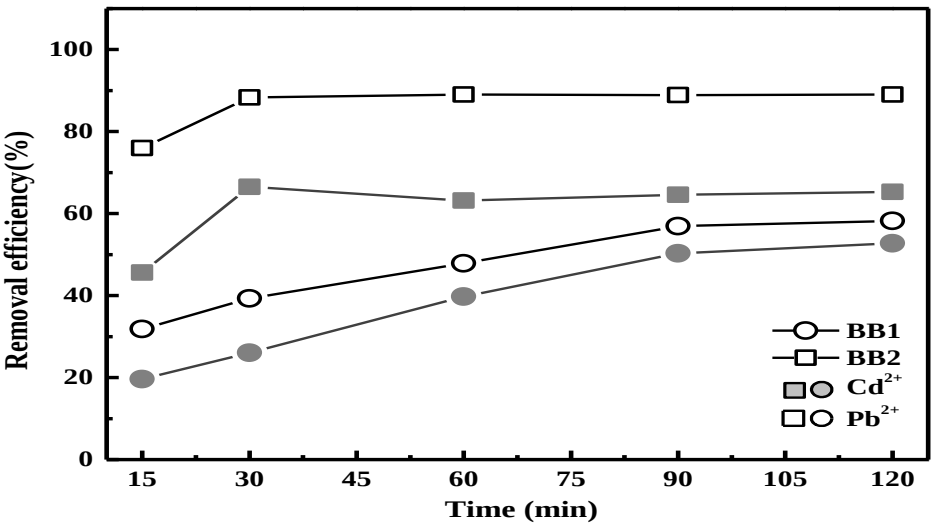

Figure 3: Pb^{2+} and Cd^{2+} removal efficiency of treated mixed pineapple waste in tight packed (BB1) and loose packed (BB2) adsorbents at various absorption time points

APPLICATION OF ADSORBENTS

For easy adsorbent recovery after use in practical applications, two types of packaging in a cloth bag, tightly packed (BB1) and loosely packed (BB2) (Figure 1), were studied in batch adsorption experiments.

It can be seen from Figure 3 that Pb^{2+} and Cd^{2+} removal efficiency using NaOH treated mixed pineapple waste in the loose packing is higher than in the tight packing. The Pb^{2+} removal efficiency by treated waste remained higher than Cd^{2+} removal efficiency as observed in other experiments. On the other hand, the time needed for

the adsorption to reach equilibrium was shorter for the loosely packed adsorbent (30 minute) than for the tightly packed adsorbent (90 minute). This is because the diffusion resistance to mass transfer is greater for tightly packed adsorbent. The loose packing allows very fast removal kinetics since the adsorption is primarily a surface phenomenon [22].

CONCLUSION

The results of this research show that adsorbents prepared from pineapple wastes by treatment with sodium hydroxide have higher adsorption efficiency for cadmium and lead ions than untreated pineapple wastes. This demonstrates that sodium hydroxide is a good reagent for the conversion of pineapple waste to high efficiency metal ions adsorbents. The increase in adsorption efficiency observed upon the treatment is on the order of 50-100%. In addition, it can also be concluded that the efficiency of Pb^{2+} adsorption is higher than that of Cd^{2+} adsorption for both NaOH treated and untreated waste materials. The adsorption efficiency of Pb^{2+} and Cd^{2+} ions of untreated and treated fruit waste are lowest. The adsorption efficiencies for leaf, stem, and mixed wastes are higher but not significantly different from each other. This result was attributed to the content cellulose in the waste materials. It was also found that the Pb^{2+} and Cd^{2+} adsorption on treated waste materials reaches equilibrium in 30 and 60 minutes, respectively. Furthermore, the adsorption rate at 60°C is higher than at 30°C. This shows that Pb^{2+} and Cd^{2+} ion adsorption by NaOH treated pineapple waste materials is endothermal adsorption process. As for the effect of pH, times needed to reach equilibrium for Pb^{2+} and Cd^{2+} adsorption on NaOH treated mixed pineapple waste are 30 minutes and 60 minutes at pH 2, respectively. This is slower than at pH >4. The Cd^{2+} and Pb^{2+} adsorption efficiency increases above pH 2 and reaches maximum at pH 4. A slight decrease was then observed at pH 6. Finally, for practical use of the waste materials, it was found that Pb^{2+} and Cd^{2+} removal efficiency with NaOH treated mixed pineapple waste is higher with loose packing than with tight packing. The equilibrium adsorption state is also reached faster with the loosely packed materials (30 minute) than with the tightly packed ones (90 minute). Therefore it can be concluded that pineapple wastes, which are cheap, easily available, and can be used more economically on large scale, have high potential for conversion to Pb^{2+} and Cd^{2+} ion adsorbents by treatment with NaOH.

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REFERENCES

[1] Rafatullah, Mohd., Sulaiman, O., Hashim, R., and Ahmad, A., 2010, "Adsorption of methylene blue on low-cost adsorbents: A review," J. Hazard. Mater., 177, 70–80.

[2] Liu, X., and Lee, D.-J., 2014, "Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewaters," Bioresource Technol., 160, 24–31.

[3] Tran, V. S., Ngo, H. H., Guo, W., Zhang, J., Liang, S., Ton-That, C., and Zhang, X., 2015, "Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water," Bioresource Technol., 182, 353–363.

