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Modified Sunflower Seed Husks for Metal Ions Removal from Wastewater

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Metal ion contaminated wastewater from small factory are interested. Finding of new and cheap adsorbent for wastewater treatment can increase the quality of the environment in the effected localities and thus prevent adverse effect on environment and human being. Adsorption techniques belong to a cost effective methods that are able to effectively remove metal ion from solution. For the overall understanding of adsorptive removal, factors affecting removal capacity is necessary examined.
This study aimed to evaluate the removal efficiency of heavy metal ions in aqueous solution by modified sunflower seed husk (MSSH) for industrial wastewater treatment. Removal of lead (Pb(II)), nickel (Ni(II)), zinc (Zn(II)), and cadmium (Cd(II)) from aqueous solution using activated carbon prepared from sunflower seed husks (SSH), an agricultural waste was studied in batch experiment. Sunflower seed husks were modified by chemical activation with potassium carbonate (K_2CO_3) and zinc chloride ($ZnCl_2$) solution followed by carbonization. The concentration of both chemicals was varied between 0.4 and 1.2 M, and the temperature was ranged from 400 °C to 700 °C. The initial concentration of each metal ion used in this experiment was 200 mg/g. The experimental data showed that the 0.8 M K_2CO_3 and $ZnCl_2$ gave the optimum metal ions removal. The maximum removal of Pb(II), Ni(II), Zn(II), and Cd(II) ions occurred using 400°C-K_2CO_3 modified husks with 99.61, 98.07, 98.75, and 92.99 percent, respectively. Furthermore in $ZnCl_2$ activation, 400°C-$ZnCl_2$ modified husks showed the maximum removal of Pb(II), Ni(II), Zn(II), and Cd(II) ions with the values of 75.68, 51.79, 28.07, and 50.33 percent, respectively. The adsorption process conformed to Langmuir adsorption isotherm with the maximum adsorption (q_m) of Pb(II), Ni(II), Zn(II), and Cd(II) of 19.92, 18.56, 19.76, and 19.62 mg/g, respectively and K_L of 0.1640, 0.1585, 0.1005 and 0.1918 L/mg, respectively. The results indicated that the 400°C-K_2CO_3 MSSH could be employed as a promising biosorption for industrial wastewater treatment.

1. Introduction

Disposal of heavy metals into aquatic environment is increasing rapidly due to industrialization and unconcerned polluted process. Some metals are classified as toxic to human and living environment. They are of particular concern in the treatment of industrial wastewaters including arsenic(III) and arsenic(V), cadmium(II), chromium(III) and chromium(VI), cobalt(II), copper(II), lead(II), mercury(II), manganese(II), nickel(II), and zinc(II). Adsorption of Cr(VI) on sunflower seed hull derived porous carbon was studied (Zou et al., 2015). The use of activated carbon, (AC), has been proved to be one of the most convenient technique for metal ion removal. Foo and Hameed (2011) also prepared and characterized activated carbon from sunflower seed oil residue via microwave assisted K_2CO_3 activation for metal ion removal. Feizi et al. (2015) as well as Shah et al. (2015) also used the activated carbon from biomaterials as adsorbent for metal ion removal. There are many kinds of biomaterials available in large quantities in Thailand from agricultural operations including coconut shell, wood, palm shell, and sunflower seed husks. Sunflower seed husk (SSH) in Thailand is disposed as waste or used as biofuel or fertilizer. SSH was used as adsorbent for dye removal by Srisorrachatr (2012) and also has been used as low cost adsorbent for dye removal by Srisorrachatr and Sriromreun (2013). Balintova et al. (2016) also studied sorption removal of Cu(II), Zn(II) and Fe(II) from acidic solutions by the various kinds of wood sawdust. Removal of some metal ions by activated carbon prepared from *Phaseolus aureus* hulls were studied Madhava *et al*. (2009). In addition, activated carbon prepared from coirpith was used to remove Pb(II) and other heavy metals from industrial wastewaters by Kadirvelu *et al.* (2001). Removal efficiency of Pb(II) from synthetic and industrial wastewaters by using biomass fly ashes also studied by Barbosa *et al*. (2014) and Mishra et al. (2009). Recently, adsorptive removal of Pb(II) using spent coffee ground also investigated by Lavecchia et al. (2016). The aim of this research was to study the removal efficiency of metal ions; Pb(II), Zn(II), Ni(II), and Cd(II), from solution by using modified sunflower seed husk via K_2CO_3, $ZnCl_2$, and heating temperature.

