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Biosorption of Removal Heavy Metal using Hybrid Chitosan-Pandan

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ABSTRACT

The adsorption performance on Chromium(VI) ions from aqueous solution by hybrid chitosan- pandan (ChiPandan) was investigated. The effect of contact time, temperature, pH solution and biosorbent dosage has been studied. ChiPandan gave optimal adsorption performance when operated at 0.1g of adsorbent with pH of 6 at ambient temperature for 60 minutes of contact time. Whereas, raw Pandan was found to give a better performance at 2.0g of adsorbent, pH of 5, 60˚C and 90 minutes of contact time. Raw Chitosan needed 1.0g of adsorbent, pH 5, 70˚C with 120 minutes of reaction time for a maximum Chromium(VI) ions removal performance. From these result, it can concluded that ChiPandan could be a good adsorbent for the Chromium(VI) ions removal from aqueous solution.

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INTRODUCTION

The pollution of heavy metal is becoming a serious environmental issue. Due to economic change, the rapid development industries had caused tremendous increased disposal heavy metals into the environment. This heavy metal will associate with several of problematic health to human kind. The permitted limit amount intake chromium in drinking water, according to the EPA is 0.1mg/L or 10 ppm which is considered safe.

The chromium can change its oxidation number in water or in the human body, depending on environmental conditions. The source of chromium may come from human activities or even natural source. Through human activities, the chromium emitted from electroplating, leather tanning and metal-finishing plant industries. The source of chromium also can find from naturally in rocks, plants, soil and volcanic dust, humans and animal faeces.

The wastewater that consist chromium compound will go to landfill or surface water, which will distort ecosystem and environment. Therefore is it essential to do the treatment of wastewater from chromium before it is released into the environment. Otherwise, this will give a severe toxicity to human being and aquatic biota.

Chitosan is bio-polymer that comes from treating shrimp and other crustacean shells with the alkali sodium hydroxide. It has many natural characteristics such as highly hydrophilic, excellent chemical-resistance properties, biodegradable, low cost and easily available which in recognition as effective biosorbent. It is known as good absorbent due to presence of reactive hydroxyl and an amino group. These groups act as active site on the surface of sorbet, which is used to bond with heavy metal ions.

The drawback of Chitosan is it has low adsorption heavy metals capacities to be used in large scales. There scientist had brought a lot of researches about modification of Chitosan using various compounds and methods for improvement adsorbent in term of chemical and mechanical. But the problem is there are still lacking in term cost, energy and eco-environment.

Therefore, with hybridization of Chitosan and Pandan compounds will give a new alternative bio-sorbent that helps to enhance the bio-sorption process.

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Experimental:
Materials:

Fresh Pandan, conventional Chitosan, pure ethanol (99.9%), 0.1M sodium hydroxide (NaOH) solutions, 0.1M hydrochloric acid (HCl) solution, distilled water and Potassium Dichromate powder to obtain Cr6+ ion solution.

Method:
Extraction of Pandan Leaves:

The Pandan leaves were treated prior to extraction process. First, approximately 200g of Pandan leaves were cleaned, cut into small pieces and immediately dried in an oven at 45oC for 48 hours. Lastly, the Pandan leaves were grounded using a grinder into 150 micron. Etahanol was used as solvent to carried out the solvent extraction. 5g of Pandan Leaves were soaked with 100mL pure ethanol for 24 hours as a stock solution.

Hybrid of Chitosan and Pandan:

Hybrid of Chitosan and Pandan sorbent was prepared via wet impregnation method. 0.1g of Chitosan was dissolved in 50mL of extract Pandan leave for 24 hours at room temperature. Then, the solution was filtered by using a filter paper. The solid residue obtained was dried naturally at room temperature for 48 hours. The dried sample obtained was referred as ChiPandan sorbent.

Heavy Metal Solution Preparation:

The heavy metal ions that tested in this study are Cr6+ and the initial concentration of Cr6+ was set at 1ppm of stock solution. The Cr6+ ion solution was prepared by diluting approximate 0.01g of Potassium Dichromate powder with 1 litre of distilled water. The analytical grade of HCl and NaOH solutions were used for pH adjustment.

Adsorption Study:
Reaction Time:

The initial experiment was carried out by setting the ChiPandan dosage, solution pH, initial concentration of chromium ions and solution temperature at 0.1g, pH 7, 1ppm and room temperature, respectively. The 0.1g of ChiPandan was added into a 15 mL aqueous solution that contained 1 ppm of chromium ions. The mixture was stirred and the sample was collected for 30 minutes. The collected sample was determined it removal of chromium ions in aqueous solution after bio sorption process using COD and Multiparameter Photometer. The reaction was stop after the removal of chromium reaches equilibrium. The percentage removal of chromium was calculated.

