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The Use of K_2CO_3 Modified Sunflower Seed Husks for Removing of Metal Ions from Industrial Wastewater

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Activated carbons which prepared from residual or waste biomaterials are widely examined as low-cost adsorbents for wastewater treatment, as well as heavy metal ions in wastewater have become a serious environmental problem. In addition, the removal efficiency of new cheap modified adsorbent from agricultural waste is important and would probably increase the quality of the environment. Therefore, it is necessary to investigate the understanding of adsorptive removal mechanism and removal efficiency of the adsorbent.
This study is aimed to evaluate the removal efficiency of Pb(II), Ni(II), Zn(II), and Cd(II) in aqueous solution by using a modified sunflower seed husk (MSSH) for industrial wastewater treatment. The husk as an adsorbent was treated by 0.8 M K_2CO_3, afterward; it was heated at 400 °C, sieved to a size of 500 to 710 µm (400-K_2CO_3MSSH). As a result, it was found that the Methylene blue number of 400-K_2CO_3MSSH was 50.80 mg/g and the Iodine number was 808.54 mg/g. The adsorption experiments were conducted with an initial metal ion concentration of 100 mg/L and pH of 5. In a batch experiment of single metal ion synthetic wastewater, it was observed that the adsorption percentage of Ni(II), Zn(II), Pb(II), and Cd(II) were 96.50, 97.03, 96.98, and 97.54, respectively. For mixed synthetic wastewater, the adsorption percentage of Ni(II), Zn(II), Pb(II), and Cd(II) were 87.16, 94.30, 98.02, and 97.01, respectively. Competitive adsorption decreased the removal of metal ions, and the equilibration time was showed longer result than that in the single system. Wastewater from the automotive industry was consisted of Ni(II), and Zn(II) which had the percentages of removal at 75.25 and 87.50, respectively. Whereas the lathe work demonstrated the percentage of Zn(II) and Pb(II) at 78.18 and 88.34 of removal. Experimental results were found that the Langmuir isotherm model was matched with a monolayer adsorption capacity per g adsorbent of 79.37 mg Ni(II), 76.34 mg Zn(II), 74.07 mg Pb(II), and 81.97 mg Cd(II). From our results, it can be concluded that 400-K_2CO_3MSSH could be potentially used as an attractive low-cost adsorbent for Ni(II), Zn(II), Pb(II) and Cd(II) containing industrial wastewaters.

1. Introduction

Trace concentration of Pb(II), Ni(II), Zn(II), and Cd(II) is very important for physiological function of living organism and human health. These ions are found in various industrial activities such as manufacturing of alloy, batteries, lathe work, automotive industry, chemical catalyst and so on. Release of untreated industrial wastewater into the environment decreased the quality of water resources (Gogoi et al., 2018). Although there are regulations and law for industrial effluent discharge, it is presented in small scale of effluent or low metal ion contaminated. Hence, it may be practical to use some cheap adsorbent derived from biomaterials. There are many methods for removing metal ions from wastewater such as reverse osmosis, membrane filtration, adsorption, ion exchange, and precipitation (Fu and Wang, 2011), the adsorption seems to be popular technique regarding to its simplicity, economics and effectiveness.
Adsorptions through biomaterials are widely studied for metal ion removals. Activated carbon which prepared from agricultural solid waste was used to remove Pb(II) and other heavy metals from industrial wastewaters according to Kadirvelu et al. (2001). Coffee grounds also was applied as an adsorbent for Pb(II) removal (Lavecchia et al., 2016). Moreover, activated carbons which prepared from lignocellulosic waste materials were examined for their adsorption, properties of dyes, metals and anions (Lahti et al., 2017), and it showed high removal ability. Recently, many researchers have focused on new modified or fabricated nanocomposite to

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remove Pb(II), Cd (II) and Cu(II) ions from polluted water (Saad et al., 2018), which chemically modified cellulose for Cd^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Cu^{2+} removal (Fakhre and Ibrahim, 2018). However, these techniques are quite expensive and difficult to conduct as well as there are many kinds of biomaterials/agricultural waste available with large quantities in Thailand. The agricultural waste such as coconut shell, wood, palm shell, and sunflower seed husks were explored as a low-cost adsorbent. Sunflower seed husk (SSH) was used as an adsorbent for dye removal by Srisorrachatr and Sriromreun (2013). Furthermore, SSH was used as an adsorbent for Ni^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}removals and also modified by chemicals in order to enhance the removal efficiency for metal ions from aqueous solution (Srisorrachatr, 2017). It was observed that different kinds of chemical modifications were able to improve altered properties and capacities of adsorption. SSH modified by K_2CO_3 and carbonization at 400 °C (400-K_2CO_3MSSH) showed a greater removal capability than that of SSH modified by $ZnCl_2$. Hence, the further experiment of metal ion removal must be explored for real industrial wastewater using 400-K_2CO_3MSSH as an adsorbent.