2. Materials and methods

2.1 Chemical and materials

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 $Cd(NO_3)_2$. Standard solution of Zn(II), Pb(II), Cd(II) and Ni(II) was 1000 mg/L AAS standard (Spectrosol) whereas potassium carbonate (K_2CO_3) and zinc chloride ($ZnCl_2$) are analytical reagent grade. Sunflower seed husk was industrial waste obtained from Flower Food Co. Ltd., Thailand.

2.2 Procedure of adsorbent preparation and activation

Sunflower seed husks were collected from Flower Food Co., Ltd., (Bangkok, Thailand). The raw sunflower seed husks were repeatedly washed with distilled water to remove dirt, dust, and other impurities. The washed husks were then sundried and also dried overnight (SSH) in an oven around 100 °C. The dried hulls were divided into 2 portions for two chemical treatments; K_2CO_3 and $ZnCl_2$ solution. The modified husks was prepared by soaking in 0.4 to 1.2 M K_2CO_3 or $ZnCl_2$ solution for 24 hours. After treatment, the husks were washed by distilled water until the filtrate reached neutral pH. After that, the resulting husks were air dried. The dried treated husk were then carbonized at a desired temperature; 400, 500, 600, or 700 °C for an hour in oxygen deficient conditioned muffle furnace (Fisher Scientific Isotemp Muffle Furnace, England). The modified sunflower seed husks [MSSH] then were reduced in size and sieved (Retsch, model Rheinische str 36, Germany) for size of 500-710 micrometre and kept in desiccator.

2.3 Batch adsorption studies

All experiments in this study were examined as batch adsorption at room temperature and all the chemical used was of analytical reagent grade. The parameters affecting on the removal capacity were investigated, such as modified adsorbents, pH of the solution, and adsorbent size. A working solution of 200 mg/L metal ion was prepared for initial concentration and actual metal ion concentration was calculated from the calibration curve using Atomic Absorption Spectrophotometer (AAS, model GBD 908 AA, GBC Scientific, Equipment, Pty., Australia). The pH of the metal ion solution was adjusted to desired value by addition of dilute H2SO4 or NaOH solutions. For batch study, 1.0 grams of MSSH was mixed with 100 mL of 200 mg/L metal ion in conical flask. The mixture was shook on orbital shaker (Gallenkamp orbital shaker, England) with constant speed of 150 rpm at room temperature. Samples were then taken out at determined time interval periodically and separated from the adsorbents by micro-syringe filtration. The resulting ion solution was determined by AAS and then metal ion removal capabilities can be analyzed. The effect of chemical modification and heating temperature of sunflower seed husks on metal ion removal were studied. The effect of pH on removal capability was also studied over pH range of 2-6. The percentage of metal ion removal (% removal) and amount of adsorbed ion at equilibrium (q_e) were calculated by the following equation:

$$\%\,removal = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

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

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 amount metal ion adsorbed at equilibrium (mg/g).

2.4 Adsorption isotherm

The adsorption isotherm experiment was carried out by mixing 1 gram of 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 adsorption isotherm model and Freundlich adsorption isotherm model.
Langmuir model:

$$q_e = \frac{q_m K_L C_e}{(1+K_L C_e)}$$

and can be linearized to be $$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (3)$$

Freundlich model:

$$q_e = K_F C_e^{\frac{1}{n}}$$

which can be written in the linear form as

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

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 using linear least-squares fitting.