[4] Soltani, N., Bahrami, A., Pech-Canul, M. I., González, L. A., 2015, "Review on the physicochemical treatments of rice husk for production of advanced materials," Chem. Eng. J., 264, 899–935.

[5] Bhatnagar, A., and Sillanpää, M., 2010, "Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review," Chem. Eng. J., 157, 277–296.

[6] Miretzky, P., and Fernandez Cirelli, A., 2010, "Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review," J. Hazard.Mater., 180, 1–19.

[7] Nguyen, T. A.H., Ngo, H. H., Guo, W. S., Zhang, J., Liang, S., Yue, Q. Y., Li, Q., and Nguyen, T. V., 2013, "Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. Bioresource Technol. 148, 574–585.

[8] Guo, H., Zhang, S., Kou, Z., Zhai, S., Ma, W., and Yang, Y., 2015, "Removal of cadmium(II) from aqueous solutions by chemically modified maize straw," Carbohyd. Polym., 115, 177–185.

[9] Chand, P., Shil, A. K., Sharma, M., and Pakade, Y. B., 2014, "Improved adsorption of cadmium ions from aqueous solution using chemically modified apple pomace: Mechanism, kinetics, and thermodynamics," Int. Biodeter. Biodegr., 90, 8-16.

[10] Weng, C.-H., Lin, Y.-T., Hong, D. -Y., Sharma, Y.C., Chen, S.-C., and Tripathi, K., 2014, "Effective removal of copper ions from aqueous solution using base treated black tea waste," Ecol. Eng., 67, 127–133.

[11] Ewecharoen, A., Thiravetyan, P., and Nakbanpote, W., 2008, "Comparison of nickel adsorption from electroplating rinse water by coir pith and modified coir pith," Chem. Eng. J., 137, 181–188.

[12] Senthilkumaar, S., Bharathi, S., Nithyanandhi, D., and Subburam, V., 2000, "Biosorption of toxic heavy metals from aqueous solutions," Bioresource Technol., 75, 163-165.

[13] Kengkhetkit, N., and Amornsakchai, T., 2014, "A new approach to ''Greening'' plastic composites using pineapple leaf waste for performance and cost effectiveness," Mater. Design, 55, 292–299.

[14] Chowdhury, S., Chakraborty, S., andSaha, P., 2011, "Biosorption of Basic Green 4 from aqueous solution by *Ananascomosus* (pineapple) leaf powder," Colloid. Surface. B, 84, 520–527.

[15] Ponou, J., Kim, J., Wang, L. P., Dodbiba, G., and Fujita, T., 2011, "Sorption of Cr(VI) anions in aqueous solution using carbonized or dried pineapple leaves," Chem. Eng. J., 172, 906– 913.

[16] Inari, G.N., Mounguengui, S., Dumarçay, S., Pétrissans, M., and Gérardin, P., 2007, "Evidence of char formation during wood heat treatment by mild pyrolysis," Polym. Degrad. Stabil., 92, 997–1002.

[17] Zhang, P., Dong, S.-J., Ma, H.-H., Zhangc, B.-X., Wang, Y. –F., and Hu, X. –M., 2015, "Fractionation of corn stover into cellulose, hemicellulose and lignin using a series of ionic liquids," Ind. Crop. Prod., 76, 688–696.

[18] Yang, X., and Cui, X., 2013, "Adsorption characteristics of Pb (II) on alkali treated tea residue," Water Resour. Ind., 3, 1–10.

[19] Yu, X., Tong, S., Ge, M., Wu, L., Zuo, J., Cao, C., and Song, W., 2013, "Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals," J. Environ. Sci., 25(5), 933–943.

[20] Garg, U., Kaur, M.P., Jawa, G. K., Sud, D., and Garg, V. K., 2008, "Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass," J. Hazard. Mater., 154, 1149–1157.

[21] Dax, D., Chávez, M. S., Xu, C., Willför, S., Mendonça, R. T., and Sánchez, J., 2014, "Cationic hemicellulose-based hydrogels for arsenic and chromium removal from aqueous solutions," Carbohyd. Polym., 111(13), 797-805.

[22] Pehlivan, E., Yanık, B. H., Ahmetli, G., and Pehlivan, M., 2008, "Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp," Bioresource Technol., 99(9), 3520-3527.

[23] Abdullah, A. Z., Salamatinia, B., and Kamaruddin, A. H., 2009, "Application of response surface methodology for the optimization of NaOH treatment on oil palm frond towards improvement in the sorption of heavy metals," Desalination, 244, 227–238.

[24] Zheng, L., Zhu, C., Dang, Z., Zhang, H., Yi, X., and Liu, C., 2012, "Preparation of cellulose derived from corn stalk and its application for cadmium ion adsorption from aqueous solution," Carbohyd. Polymer., 90(2), 1008-1015.

[25] Rafatullah, M., Sulaiman, O., Hashim, R., and Ahmad, A., 2009, "Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust," J. Hazard. Mater. 170, 969–977.

[26] Nasuha, N., and Hameed, B. H., 2011, "Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea," Chem. Eng. J., 166, 783–786.

[27] Demirbas, A., 2004, "Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignication," J. Hazard. Mater., B109, 221–226.