Therefore, the objective of this study is to prepare a low-cost adsorbent as well as examine the removal efficiency of modified sunflower seed husk with 0.8 M K_2CO_3 and carbonization at 400 °C for removing Ni(II), Zn(II), Pb(II), and Cd(II) from synthetic and industrial wastewater. Percentages of a single metal ions removal from solution, competitive removal among mixed metal ions in synthetic wastewater and in real industrial wastewater are investigated. Then a new cheap modified adsorbent from agricultural waste will be potentially used and practical for metal ion removal in small scale of effluent or low metal ion contaminated industrial wastewater.

2. Materials and methodology

In this section, an adsorbent from sunflower seed husks was prepared and batch adsorption experiments were carried out at room temperature. Details of materials and methodology were described below.

2.1 Chemical and materials

Standard solution of Zn(II), Pb(II), Cd(II), and Ni(II) was 1000 mg/L AAS (Spectrosol). Working solutions of Zn(II), Pb(II), Ni(II), and Cd(II) were prepared from $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Ni(NO_3)_2$, and $Cd(NO_3)_2$. Potassium carbonate (K_2CO_3) is analytical reagent grade. All chemicals are from Asia Pacific Specialty Chemical Limited. Sunflower seed husk was agricultural waste obtained from Flower Food Co. Ltd., Thailand.

2.2 Methodology

An adsorbent preparation was carried out by using cleaned raw sunflower seed husks. The dried cleaned husks were chemically modified by soaking in 0.8 M K_2CO_3 solution for 24 hours and then were washed with distilled water until the filtrate reached neutral pH (K_2CO_3MSSH). After that, the resulting husks were air-dried and were subsequent carbonized at 400°C for an hour in oxygen-deficient conditioned muffle furnace (Fisher Scientific Isotemp Muffle Furnace, England). The modified sunflower seed husks then were reduced in size and sieved (Endecotts, England) for size of 500-710 µm (400-K_2CO_3MSSH) and kept in desiccator.

For the batch study, 1.0 g of 400-K_2CO_3MSSH (500 - 710 µm) was mixed with 200 mL of 100 mg/L metal ion solution, pH 5, in a conical flask and then mixture was shaken on an orbital shaker (Gallenkamp orbital shaker, England) at 150 rpm. An aliquot of sample was then taken out at a desired time interval and filtered. The remaining metal ions in the filtrate was determined using Atomic Absorption Spectrophotometer (AAS, model GBD 908 AA, GBC Scientific, Australia). The wavelengths used for monitoring Zn(II), Pb(II), Cd(II), and Ni(II) were 213.90, 283.30, 228.80, and 341.50 nm, respectively. Then metal ion removal capabilities were analysed. The method and procedure of the batch experiment were presented in Figure 1(a).

Removal capacity of metal ions in synthetic and real wastewater by 400-K_2CO_3MSSH was investigated. Synthetic wastewater was then prepared in 2 categories as single and mixed metal ion with metal ion in total initial concentration of 100 mg/L and pH 5. The mixed ion synthetic wastewater was used as representative of industrial wastewater without contaminants. For industrial wastewater, the samples of wastewater were collected from an automotive waste management unit in Samut Sakhon Province, and metal lathe work in Nakhon Nayok Province, Thailand. The industrial wastewater also was adjusted to pH 5 and then the batch adsorption experiments were conducted. The diagram of wastewater study plan was shown in Figure 1(b).

Langmuir and Freundlich adsorption isotherm model were investigated for single metal ion removal from solution in order to verify a characteristic of interaction between adsorbent and adsorbate. The experiment was carried out by mixing 1 g of an adsorbent and 100 mL of metal ion solution of various concentration; 200-600 mg/L with pH 5, shaking at 150 rpm about an hour for reaching equilibrium. Then the remaining concentration of metal ion in solutions were examined using AAS for Langmuir and Freundlich adsorption isotherm model.

