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CHARACTERIZATION AND OPTIMIZATION OF HEAVY METALS BIOSORPTION BY FISH SCALES

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ABSTRACT

Heavy metals are highly toxic and cumulative poison. Once in the environment, it is difficult to recover and can adversely affect human health. The tremendous increse in the use of heavy metals over the past few decades has inevitably increased the metallic contents in the aquatic life. Heavy metals ions are of great concern, due to their mobility in natural water ecosystems and due to their toxicity.Removal of nickel from aqueous solution using tilapia fish scale as biosorbent was studied. This study was focused on the evalution of the impact of amount of biosorbent, pH and contact time on nickel ions removal from aqueous solution using tilapia fish scale as biosorbent. The optimum percentage removal value was found as 71.25% with the amount of 2g tilapia fish scale biosorbent. Optimum percentage uptake was found to occur at alkaline equilibrium reached after four hours contact time with 70% and 1.4 mg/g respectively.The finding indicated that promising biosorption of nickel using tilapia fish scale as biosorbent.

***Keywords**: Biosorbent, fish scale, nickel*

INTRODUCTION

The uses of water in lakes, river and streams are greatly depand on the quality of the water. Water of high quality is important which is needed for potable water supplies and also for biological community living in these water bodies. Nowadays, human activities use a lot of the water sources. The activities included industries that the effluent contain varies of pollutant which caused a serious degrading on water quality. Most of pollutants deposited by industrial waste are toxic metal and toxic organic chemical. Many industries such as metallurgical, galvanizing, metal finishing, electroplating and electronic device manufacturing produce large quantities of wastewater containing metals [1].

Industrial effluent must be treated prior to the level stipulated by regulation prior to being discharged to the receiving environment. Due to the stringent regulations, there is an increased in demand for new technologies for metal removal from industrial wastewater. This has resulted in an inflow of foreign technologies into Malaysia. Most of the treatment methods are chemical and physical treatment. Chemical treatment for heavy metal removal in industrial wastewater is often limited by costly operation and also less efficiency at low metal concentration. This removal method is expensive because the installation of new infrastructures and are not environmentally friendly since the process increase the volume of chemical sludge due to the additional chemicals during the treatment [2]. Physical treatment such as sedimentation and filtration, although it is more cost effective and low energy consumption, some small and micro particles called colloid and bacteria still can pass through which still makes it unsuitable for drinking. As for biological treatment, it has more advantages than the other two methods. Therefore, technology utilizing locally available biomaterial must be developed.

Biosorption is one of the biological treatment alternatives for the removal of toxic metal from industrial wastewaters. This technology has more advantages compared to chemical and physical methods, as it is nonpolluting, easy to operate and gives a high efficiency of wastewater treatment. Biosorption process use inexpensive biomass as sorbent where certain living or dead biomass has the ability to bind with metals and also having a good absorption properties. The biosorption process involves a solid phase which is the sorbent and liquid phase which is normally water containing material to be sorbed such as the metal ion. Many kinds of biomass have been investigated as sorbents for the removal of metals from waters. From recent study, algae, bacteria and agricultural wastes show that they have the ability to remove large amounts of toxic metals [3].

There are wide ranges of biomass available to be used as biosorbent ranging from natural to waste product. Among natural product that had been used as biosorbent are sunflower stem [4] and black leave tea as a sorbent for chromium ions adsorption [5]. Waste product such as egg shell also shows a relatively high sorption of chromium ions. There are other previous research on biosorption that use cynobacteria a kind of bacteria which gets its energy from photosynthesis [6] and wool as sorbent [7]. Recently, the interest in sorbent selection has moved to more low cost of waste product, available in abundance and inexpensive. Fish scale waste from wet

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market has shown high potential to be used as biosorbent. However research in Malaysia has not focus significantly in this area. In the present work three objectives have been highlighted namely, to study the effect of biosorbent amount, contact time and pH in removal of nickel using biosorption process, to determine the optimum value for biosorbent amount, contact time and pH in removal of nickel using biosorption process and to determine the efficiency of fish scale as a biosorbent.

