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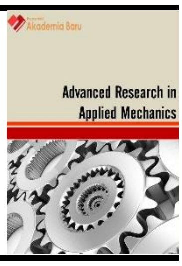

Application of Palm Kernel Shell as Bio Adsorbent for the Treatment of Heavy Metal Contaminated Water

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ABSTRACT

Contamination of heavy metal in water results are affecting on human health and living creatures. In this study, palm oil kernel shell (PKS) is applied as bio-adsorbent for the treatment of heavy metal contaminated water. Heavy metals namely; Cr6+, Pb2+, Cd2+ and Zn2+ were removed through bio-adsorption on PKS. Parameters of adsorptions namely pH of solution, adsorbent dosage, concentration of metal ions and contact time were optimized. The PKS was able to effectively remove Cr6+, Pb2+, Cd2+ and Zn2+ ions from water with percentage removal of 98.92%, 99.01%, 84.23% and 83.45%, respectively. The Freundlich and Langmuir isotherms models were applied for the adsorption interaction between metal ions and PKS. PKS was found to be very effectively bio-adsorbed for the removal of heavy metal contaminated water within two hours. This is greener approach for the treatment of heavy metal ions contaminated water.

Keywords:
Bio-adsorbent, palm kernel shell, Heavy metals, water treatment

1. Introduction

Industrialization has made our lives comfortable but at the same time it has immensely contributed to the environmental pollution such as air, water and soil pollutions. Air and water pollutions directly affects the living things as soil pollution ultimately causes food poisoning [12, 16, 18]. Life is impossible to sustain in the absence of water and water pollution is major issue to be addressed. There can various pollutants in water namely organic compounds, dyes, microbes and toxic heavy metals e.g. Cr^{6+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, As^{3+} and Hg^{2+} etc. All other contaminants can be degraded in one way or another, but toxic heavy metals are non-degradable. These heavy metals can cause skins diseases, brain damage, kidney failure, liver damage anaemia, ulcers and are also carcinogenic [15,17,19]. Millions of lives are at risk of these diseases because of water contamination. Heavy metals come in water from various sources e.g. batteries, fertilizers, pesticides, pharmaceuticals, papers and pulp industries etc. [1,17,18]. Pollution in water is shrinking the sources of drinking water [1,2]. There is urgent need to design and develop method capable of effectively remove the heavy metals from water. In this study we have utilized PKS as an effective bio-adsorbent for the treatment of heavy metal contaminated water.

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2. Literature Review

Variety of protocols are widely applied for the treatment of heavy metal contaminated water such as reverse osmosis, colorimetric, ion exchange, evaporation, precipitation, membrane and coagulation [3,6,18]. These techniques are not cost effective, require a lot of energy and are only capable of removing low concentration of metal ions. Every year millions-tons of agriculture waste is generated throughout the world. They are disposed by burning causing an environmental issue. The utilization of agriculture waste in treatment of contaminated water is novel and effective technique.

Agricultural waste is composed organic compounds containing variety of functional groups namely hydroxyl, carbonyl, amines, and carboxyl groups etc [5,10,12,14]. These functionals groups confer on the excellent adsorption properties to agricultural waste making them ideal material to be applied for the bio-adsorbents of impurities from water especially heavy metal ions. Variety of agricultural waste materials have been widely applied for the treatment of heavy metal contaminated water i.e. rice husk, corn algae, cob, olive oil by products, livestock waste, egg shell, activated carbon, rice husk, sawdust, forest by-products and waste etc [1,8,9].

3. Materials and methods

Palm kernel shells (PKS) were collected from Seri Ulu Langat Palm Oil Mill, Dengkil, Selangor Malaysia. The metal ions Cr^{6+}, Cd^{2+}, Pb^{2+} and Zn^{2+} solutions standards of 1000 mg/L, NaOH, HCl were purchased from sigma Aldrich (St. Louis, MO, USA). The deionized water (18.2MΩ/cm^{-1}) was used during all experiments.

3.1 PKS adsorbent preparation

PKS were cleaned tape water followed by washing with deionized water. PKS were then dried in an oven for 48 hours at 70 $^{\circ}$C. After that PKS fine powder formed by applying stable arm grinder and the fine powder was selected for the adsorption studies.

3.2 Experimental set up for batch studies

For the adsorption batch studies, different standard solutions (5ppm, 10ppm, 15ppm, 20ppm and 25ppm) of metal ions; Cr^{6+}, Pb^{2+}, Cd^{2+} and Zn^{2+} were prepared and kept in a refrigerator to maintain the volume and concentration. The adsorption experiments were carried out in flasks 250 mL containing 100 mL metal ions solutions of various concentrations, dosages of PKS powder, pH and contact time. Samples were shaken at previously optimized rate i.e. 200 rpm using a thermostat incubator at room temperature for two hours [1].