Temperature:

Different temperature was used for temperature 30, 40, 50, 60 and 70℃. Then, the solution was analyzed for the percentage removal of chromium ions. The temperature with the highest percentage of chromium ion removal was selected as the best temperature and used for the next experiment.

pH:

Different pH solution was used for pH 5, 6, 7, 8 and 9. Then, the solution was analyzed for the removal percentage of chromium ions. The pH with highest percentage removal was determined as the optimal pH for the next experiment.

Dosage Biosorbent:

Different dosage was used for 0.1g, 1.0g and 2.0g. Then, the solution was analyzed for the removal percentage of chromium ions. The dosage with highest percentage removal chromium ions was determined as the optimal dosage biosorbent. The steps were repeated using raw Chitosan and raw Pandan.

RESULTS AND DISCUSSION

Characterization by FTIR analysis:

The FTIR spectroscopic analysis of Chitosan, Pandan and ChiPandan is shown in Figure 1.

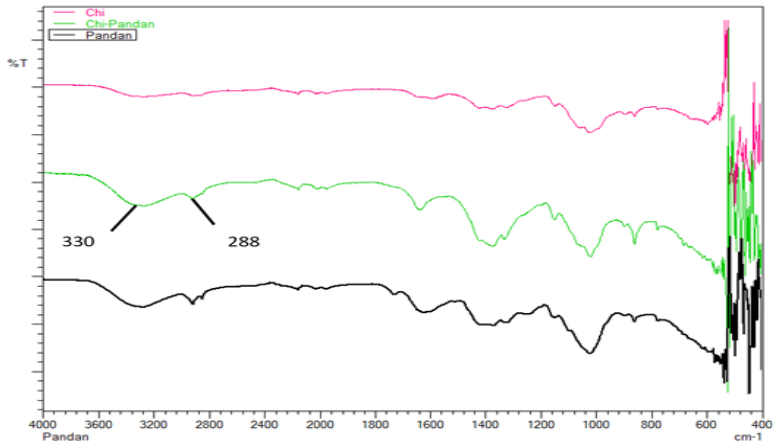

Fig. 1: IR Spectrum of ChiPandan, Chitosan and Pandan

Different stretching vibration bands were observed, 3300cm^{-1} related to N-H group in amine and 3200-3400cm^{-1} were assigned to presence of N-H group and O-H group. It is shows that all the absorbents had the presence of N-H group and O-H group. However, the ChiPandan has the highest peak compared to Pandan and Chitosan. Meanwhile, for band at 3000 cm^{-1} the broad of acid O-H group was presence because of stronger hydrogen bonding between acid molecules. Besides, the peak at 2923 cm^{-1} was shown due to aromatic C-H stretching vibrations. The sharp peak at 1614 and 1477 cm-1 may be due to C=C or N-C stretching. Therefore, the presence of O-H and N-H groups is important for adsoption process because these groups used to interact with chromium ions.

Effect of Reaction Time:

The effect of contact time on the adsorption of chromium ions by ChiPandan, Pandan and Chitosan is shown in Figure 2.

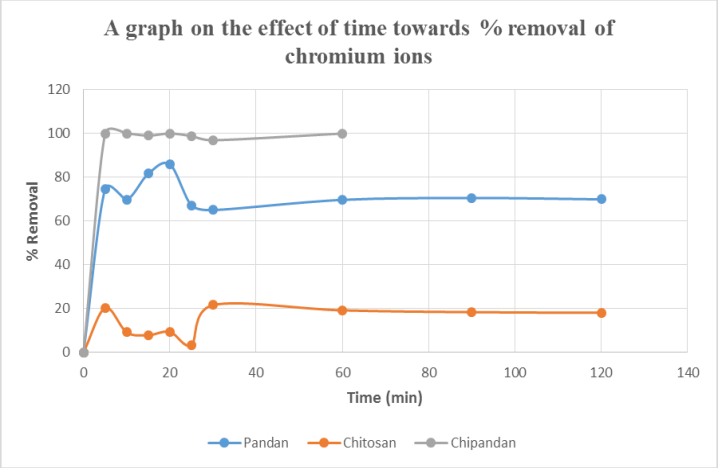

Fig. 2: The effect of contact time towards % removal of chromium ions

As can be seen, ChiPandan gave a better adsorption performance towards chromium ions removal compared to Pandan and Chitosan. Based on the result obtained, ChiPandan Pandan and Chitosan showed that the adsorption of chromium ions was fluctuate at the early minutes because of fast adsorption of chromium ions due to the presence of numerous active site on the adsorbent surface [1] but gradually slow down until it reached the equilibrium at time of 60 minutes (100%), 90 minutes (71%) and 120 minutes (18%) respectively. Thus, these equilibrium time obtained were used for further studied for biosorption process.