MATERIAL AND METHODS

Fish Scale Preparation

Fish scale of tilapia is obtained from fish market in Parit Raja.Fish scale is first cleaned with nitric acid to remove surface contaminant and odour [8]. Then, it is cleaned with distilled water for three times and three times and continuously dried in oven at temperature of 60^{o}C. The dried fish scale is then grinded to powder and then sieved through sieve 100µm mesh [8]. Fish scale retained on sieve is used for experiment.

Aqueous Solution Preparation

Nickel solutions used in this study are prepared by adding 0.2 g of nickel nitrate, $Ni(NO_3)_2$ in 1000 ml of ultra-pure water to produce 200 ppm Nickel solution. The reagent used in this study was of analytical reagent grade. The stock solution are diluted from 200 ppm to the desirable concentration.

Experimental Design

A laboratory scale of wastewater treatment is made to determine the optimum condition of nickel removal in wastewater by varying the fish scale amount, settling time and pH level. All experiments were conducted using batch mode. The samples were shaken at 125rpm. In order to study the influence of biosorbent amount on nickel removal by fish scale the amount of biosorbent were varied from 0.3g, 0.5g, 1g, 2g, 3g and 4g. The contact times chosen for the time dependence study were 30 minutes, 45 minuftes, 1 hours, 2 hours, 3 hours and 4 hours. Experiments were also carried out at different initial pH value namely, 3, 5, 7, 9 to 11.

Sample Analysis

After biosorption treatment was completed under the specific condition, the solution were filtered using filter paper No. 40 which was used specifically for AAS method. The extraction of biosorbent from solution was to avoid any further sorption which will influence the result. Solution which now free from biosorbent was analyzed using flame atomic absorption spectroscopy (AAS) to determine the concentration of nickel ion in aqueous solution before and after treatment respectively.

RESULTS AND DISCUSSION

This study was carried out to determine the capabilities of tilapia fish scale in removing nickel in wastewater. The experiment was divided into three phases by varying the amount of fish scale used, contact time and pH level to check the effect and efficiency of each parameter towards the heavy metal sorption. All samples were done in duplicate to reduce error.

Effect of Fish Scale Amount on Nickel Removal

It was shown that the tilapia fish scale biosorbent was able to remove nickel from aqueous solution as shown in Figure 1. Nickel removal depends on biosorbent. Increase in amount of biosorbent lead to an increase in nickel removal. The removal of nickel by tilapia fish scale as biosorbent from aqueous solution ranged from 63% to 72%. The optimum nickel removal of 71.25% was achieved at 2 g of biosorbent.

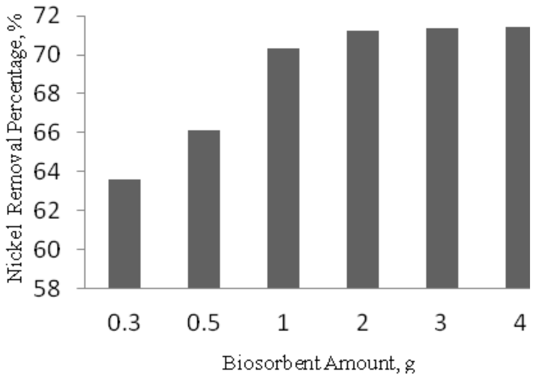

Figure 1:.The removal of nickel by tilapia fish scale as biosorbent from aqueous solution.

This is as expected because the increase in nickel ions removal with the biosorbent amount could attributed to increase in surface area and the availability of more sorption site. The percentage removal increase as the amount of biosorbent was increased and reaches a saturation level at high amount for nickel ion removal [9]. As the saturation level is high, the sorption became slower which show a very small increment in nickel removal percentage after the application of 2 g of tilapia fish scale.

The specific uptake for nickel is shown in Figure 2. The graph shows that at a given equilibrium concentration, the biosorbent takes up more metal ions at lower biosorbent amount. The biosorption specific uptake decrease from 4.24 to 0.357 as biosorbent amount was increased from 0.3 g to 4 g for the equilibrium time of 1 hour.