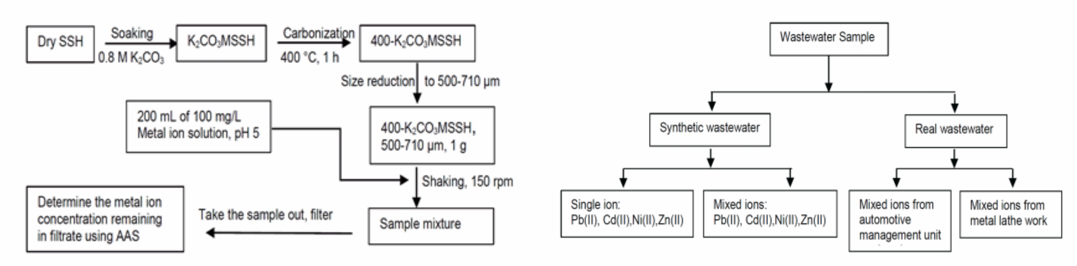

Figure 1: (a) Diagram of experimental procedure and (b) wastewater preparation.

3. Analysis of data

The experimental data obtained from the batch studies were used to calculate the percentage removal and adsorption capacity of the metal ions by using mass balance equation (1) and equation (2).

$$\% \mathit{Removal} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

$$q_e = \frac{C_i - C_f}{W} \times V \tag{2}$$

where C_i and C_f are the initial and final concentrations (mg/L) of metal ions, W is the mass (g) of adsorbent, V is the volume of metal ion solution (L) and q_e is the amount metal ion adsorbed at equilibrium (mg/g).
For Langmuir and Freundlich adsorption isotherm model, the experimental data was used to verify the model by fitting equation (3) and equation (4), respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where C_e is equilibrium concentration (mg/L), q_e is adsorption capacity (mg/g), q_m is maximum adsorption capacity (mg/g), K_L is Langmuir adsorption constant and K_F is Freundlich adsorption constant. The plot of C_e/q_e versus C_e for Langmuir's adsorption model will give the straight line with slope of $1/q_m$ and intercept of $1/(K_L\ q_m)$. For Freundlich's adsorption model, plot of *log* q_e against *log* C_e also will be linear relationship. The relative coefficients of these models were calculated by using linear least-squares fitting.

4. Results and discussion

From our preparation of the adsorbent, monitoring its removal capacity for Ni(II), Zn(II), Pb(II), and Cd(II) from wastewater, the experimental results and data analysis were presented as below.

4.1 Physical properties of modified sunflower seed husks

The adsorbent, 400-K_2CO_3MSSH, was prepared from sunflower seed husk (SSH) activated with 0.8 M K_2CO_3 and carbonized at 400 °C, with particle size of 500-710 µm. Color of SSH was changed from brown to dark brown after 0.8 M K_2CO_3 treatment, and became black subsequent to carbonization and their pictures were showed in Figure 2.
Methylene blue number (MB_N) and Iodine number (IN) are significant parameters for characterizing adsorptive capability of adsorbents. The IN is a measure of micro-pore capacity (Itodo et al., 2010) and suitable for small molecules while MB_N is related to the macro- and meso-pore capacity (Raposo et al., 2009) and fitting for larger molecules. Therefore, 400-K_2CO_3MSSH were investigated both MB_N and IN followed by Nunes and Guerreiro (2011) and ASTM D 4607-94, respectively. It was observed that the MB_N of 400-K_2CO_3MSSH was 50.80 mg/g and IN was 808.54 mg/g. Whereas, Srisorrachatr (2017) found that, 500-K_2CO_3MSSH had MB_N of 134.64 mg/g and IN of 1075.02 mg/g, respectively. However, 400-K_2CO_3MSSH was preferred using as adsorbent to 500-K_2CO_3MSSH according to the optimal condition of metal ion removal capability. With these values of MB_N and IN, it can be emphasized that this 400-K_2CO_3MSSH can be used as an adsorbent. Thus, the 400-K_2CO_3MSSH was used in the batch adsorption for metal ion removal.

(a) (b) (c) (d)

Figure 2: (a) Sunflower seed husk (SSH), (b) SSH soaked with 0.8 M K_2CO_3 (K_2CO_3MSSH), (c) K_2CO_3MSSH carbonized at 400 °C (400-K_2CO_3MSSH) and (d) 400-K_2CO_3MSSH with particle size of 500-710 µm.

4.2 Removal of metal ions from synthetic wastewater

The experimental results of metal ion removal from single ion synthetic wastewater were presented in Figure 3, on the left. The removal percentage of Ni(II), Zn(II), Pb(II), and Cd(II) were 96.50, 97.03, 96.98 and 97.54, respectively. Ni(II) showed the most active in removal among them, and all metal ions reached equilibrium within 6-8 minutes. The removal percentage of Ni(II), Zn(II), Pb(II), and Cd(II) from the mixed ion synthetic wastewater were 87.16, 94.30, 98.02, and 97.01, respectively, as showed in Figure 3, on the right.