3. Results and discussion

3.1 Effect of temperature activation on adsorption capacity

Sunflower seed husk was studied as adsorbent for metal ion removal in forms of SSH, K_2CO_3-MSSH and $ZnCl_2$-MSSH with variation of temperature between 400 °C and 700 °C. The effect of temperature activation of SSH on adsorption capacity was carried out at room temperature. From the experiment, it was found that MSSH activated at 400, 500, 600, and 700 °C can adsorb Zn(II), Ni(II), and Pb(II) from solution with maximum value at pH 5 and Cd(II) at pH 6. These percentage adsorptions are 49.57, 45.84, 45.00, and 42.44 for Pb(II); 49.36, 48.12, 47.57, and 47.98 for Zn(II) ; 49.44, 46.49, 45.32, and 43.55 for Cd(II) ; 44.00, 49.92, 45.11, and 41.40 for Ni(II), respectively. The data are plotted in Figure 1. It can be concluded that the optimum temperature was 400 °C and this temperature will be used for further experiment.

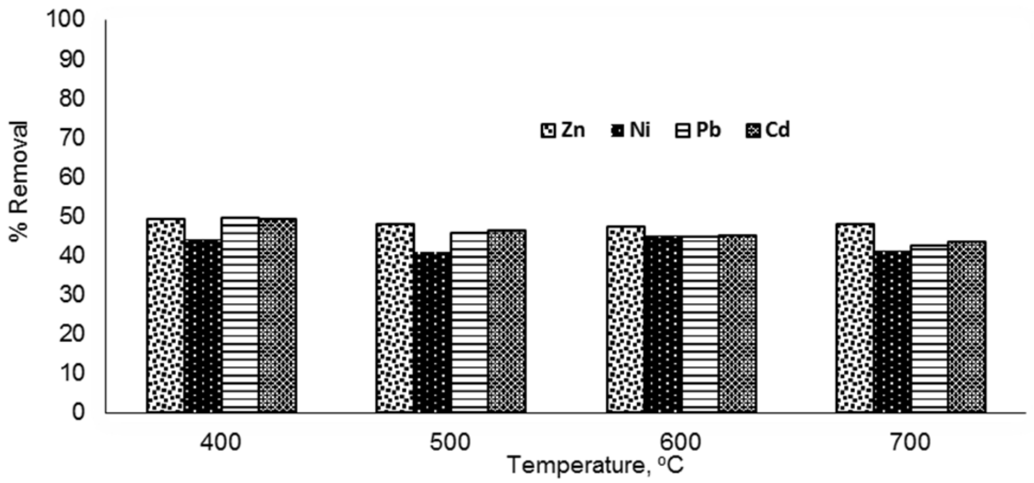

Figure 1: Effect of concentration of K_2CO_3 on removal capacity of Zn(II), Ni(II), Pb(II), and Cd(II) from solution.

3.2 Effect of K_2CO_3 and $ZnCl_2$ concentration on removal capacity

In this part, SSH was modified by soaking with various concentration of 0.4, 0.8 and 1.2 M K_2CO_3 and then heat at at 400°C or $ZnCl_2$ at 500°C in insufficient oxygen furnace; these are named 400°C-K_2CO_3 MSSH or 500°C- $ZnCl_2$MSSH. After that, the 400°C-K_2CO_3 MSSH or 500°C- $ZnCl_2$MSSH was used to remove Zn(II), Ni(II), and Pb(II) at pH 5 and Cd(II) at pH 6 from solution. From the experiment, with variation of 0.4, 0.8 and 1.2 M K_2CO_3 and heat at modification it was found that the removal percentages of are 71.12, 99.61, and 99.71 for Pb(II); 82.47, 98.48, and 98.75 for Zn(II); 82.51, 98.07, and 98.12 for Ni(II) and 75.92 92.99 and