3.3 Characterization

Functional group analysis was carried out using a Fourier transformed infrared (FTIR) spectrometer, Perkin-Elmer 100 series (Waltham, MA, USA). Surface morphology was determined using a Field emission scanning electron microscope (FESEM) JOEL JSM-6400 (Tokyo, Japan). Metal elemental analysis was done using the inductively coupled plasma (ICP), Optical Emission Spectrometer, Optima 2100 DV Perkin Elmer.

4. Results and Discussion
4.1 FTIR Analysis

Figure 1 shows the infrared spectra of the samples PKS and after its treatment with PKS-Pb^{2+}, PKS-Cd^{2+}, PKS-Zn^{2+} and PKS-Cr^{6+}. FTIR showed OH group bands in PKS at 3338 cm^{-1} and a change in the position of this band has been observed after the treatment with metal ions. The OH band positions were shifted to 3313 cm^{-1}, 3324 cm^{-1}, 3325 cm^{-1} and 3319 cm^{-1} after the adsorption of metal ions; PKS-Cr^{6+}, PKS-Cd^{2+}, PKS-Pb^{2+} and PKS-Zn^{2+}, respectively. The PKS after the treatment with metal ions, new twin bands for Cr^{6+} at 2328 cm^{-1} and 2279 cm^{-1}, for at Cd^{2+} 2320 cm^{-1} and 2284 cm^{-1}, for Pb^{2+} at 2316 cm^{-1} and 2287 cm^{-1} and for at Zn^{2+} 2320 cm^{-1} and

2292 cm^{-1}. For PKS alone, these infrared bands are absent, as these new bands appears due the adsorption of metal ions on the carbonyl groups [1,11]. Before the treatment with metal ions PKS showed the carbonyl band at 1701 cm^{-1} this band has been shifted to higher wavenumber of 1717 cm^{-1}, 1718 cm^{-1}, 1716 cm^{-1} and 1710 cm^{-1} after the adsorption of Cr^{6+}, Cd^{2+}, Pb^{2+} and Zn^{2+} ions, respectively. Rest of the changes can also be observed in the Figure 1. The shits in the position of infrared bands can ascribed the adsorption of heavy metal ions.

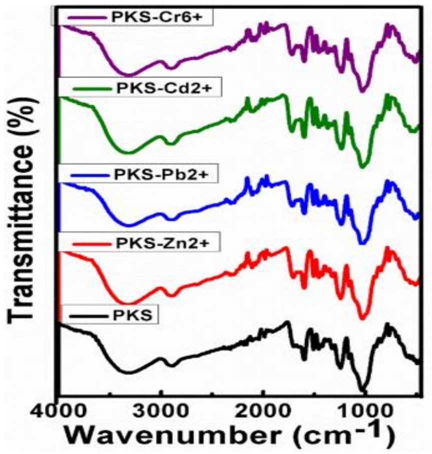

Fig. 1. FTIR Spectra of PKS Before and After The Treatment With Cr^{6+} (PKS-Cr^{6+}), Zn^{2+} (PKS-Zn^{2+}), Cd^{2+} (PKS- Cd^{2+}) And Pb^{2+} (PKS- Pb^{2+})

4.2 FESEM Analysis

Figure 2 shows the FESEM micrographs of PKS before and after the treatment with heavy metal contaminated water. Morphology of PKS before the bio-adsorption process looks like rough with layers stacking on top of one another as described in the literature [13]. Bio-adsorption of heavy metal ions e.g. Cr^{6+}, Zn^{2+}, Cd^{2+} and Pb^{2+} resulted in the change in morphology of PKS slightly having smoother surface as shown in the Figure 2.