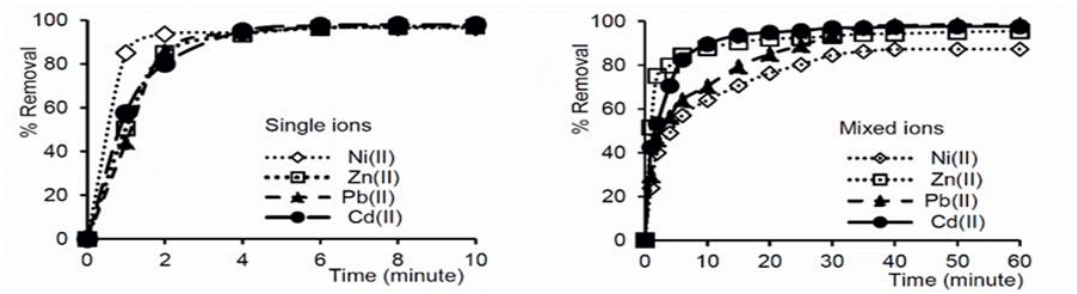

Figure 3: Metal ion removal percentage from synthetic wastewater for single and mixed ions using 400-K_2CO_3MSSH.

It was observed that competitive removal was occurred among them in mixed ions (Figure 3, the right) and it decreased the removal of metal ions comparing to single system (Figure 3, the left). The Ni(II) showed the lowest removal percentage and slowest removal rate followed by Pb(II), whereas Zn(II) and Cd(II) got high removal rate. The equilibrium competing time was around 50 minutes. The equilibrium time of the ions in mixed synthetic wastewater also took longer than the wastewater of single ion. The values of removal capability of metal ions from synthetic wastewater were tabulated in Table 1.

Table 1: Removal ability of metal ions from synthetic wastewater using 400-K_2CO_3MSSH at pH 5.

Synthetic wastewater	Metal ion	Equilibrium time (minute)	Adsorption capacity (mg/g)	% Removal
Single ion	Ni(II)	6	9.60	96.50
	Zn(II)	8	9.65	97.03
	Pb(II)	8	9.70	96.98
	Cd(II)	6	9.76	97.54
Mixed ions	Ni(II)	50	2.175	87.16
	Zn(II)	50	2.204	94.30
	Pb(II)	40	2.378	98.02
	Cd(II)	40	2.377	97.01

These behaviors were also found in the competitive removal of Fe, Mn, Cd, Zn, Cu, and Fe in aqueous solution using sunflower, potato, canola, and walnut shell residues (Feizi et al., 2015).

4.3 Removal of metal ions from industrial wastewater

Removal of metal ions from real industrial wastewater by 400-K_2CO_3MSSH is very important and meaningful. Since initial metal ion concentration in industrial wastewater cannot be controlled, which depends on sources, and there are also many mixed contaminants. The concentration of each metal ion was monitored before and after conducting the batch adsorption. It was observed that wastewater from the automotive contains only Ni(II) and Zn(II) with different concentration. The 400-K_2CO_3MSSH removed Ni(II) and Zn(II) from the wastewater with removal percentages of 75.25 and 87.50 and had equilibrium time around 40-50 minutes, as shown in the left on Figure 4. It can be noted that the sequent rate of metal ion removal in Ni(II) and Zn(II) from industrial wastewater is the same magnitude as in the mixed ions synthetic wastewater. Whereas wastewater from the lathe work which contained Zn(II) and Pb(II) with different initial concentration, had the removal percentage of 78.18 and 88.34, respectively, as shown on the right of Figure 4. The calculated data were presented in Table 2. For this case, it can be seen that the sequence of removal activity was not same as those mixed ions synthetic wastewater. These incidents may due to unfixed initial concentration of metal ions in real wastewater and other ions or contaminants also presented in the wastewater (Kadirvelu et al., 2001). The main ions, more concentrate metal ions, also can compete to others and undergo predominant removal ability**.**