92.40 for Cd(II) respectively. The data were shown that 400°C heated with 0.8 M K_2CO_3 [400°C-K_2CO_3 MSSH] was the optimal condition for modification. The experimental results were plotted in Figure 2. Effect of $ZnCl_2$ concentration with 500°C heated SSH modification [500°C- $ZnCl_2$ MSSH] was also monitored for metal ion removal. It was observed that with 0.4, 0.8 and 1.2 M $ZnCl_2$ the removal percentages were as follows: 29.66, 59.79, and 59.53 for Pb(II) ; 42.32, 50.05, and 50.33 for Zn(II); 20.29, 28.07, and 28.28 for Ni(II); and 32.96, 51.79, and 52.38 for Cd(II) respectively. From the data it can be concluded that he removal of metal ions by 0.8 M $ZnCl_2$ with 500°C heated one [500°C- $ZnCl_2$MSSH] was the optimal condition for modification. However, 400°C-K_2CO_3 MSSH showed higher removal percentage than that of 500°C- $ZnCl_2$MSSH.

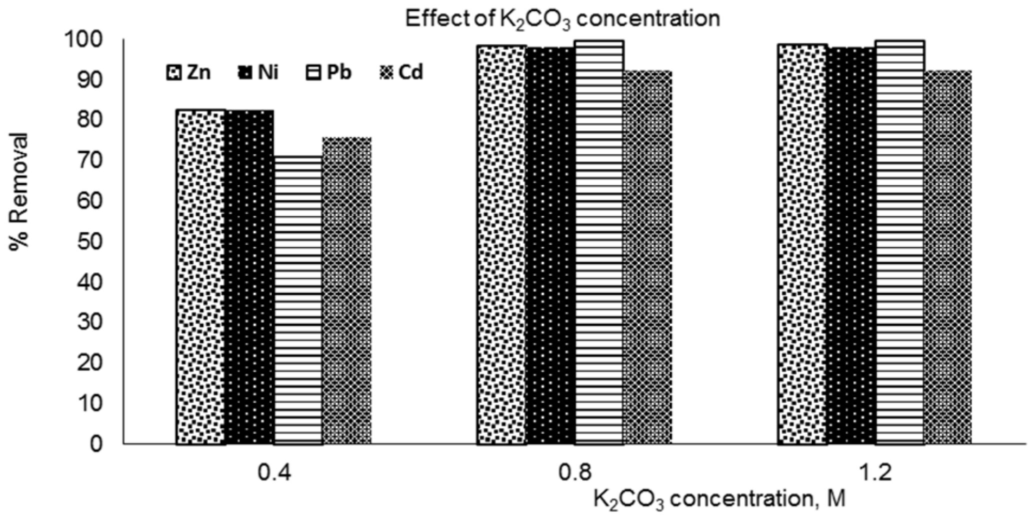

Figure 2: Effect of concentration of K_2CO_3 on removal capacity of Zn(II), Ni(II), Pb(II), and Cd(II) from solution.

3.3 Effect of heating temperature of K_2CO_3-MSSH and $ZnCl_2$-MSSH on removal capacity

Effect of heating temperature of K_2CO_3-MSSH and $ZnCl_2$-MSSH on removal capacity was studied by using K_2CO_3-MSSH and $ZnCl_2$-MSSH to a certain temperature: 400 °C, 500 °C, 600 °C, and 700 °C for metal ion removal. It was found that the removal percentage of Zn(II), Ni(II), and Pb(II) from solution by various heated K_2CO_3-MSSH at pH 5 and Cd(II) at pH 6 were 99.61, 93.22, 83.90, and 58.15 respectively for Pb(II); 95.99, 98.75, 98.62 and 78.20 respectively for Zn(II); 98.07, 95.48, 86.22, and 80.66 respectively for Ni (II); and 81.22, 92.99, 92.40, and 51.99 respectively for Cd(II). The experimental data are shown in Figure 3 and it can be concluded that the optimal temperature is 400 °C.