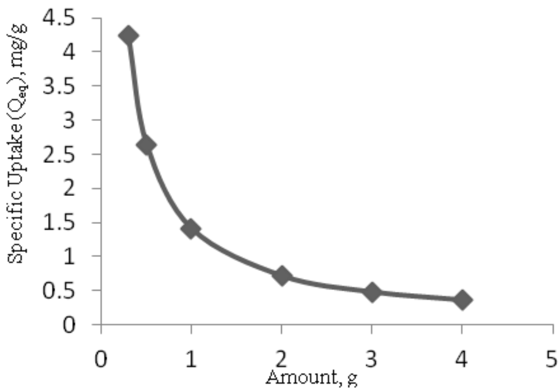

Figure 2: .Effect of amount of biosorbent on nickel ion uptake using tilapia fish scale as biosorbent.

Specific uptake was influenced by factors affecting the mass transfer from bulk solution into binding site. The process involves three steps. First, bulk transport of metal ion takes place from the solution phase to surface of binding, which was usually fast because of mixing and flow [10]. It was followed by film transport, which involves diffusion of metal through a hydrodynamic boundary layer around the biosorbent surface and finally actual adsorption of metal ion takes place into the active sites of the biosorbent [11]. The decrease in specific uptake can be explained by the formation of aggregates during biosorption, which occurs at a high biomass concentration, causing a decrease of the effective adsorption area [12] or due to interference between the binding sites at higher concentration [13].

The study by Huang [9] also yielded a similar result where the highest specific uptake of copper occurred with the smallest biosorbent to copper ratio. With the increasing biomass concentrations, the metal ions in solution became insufficient to available binding sites. Higher specific uptake at lower biomass concentrations was due to increased metal ion to biosorbent ratio, which decreases as the biomass concentration increases.

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Effect of Contact time on Nickel Removal

Removal of nickel ion from aqueous solution using tilapia fish scale as biosorbent is carried out at different contact time. The contact time chosen for the time dependence study were 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours and 6 hours. Figure 3, 4 and show the biosorption efficiency of nickel by tilapia fish scale as a function of contact time.

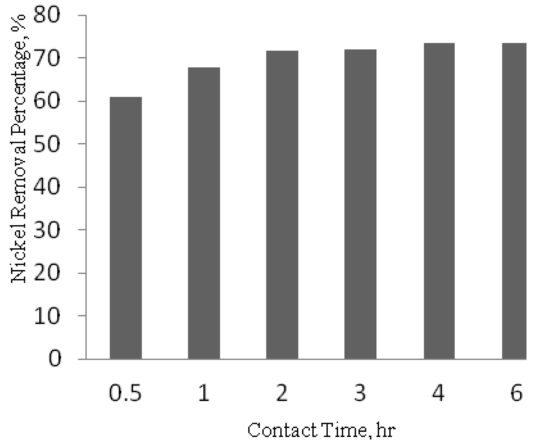

Figure 3; The removal of nickel by tilapia fish scale as biosorbent from aqueous solution.

This study investigated the effect of contact time to nickel ion removal in aqueous solution. As shown in Figure 3, nickel removal depended on the time of treatment. The removal of nickel by varying the contact time ranged from 60% to 75%. The optimum nickel removal of 73.38% was achieved at 4 hours of contact time. The effect of contact time on uptake capacity is shown in Figure 4. The graph shows that the metal uptake increased as the contact time was increased. The range of metal uptake was from 1.3 to 1.5. The uptake capacity reaches the equilibrium state at 1.468 during 4 hours of contact time.

The result is expected as the longer the contact time, the higher the nickel removal percentage. This can be attributed to more nickel was allowed to bind with surface area. As the metal sorption reached a certain point of equilibrium time, there was a reduction in metal removal capacity which could be attributed to complexation of metal ions in solution which introduces competition between surface and soluble active sites for the binding of metal ions [14].

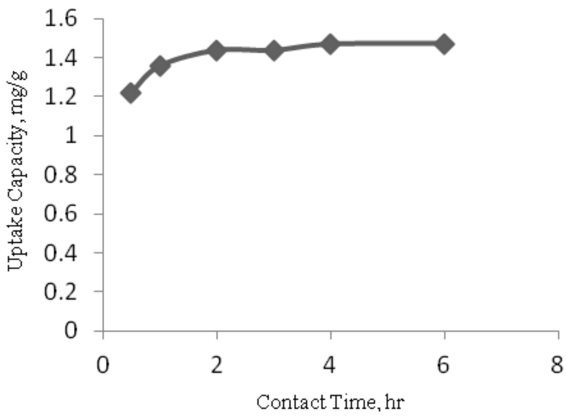

Figure 4:.Effect of contact time on nickel ion uptake using tilapia fish scale as biosorbent.