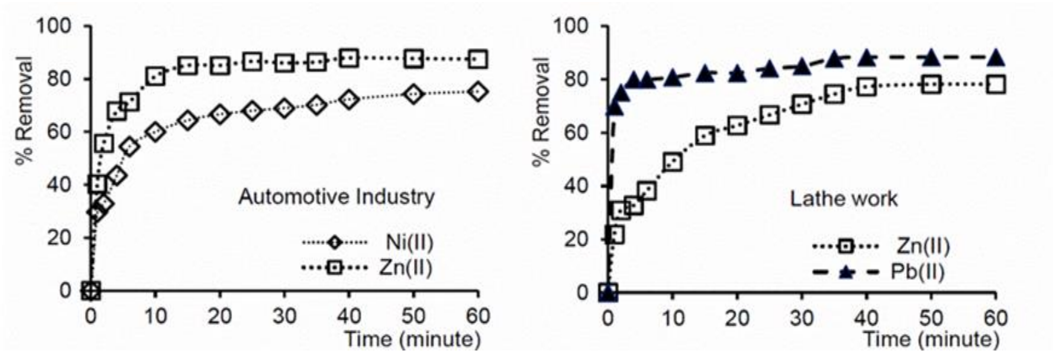

Figure 4: Removal percentage of metal ions presenting in industrial wastewater using 400-K_2CO_3MSSH.

Table 2: Removal ability of metal ions from industrial wastewater using 400-K_2CO_3MSSH at pH 5.

Industrial wastewater	Metal ion	Initial concentration (mg/L)	Adsorption capacity (mg/g)	% Removal
Automotive	Ni(II)	4.550	0.34	72.25
	Zn(II)	2.895	0.40	87.25
Lathe	Zn(II)	0.603	0.13	78.18
	Pb(II)	3.158	0.19	88.34

4.4 Langmuir and Freundlich adsorption isotherm

Since adsorption isotherm describes the interaction between adsorbate and adsorbent materials. The data were fitted to Langmuir's adsorption model (3) and Freundlich's adsorption model (4). Maximum adsorption capacity (q_m) and Langmuir adsorption constant (K_L) can be calculated by Langmuir adsorption isotherm (3).
From Table 3, it can be seen that the calculated values fitted to Langmuir adsorption model for all ions with R^2 approaching unity. Maximum adsorption capacity, q_m, were 79.37, 76.34, 74.07, and 81.97 mg/g for Ni(II), Zn(II), Pb(II), and Cd(II), respectively.

Table 3: Values of parameters calculated from adsorption model of metal ions by 400 °C-K_2CO_3MSSH, pH5

Ions	Langmuir model					Freundlich model				
	Slope	Intercept	q_m (mg/g)	K_L (L/g)	R^2	Slope	Intercept	n	K_F	R^2
Ni(II)	0.013	0.285	79.37	0.044	0.931	0.501	0.863	1.99	7.291	0.834
Zn(II)	0.013	0.411	76.34	0.032	0.998	0.491	0.898	2.04	7.900	0.822
Pb(II)	0.014	0.584	74.07	0.023	0.983	0.503	0.801	1.99	6.323	0.815
Cd(II)	0.012	0.364	81.97	0.033	0.986	0.511	0.914	1.96	8.196	0.764

Therefore, it can be interpreted that the interaction at 400-K_2CO_3MSSH and these ions were ionic interaction with monolayer adsorption. Removal of toxic metal ions from wastewater using ZnO@Chitosan core shell nanocomposite was studied and found that it was fitted Langmuir adsorption isotherm model with q_m of 476.1, 135.1 and 117.6 mg/g, for Pb(II), Cd(II) and Cu(II), respectively (Saada, 2018). Even though the q_m at 400-K_2CO_3MSSH is rather smaller capacity than the ZnO@, but preparation of 400-K_2CO_3MSSH is simpler and easier to produce as well as cheaper than the ZnO@.

5. Conclusions

In this study, modified sunflower seed husk with K_2CO_3 and carbonization at 400 °C (400-K_2CO_3MSSH) was prepared with the IN and the MB_N at 808.54 mg/g and 50.80mg/g, respectively. Metal ion removals from synthetic and industrial wastewater by 400-K_2CO_3MSSH were monitored, and found that the competitive adsorption occurred and the removal decreased in mixed ion synthetic wastewater as compared to single ion wastewater. It was also demonstrated that 400-K_2CO_3MSSH removed Ni(II) and Zn(II) from the automotive and Zn(II) and Pb(II) from the lathe industry effectively. The experimental results of single metal ion synthetic wastewater were found to match the Langmuir isotherm model with a monolayer adsorption. It can be concluded that 400-K_2CO_3MSSH can be potentially used as attractive low-cost adsorbent for Ni(II), Zn(II), Pb(II) and Cd(II) removal from industrial wastewaters. In addition, removal of the mixed ions from solution using fixed bed column will be study for real industrial wastewater application.

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