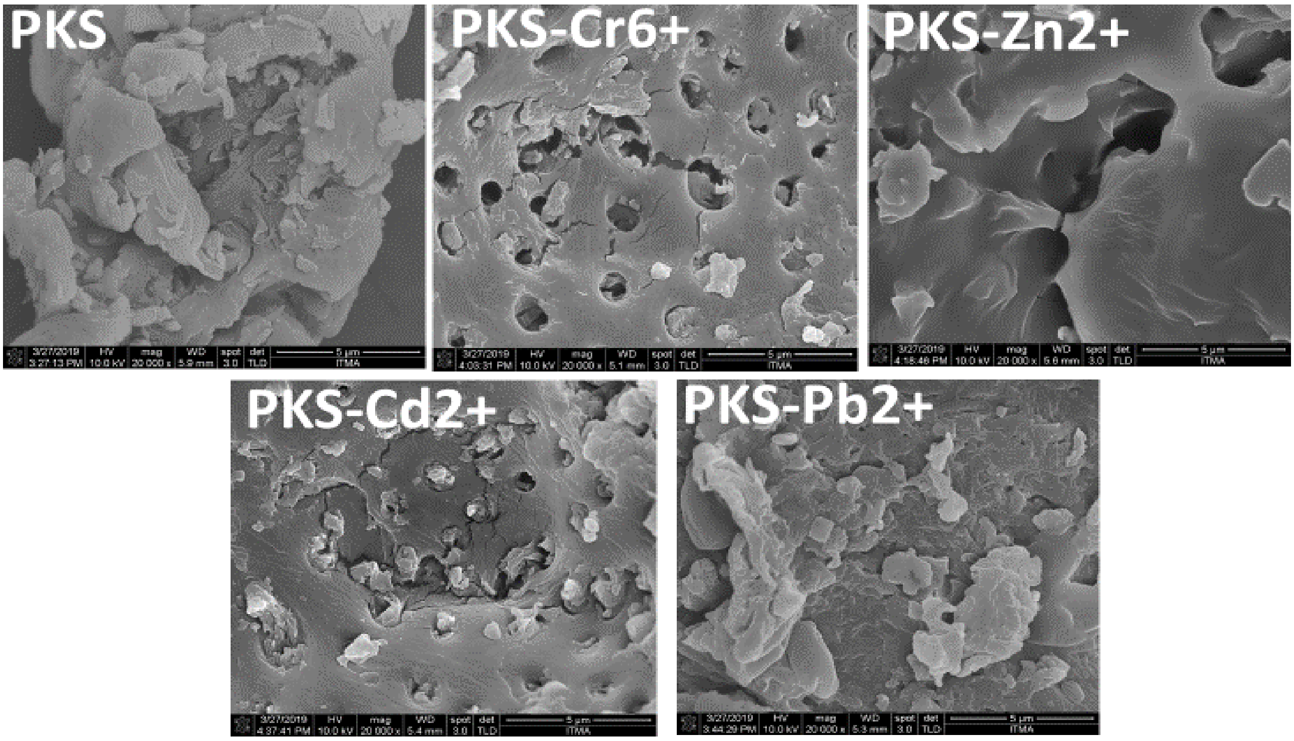

Fig. 2. FESEM Micrographs of PKS Before and After the Adsorption Process With Cr^{6+} (PKS-Cr^{6+}), Zn^{2+} (PKS-Zn^{2+}), Cd (PKS-Cd^{2+}) and Pb^{2+} (PKS-Pb^{2+})

4.3 Effect of pH on the Bio-adsorption of Heavy Metal Ions

The interactions of metal ions and bio-adsorbent rely upon the pH of [22, 23]. In order to optimized the pH conditions for the maximum adsorption different pH were applied e.g. the pH e.g. pH 3, pH 4, pH 5, pH6, pH7, pH8 and pH9 of each of the metal ions; Cr^{6+}, Pb^{2+}, Cd^{2+} and Zn^{2+}. The maximum adsorption was observed in basic pH i.e. above pH7 as shown in Figure 3. But under basic conditions precipitation of metal ions as their respective hydroxide may effect adsorption process, that is why maximum adsorption under acidic environment e.g. < pH 7 [24-26]. The Pb^{2+} ions showed the maximum adsorption of 95 % at pH 4 and the remaining three metal ions Cr^{6+}, Cd^{2+} and Zn^{2+} showed maximum adsorption at pH 6 e.g. 90.20 %, 75.50 % and 67.30 %, respectively. For the remaining batch experiments, pH 4 for Pb^{2+} ions and pH 6 were selected. Figure 3 Shows the Effect of pH on the adsorption process of these metal ions.

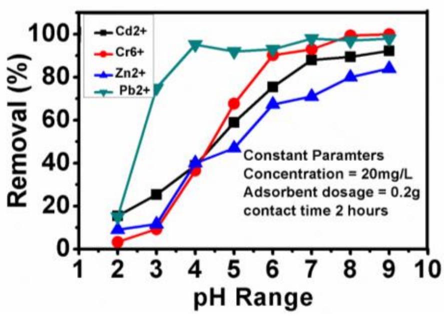

Fig. 3. Effect of pH on the bio-adsorption of heavy metal ions

4.4 Effect of PKS Dosage on the Bio-adsorption of heavy metal ions

Different dosages of PKS powder e.g. 0.25g, 0.50g, 1 g, 1.50g and 2g in 100 mL in 20 ppm metal ions solution were used to determine the minimum possible dosage for the bio-adsorption of heavy metal ions. These experiments were carried out at optimized pH conditions for determined in previous experiment. Figure 3 shows the effect dosage on the bio-adsorption heavy metal ions. It can be observed that the bio-adsorption was increased by increasing the dosage. The maximum adsorption was achieved at the dosage of 1.5-2g Figure 4 shows the effect of PKS dosage on the bio-adsorption of heavy metal ions.