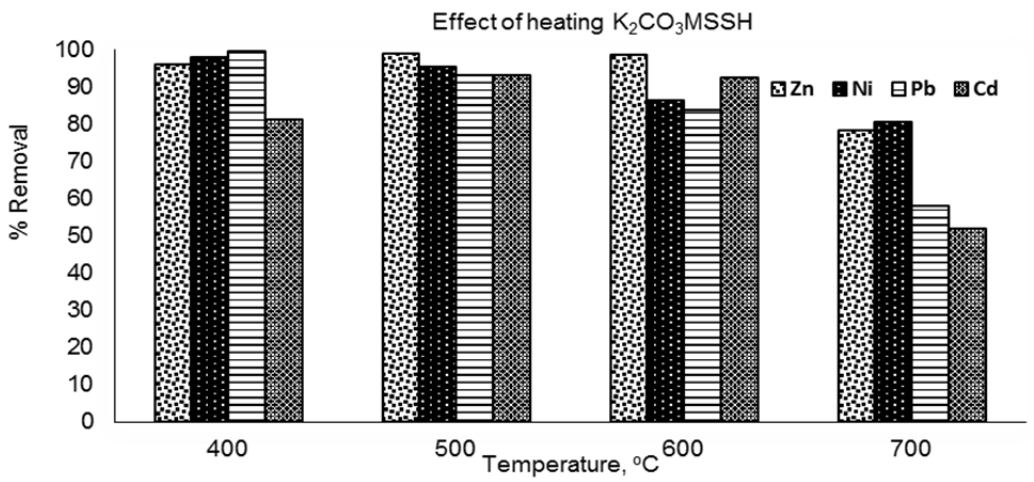

Figure 3: Effect of heating temperature of K_2CO_3-MSSH on removal capacity of Zn(II), Ni(II), Pb(II), and Cd(II) from solution.

The removal percentage of Zn(II), Ni(II), Cd(II), and Pb(II) from solution by various heated temperature for $ZnCl_2$-MSSH also was examined. It was observed that the removal percentage of Zn(II), Ni(II), and Pb(II) from solution by 400 °C, 500 °C, 600 °C, and 700 °C heated $ZnCl_2$-MSSH at pH 5 were 75.68, 59.79, 27.83, and 21.44 respectively for Pb(II); 43.04, 47.01, 46.74, and 50.33 respectively for Zn(II) ; 28.07, 26.59, 24.37, and 23.62 respectively for Ni(II); and 51.79, 37.08, 32.96, and 26.48 respectively at pH 6 for Cd(II). From our results, the optimal temperature is around 400-500°C. It can be seen that K_2CO_3-MSSH can remove the metal ions from solution higher percentage than that of $ZnCl_2$-MSSH. It can explain that soaking heated SSH in K_2CO_3 and can assist the penetration of K_2CO_3 with in the heated SSH matrix, which creates more porous structure by opening of previously closed pores and formation of new pores (Foo and Hameed, 2011).

3.4 Langmuir and Freundlich adsorption isotherm studies

Since the relationship between the amount of substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in equilibrium, adsorption isotherm, is very important in determining the adsorption capacity of metal ions onto the adsorbent (Madhava et al.,2009). Adsorption isotherm describes the interaction between adsorbate and adsorbent materials. The experimental results were fitted to the equations according to Langmuir adsorption model and Freundlich model as Eq(3) and Eq(4), respectively. And the experimental data and calculated values are in Table 1. As shown in Figure 4 and regression coefficient in Table1, the experimental data fitted to Langmuir's adsorption model with R^2 around 0.99 and also fitted to Freundlich's adsorption model with R^2 around 0.73 as shown in Figure 4 for Pb(II). It can be seen that the adsorption capacity of Pb(II), Ni(II), Zn(II), and Cd(II) are quite the same magnitude. However, the values of K_L for Pb(II), Ni(II), Zn(II), and Cd(II) adsorption are obvious different, the order of K_L are Cd(II) > Pb(II) > Zn(II) > Ni(II) respectively.