The study by Huang [9] founded that a 100% percent heavy metal removal was possible. The process of removing 100% of copper in a certain volume of industrial effluent with the application of biosorbent amount with ratio of biosorbent to copper at 5.00 required a total contact time of 12 days. Another study done by Mustafiz*et* [15] suggested that microbes were responsible in heavy metal removal with the application of fish scales as a biosorbent. It was possible that a longer contact time allowed the microbes to be released into the solution. The microbes needed to be in solution for a longer time in order to absorb heavy metal ions. As the result, shorter contact time did not allow enough time for heavy metal sorption abilities of the microbes in the biosorbent.

The removal rate of nickel is shown in Figure 5. The graph shows that at a given equilibrium concentration, the removal rate of metal ions was highest at smaller contact time. The biosorption removal rate decrease from 24.44 to 2.45 as contact time was increased from 0.5 hour to 6 hours for the equilibrium biosorbent amount at 1 g.

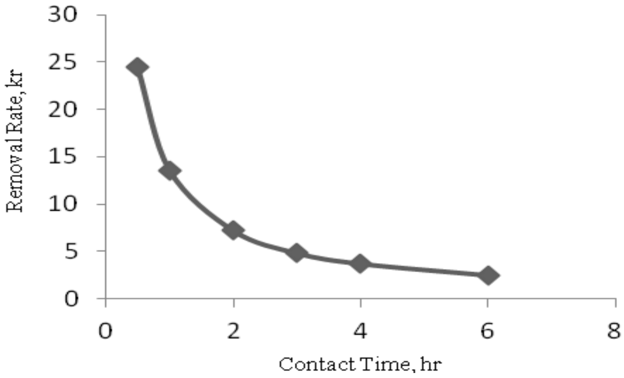

Figure 5: .Effect of contact time on nickel removal rate using tilapia fish scale as biosorbent.

The nickel removal rate was rapid at the beginning of treatment since there was abundant available area for metal binding. As the contact time added, the ratio of free surface area to available metal ion in aqueous solution decreased. As the time continued, lesser metal ions are available in solution for further metal sorption causing the removal rate decreased with time [9].

Effect of pH Level on Nickel Removal

The pH parameter plays an important role for the biosorption process of heavy metal ions from aqueous solution. Effect of pH on nickel removal was evaluated at pH 3, 5, 7, 9 and 11 as shown in Figure 6.

Figure 6 shows nickel removal depended on the pH level of aqueous solution. The removal of nickel by varying the pH ranged from 65% to 71%. The optimum nickel removal of 70% was achieved at pH 9. The effect of pH level on uptake capacity is shown in Figure 7. The graph shows that the metal uptake increased as the pH was increased. The range of metal uptake was from 1.3 to 1.5 mg/g. The uptake capacity reaches the equilibrium state at pH 9 with a value of 1.400 mg/g.

The result is expected as the higher pH level, the higher the nickel removal percentage. High metal removal at higher pH level was a result of effective competition by metal ions for negatively charged sites at the biosorbent surface. The solution pH affects the surface charge of the adsorbent and the degree of ionization. The adsorption of metal ion occurred mainly due to oppositely charged ionic attraction. As pH level decreased, the cell surface became more positively charged, therefore reducing the attraction between biosorbent and metal ions [16]. In contrast, higher pH results in higher metal uptake, since the cell surface was more negatively charged and more metal bindings were allowed.