The ChiPandan required a shorter time to achieve a higher chromium ions removal because of the largest binding site since it adsorbed 100% of chromium ions. This binding site was required for interaction within anions and cations, which helped to improve the binding capacity of an adsorbent and adsorption proceeds rapidly [2]. From the result, a time of 60 minutes is sufficient enough to obtain optimum chromium ions

removal percentage. Therefore, 60 minutes was considered to be the equilibrium time for further studied of biosorption.

Effect of Temperature:

The effect of temperature on the adsorption of chromium ions process has been investigated over the range from ambient temperature to 90˚C, and the result are shown in Figure 3.

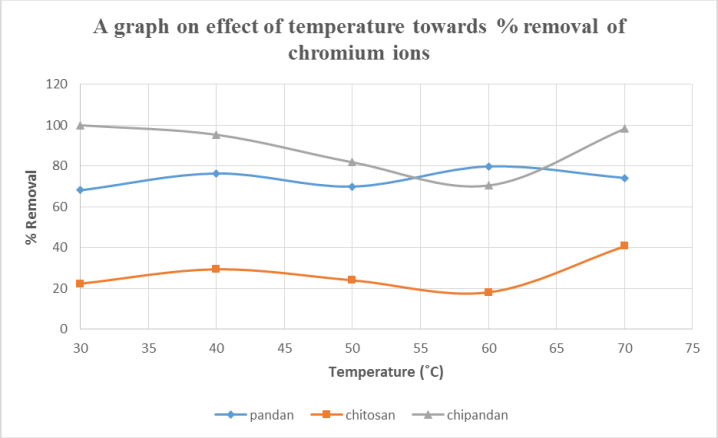

Fig. 3: The effect of temperature towards % removal of chromium ions

Based on the result obtained, it can be seen that at ambient temperature, the ChiPandan adsorbent shown 100% removal of chromium ions, while for Pandan, the highest adsorption is at 60˚C where the percentage removal obtained was up to 80%. However, for Chitosan, it needed higher temperature, which is 70˚C in order to give the highest adsorption performance, (41%). Theoretically, temperature had influence on adsorption behavior where when the temperature is increased the adsorption capacity also increased. According to [3], this might due to the generation of new active site on the surface of the absorbent and also due to the increased rate of pore diffusion of the absorbent which leads to the endothermic adsorption. Thus, as shown in the figure above, there was very little increase in adsorption efficiency with rise in temperature.

For ChiPandan adsorbent, it is less likely effected by higher temperature due to its energy- independent behavior [4] since it can adsorbed 100% chromium ions at temperature 30˚C. However, for Pandan and Chitosan, it required higher temperature to achieve higher adsorption of chromium ions. This indicates that the adsorption reaction is endothermic due to chemical interaction within chromium ions and adsorbents. As the temperature increased, the rate of intraparticle diffusion of chromium ions into the pores of adsorbents increased [5].

Effect of pH Solution:

Biosorption of chromium ions from waste water by using ChiPandan, Pandan and Chitosan was studied at pH 5 to 9. Figure 4 shows the percentage removal of chromium ions against different pH in solution.

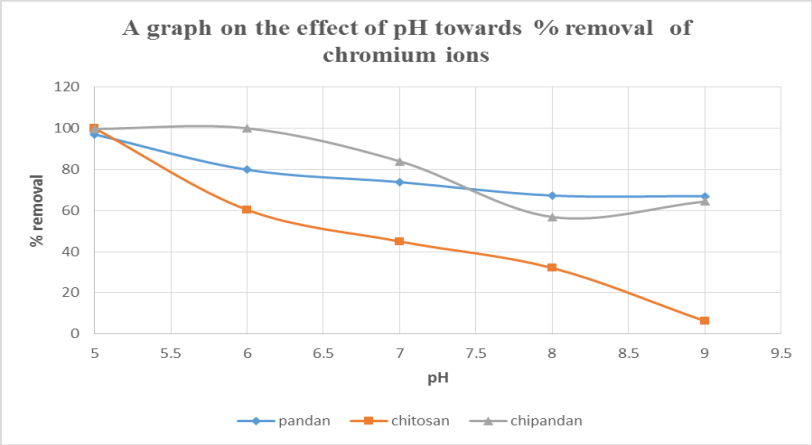

Fig. 4: The effect of pH solution towards % removal of chromium ions

The pH value plays an important role in ability of adsorption process. At pH 5, it can be seen that for Pandan and Chitosan, it had achieved a maximum adsorption rate of chromium ions at 97% and 100% respectively. Meanwhile, for ChiPandan, the maximum adsorption rate of chromium ions was achieved 100% removal at pH 6. Thus, this indicates that the highest adsorption of chromium ion occurred at acidic condition.