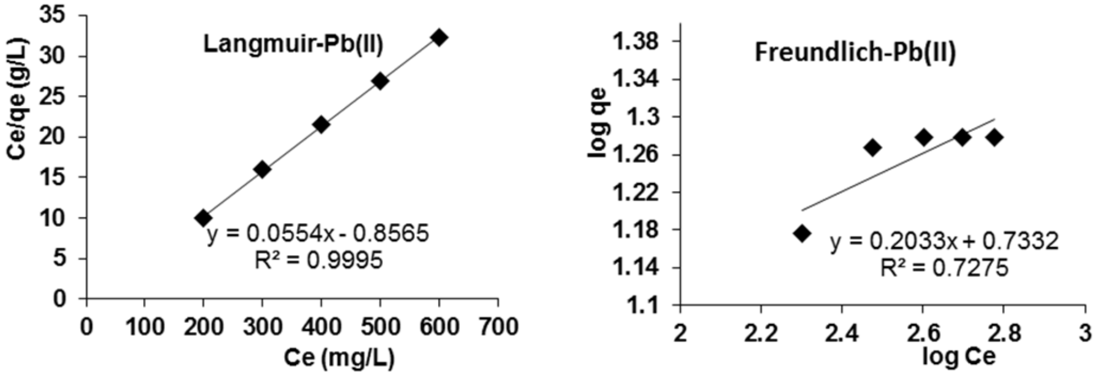

Figure 4: Adsorption plot of Pb(II) from solution at pH 5 according to Langmuir and Freundlich model

Table 1: Values of parameters calculated from adsorption model of metal ions by 400°C-K_2CO_3MSSH

Ions	Langmuir model					Freundlich model				
	Slope	Intercept	q_m (mg/g)	K_L (L/gm)	R^2	Slope	Intercept	n	K_F	R^2
Pb(II)	0.054	0.306	19.92	0.164	0.999	0.203	0.733	4.9	5.41	0.727
Zn(II)	0.054	0.306	18.60	0.158	0.998	0.203	0.733	8.0	8.79	0.777
Ni(II)	0.054	0.306	19.76	0.100	0.995	0.203	0.733	5.3	6.09	0.753
Cd(II)	0.054	0.306	19.62	0.192	0.997	0.203	0.733	5.5	6.27	0.815

From these results, it can be interpreted that the adsorption was monolayer adsorption and the maximum adsorption capacity (q_m) of those metal ions are almost same value, around 19 mg/g and Cd(II) has the highest value of K_L among these metal ions. These results agree to adsorption equilibrium of lead on SCG. Furthermore, 400°C-K_2CO_3MSSH has a higher lead removal capacity (19.92 mg/g) than that of SCG (2.46 mg/g) (Lavecchia et al., 2016).

4. Conclusions

The removal percentage of Zn(II), Ni(II), Cd(II), and Pb(II) from solution by modified SSH was investigated. The 400°C-K_2CO_3MSSH shows higher capability than that of 500 °C-SSH and 400°C-$ZnCl_2$ MSSH respectively. The percentage removal of Pb(II), Ni(II), and Zn(II) from solution at pH5 and that for Cd(II) at pH

6 by 400°C-K_2CO_3MSSH are 99.61, 98.07, 98.75, and 92.99 respectively, and followed by 500°C-SSH and then 400°C-$ZnCl_2$MSSH with the lowest capacity. The adsorption isotherm were better described by Langmuir isotherm model in comparison to Freundlich model. The maximum adsorption capacity, q_m , for Pb(II), Zn(II), Cd(II), and Ni(II) were 19.92, 18.56, 19.76, and 19.62 mg/g with K_L of 0.1640, 0.1585, 0.1005, and 0.1918 L/g respectively. Therefore, sunflower seed husk modified by soaking with K_2CO_3 and heated at 400 °C has the properties for adsorbent.
Thus these studies show that sunflower seed husks, the disposed solid waste, can be effectively used as an alternative for commercial activated carbons for the removal of heavy metal ions from water and wastewater.

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