The study by Kandah*a,* [17]shares a similar result. The study about the removal of nickel ions from water by multi-walled carbon nanotubes. The studies founded that as the pH increases, the adsorption uptake increases due to the increase in the electrostatic attractive forces between OH^{-} and Ni^{2+}. At a lower pH level, the adsorption uptake was very weak due to the competition between Ni^{2+} and H^{+} in the solution

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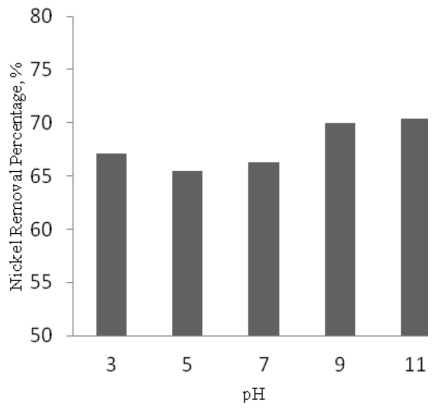

Figure 6: The removal of nickel by tilapia fish scale as biosorbent from aqueous solution.

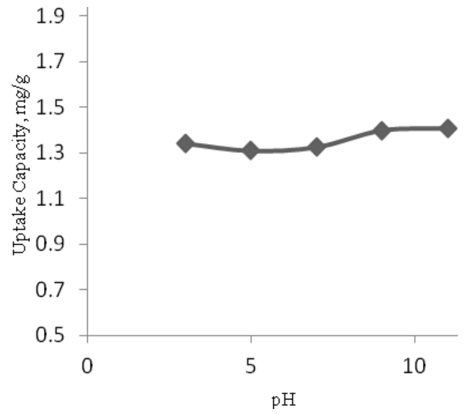

Figure 7: .Effect of pH on nickel ion uptake using tilapia fish scale as biosorbent.

Nickel Removal Under Optimum Condition.

From this study, three parameters were examined where each of parameter was tested to get the optimum condition. Experiment was conducted under the application of all the optimum value obtained from each parameter. Three samples were prepared using 100 ml nickel solution with 20 ppm concentration. All samples received the same treatment where pH level was adjusted to 9; mixed with 2 g of tilapia fish scale and shaken at a speed of 125 rpm for a contact time of 4 hours.

This study investigated the nickel ion removal in aqueous solution under the optimum condition. Mean value was obtained from the three samples. In optimum condition, the result was 74.58% which was the maximum nickel removal percentage. The maximum uptake capacity of 1.492 mg/g was achieved. The nickel removal percentage depended on the optimum condition during biosorption process.

It is as expected where all the parameters involved which were in optimum state would give the maximum value for nickel removal. Optimum condition is the state where the metal bindings reach their equilibrium state. This is the state where the treatment became stable and further adsorption could not take place because the surface area has reached the saturation point. Therefore, biosorption process done under all the optimum parameter yielded a maximum metal ions removal and further treatment only increased the metal removal at a very little amount.

The Efficiency of Fish Scale as a Biosorbent.

From Figure 2, the nickel ion uptake decreased with added amount of tilapia fish scale. Specific uptake was highest at 0.3 g of fish scale. Highest specific uptake was achieved with the application of smaller amount of biosorbent. It was most efficient to use a smaller amount of biosorbent because the efficiency is high under these conditions, although it did not give a desirable level of nickel removal in the treatment.

Removal rate is a value to determine the efficiency of nickel sorption over a period of time [9]. Figure 5 shows that the efficiency of nickel removal is decreasing with time. Removal rate is highest on the first 30

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minutes of treatment at 24.44. From the graph, efficiency was great under 2 hours of contact time but became very low after 4 hours. It is expected that even if the treatment was continued, the experiment will be impractical due to very low removal rate over the time spent on the treatment.

pH level also contribute to metal removal efficiency. The study done by Mustafiz*et* [15] stated that higher pH level yielded higher metal removal efficiency. Higher pH level would give better metal removal efficiency because more positively charged metal ions were allowed to bind with the negatively charged surface area.

CONCLUSION

The biosorption efficiency of tilapia fish scale in removal of nickel ions from aqueous solution has been studied. The result obtain in this work indicate that tilapia fish scale can be used as biosorbent for nickel ions removal in aqueous solution. The range of removal efficiency obtained was 70% to 75%. Adsorption of nickel ions onto tilapia fish scale biomass depended significantly on the amount of biosorbent, pH and contact time. Optimum biosorption of nickel ion was observed at 2g of tilapia fish scale as biosorbent, pH 9 and four hours contact time.

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