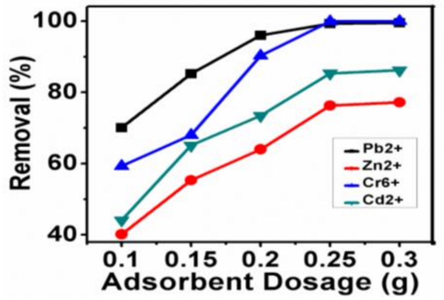

Fig. 4. Effect of PKS Dosage on the Bio-adsorption of heavy metal ions

4.5 Effect of metal ions concentration Bio-adsorption Process

Figure 5 shows the relation between bio-adsorption process and the initial concentration of heavy metal ions. To determine this relation different initial concentrations were used keeping the other optimized parameters constant. Initial metal ions concentrations of 5ppm, 10pm, 15ppm, 20ppm and 25ppm were used. For Cr^{6+} and Pb^{2+} adsorption trends are almost a straight line with percentage removal of 97.5 % and 90.4 %, respectively at the highest initial concentration of 25 ppm. But for Chromium optimum adsorption was found to be a 20ppm with 98.53 % and was decreased to 90.44 % (25 ppm initial concentration). The bio-adsorption of Cd^{2+} and Zn^{2+} ions was decreased with the increase concentration, but the overall adsorption for Cd^{2+} and Zn^{2+} was found to be 82.71 % and 60.17 %, respectively at 25 ppm. Adsorption of Zn^{2+} at 20 ppm initial concentration was 75.07 % which is still very high removal percentage. The overall adsorption efficiency decreases with the increase in the initial concentration metal ions, as the adsorption sites in PKS get saturated [27, 28]. The maximum adsorption was observed at 20mg/L and at 25mg/L the overall percentage of adsorption decreases. As the metal ions concentration increases, the adsorption decreases due to the saturation of sites for chelation or adsorption.

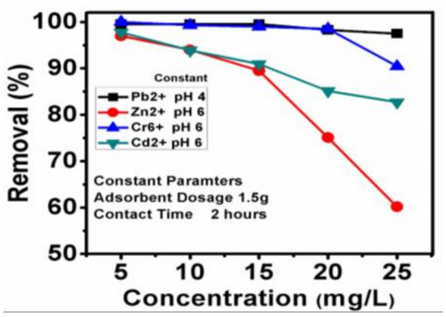

Fig. 5. Effect of metal ions concentration Bio-adsorption Process

4.6 Effect of Contact Time on Bio-adsorption of heavy Metal ions

Contact period of adsorbate and adsorbent plays key role in the bio-adsorption process [9, 29]. Batch experiments contact time e.g. 15 minutes, 30 minutes, 60 minutes, 90 minutes and 120 minutes were carried out for each metal ion and keep the all other optimized parameter constant. Figure 6 shows the effect of contact time on the adsorption of Pb^{2+}, Cr^{6+}, Cd^{2+} and Zn^{2+} on the PKS adsorbent. It can be seen in the Figure 6, that Cr^{6+} and Pb $^{2+}$ions took 60 minutes to reach the equilibrium with bio-adsorption of about 98 %. Cadmium and zinc ions took 90 minutes and 120 minutes to acquire equilibrium with maximum adsorption of about 84% and 83%, respectively.

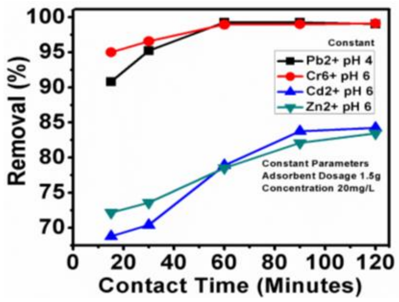

Fig. 6. Effect of Contact Time on Bio-adsorption of heavy Metal ions

5. Conclusion

In this study we have developed greener method for the treatment of heavy metal ions contaminated water by the application of agricultural waste of Kernel shell of oil Palm trees of Malaysia. Hazardous heavy metal ions namely Cr^{6+}, Pb^{2+}, Cd^{2+} and Zn^{2+} were removed by the bio-adsorption. All the parameters which can affect the bio-adsorption were optimized namely pH, metal ions concentration, adsorbent dosage and contact time. It was found that under the optimized environment about 99 % of Cr^{6+} and Pb $^{2+}$ ions and more than 83 % of Cd^{2+} and Zn^{2+} ions were bio-adsorbed by the PKS adsorbent. The process took shorter time of 1-2 hours for the complete purification of water. In this study PKS was applied as bio-adsorbent without any pre-treatment with acid/base instead it was just washed with water. The PKS bio-adsorbent is an economical, eco-friendly, renewable, and freely available in huge quantity and is produced every year in thousands of tons from oil palm plantation. This study is greener approach for the treatment of heavy metal ions contaminated water.

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