However, when the pH value increasing (pH> 6), the rate of adsorption chromium ion gradually decreased. According to [6], in acidic condition the protonated amino group (NH^{3+}) in the adsorbents and anions of chromium ($Cr_2O_7^{-2}$) OR (CrO_4^{-2}) (or are bonded by electrostatic interactions and hydrogen bonding between the two. So, it can conclude that the adsorbents in acidic solution present a higher adsorption efficiency and larger adsorption capacity. The experimental result indicates that the most suitable pH value for chromium adsorption is in the range from 5 to 6.

Effect of Dosage:

Figure 5 shows the removal of Cr(VI) by different dosages of adsorbent (0.1g, 1.0g and 2.0g) at 1ppm of Cr(VI) solution.

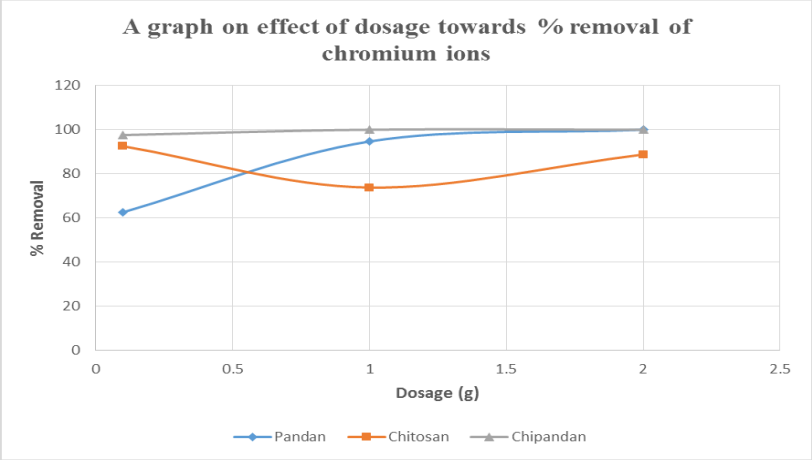

Fig. 5: The effect of dosage biosobent towards % removal of chromium ions

From the figure, it observed that the percentage of Cr(VI) removal increased from 97% to 100% with an increase in adsorbent mass from 0.1g to 2.0g of ChiPandan. The percentage removal increased with the ChiPandan adsorbent dosage up to certain limit and then it reached a constant value. Whereas for Pandan, the adsorption of Cr(VI) increased as the dosage of Pandan increased. However, for Chitosan, it can be seen that the adsorption performance of chromium ion decreased from 92.5% to 73.75% with dosage of 0.1g to 1.0g but finally it increased at Chitosan dosage of 2.0g with 88.75% of chromium removal.

Basically, the increasing in adsorption of Cr(VI) with different adsorbent dosage can be influent by increased surface area and the availability of more adsorption sites for chromium ion. [1]

Conclusion:

ChiPandan, raw Pandan and Chitosan were used as biosorbents for removal of chromium ions. In biosorption of chromium ions, the effect of contact time, reaction temperature, pH and biosorbent dosage were carried out. From FTIR results, it shows that ChiPandan, raw Pandan and Chitosan have the presence of N-H and O-H groups which interacted with chromium ions. Based on the result obtained, ChiPandan shows a good adsorption performance compared to Pandan and Chitosan. 60 minutes, 90 minutes and 120 minutes were considered to be the equilibrium time for ChiPandan, Pandan and Chitosan respectively. In temperature parameter, ChiPandan showed the 100% removal of chromium ions adsorption at ambient temperature. Meanwhile, Pandan needed temperature of 60˚C to give 80% removal of chromium ions and Chitosan gave 41% removal of chromium ions at temperature of 70 ˚C. All the adsorbents showed the maximum removal of chromium ions at acidic condition; ChiPandan at pH of 6 with the 100% removal of chroimum ions, while for Pandan and Chitosan at pH of 5 by 97% and 100% removal of chromium ions respectively. ChiPandan give a better adsorption at 0.1g adsorbent where for Pandan and Chitosan, it needed larger dosage to obtain a better performance in adsorption of chromium ion. Pandan needed 2.0g of adsorbent to give 100% removal of chromium ions while for Chitosan, it required 0.1g of adsorbent to remove 97% of chromium ions. Thus, it concluded that ChiPandan has been successfully used as a new renewable biosorbent for the removal of chromium ions from heavy metal waste water.

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