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Preliminary Study of Adsorption Copper (II) Ions from Aqueous Solution Using Aromatic Green Dwarf Waste as an Biosorbent

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ABSTRACT

Nowadays, released of heavy metals from the industries to the water stream arises a severe environmental problem to human health and water ecosystem. The conventional wastewater treatment plant is no more effective in treatingthis contamination. Furthermore, the modern wastewater treatmentplantis expensive and inefficient. Therefore, in this paper studied the suitability of aromatic green dwarf (AGD) waste as biosorbent for the copper removal. Two samples were prepared, treated and untreated AGD powdered (150-250 µm).The AGD powdered is treated with 0.1 M sodium hydroxide solutionand stirred at room temperature for 18 hours. The absorption efficiency of both samples was assessed based on the amount of copper reduction after 2 hours batch process. The concentration of copper is measured using Atomic Absorption Spectrometer (AAS) and percentage of copper removal is estimated. The result shows that the treated AGD powderedis more efficient in copper absorption than untreated. Moreover, the percentage removal shows direct proportionality to the copper solution pH.Absorption capacity is at its maximum,100% when copper solution pH is at 6whilst untreated shows only 73.12%. However, for copper solution concentration shows it otherwise, the maximum percentage removal is at 20ppm and 97.45%, whilst 67.32% for untreated. Therefore, the AGD waste shows a good potential as a low-cost and easily found biosorbent.

KEYWORDS: Aromatic Green Dwarf, Wastewater, Biosorbent, Adsorbent, Atomic Absorption Spectrometer (AAS).

INTRODUCTION

In this decade, there were many industrial processes such as mining operation, metal plating facilities, fertilizer industries, tanneries, batteries, paper industries and pesticides that release heavy metals directly or indirectly into the environment [5]. These activities maylead to the water pollution due to discharge of toxic chemicals to water sources such as river basin. There are many developed and developing countries are faced with this environmental issue such as Malaysia. According to [7], most of water pollution problems in Malaysia are caused by the discharge of industrial effluents.

Heavy metals are elements that havean atomic weight between 63.5 and 200.6, and a specific gravity greater than 5.0 [1]. It is also extremely toxic metals, non-biodegradable and tends to accumulate as metal organic complex [14]. Heavy metal must be removed in order to achieve the environmental quality standard [2]. Various methods are being employed in removing heavy metal ions from wastewater such as chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. However,some of the method has its own disadvantages such as incomplete metal removal, high reagent and energy requirements andthe generation of toxic sludge or other waste product that requires for disposal.

The absorption method employed is seems beneficial for wastewater treatment as of low cost and ease of operation, simplicity of design and insensitivity to toxic pollutants [10]. Activated carbon is a commonly used material inwastewater treatmentfor heavy metal removal. However, due to the higher cost of regeneration system, the activated carbon is less economically viable as an excellent adsorbent [9]. Therefore, natural adsorbent is an alternative to overcome high cost problem. Biosorbent from waste is an effective ways for water and wastewater treatment, since the absorbent is cheaper, renewable and abundantly available [6].

The aromatic green dwarf is cultivated and well adapted in several countries such as Malaysia, Thailand, Philippines, Brazil and other countries [11]. In Malaysia,the aromatic green dwarf is very popular for its juice as beverages in the restaurant as well as used in food industry as food flavorings. The usefulness of waste from this industryhasnot yet been discovered. Normally, they are dumped and exist in abundant thus may lead to diverse

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environmental problems. Therefore, in this paper studied the suitability of aromatic green dwarf (AGD) waste as biosorbent for the copper removal.

METHODOLOGY

Preparation of Biosorbent

Waste AGD (Figure 1 (a)) was collected from local stall in Dungun, Terengganu and the coir is dried for 8hours. Then, it was cut into small pieces and dried in an oven for 5 hours at 150°C prior togrinded to powder form (150-250 µm).This AGD was divided by two samples such asuntreated AGDand treated by soaking into 1.0M sodium hydroxide (NaOH) solution as shown in Figure 1 (b). The flask was stirred at room temperature (27°C) for 18 hours to remove acid components, separate the residual insoluble matter and leaving the lining as the final residue. After that, the supernatant was decanted and filtrated. The treated AGDis washed with distilled water to remove any NaOH excess, and it was dried at 60°C for 24 hours in a convection oven.

(a) (b)

Figure 1: Picture of (a) waste of AGD (b) treatment of untreated AGD waste with NaOH

Batch Adsorption Study: Effect of Initial pH

The effect of initial pH on the equilibrium uptake of copper ions was investigated at pH 1, 3, 5 and 6. About 1g of aromatic green dwarf coconut coir biosorbent was added to 50mL of copper (II) nitrate solution. The pH of the solution is adjusted using 2% of nitric acid (HNO_3) and 1M of NaOH. The mixture was shakento obtaina homogenous mixtureat 175 rpm for 2 hoursusing a thermostatic shaker. After 2 hours, solutions were filtered and analyzed by using Atomic Absorption Spectrometer (AAS).

Batch Adsorption Study: Effect of Initial Concentration of Adsorbate

The effect of initial concentration on the adsorption of copper ions was investigated using 20ppm, 40ppm and 50ppm copper solution. About 1g of aromatic green dwarf coconut coir is added to 50mL of copper (II) nitrate solution. The pH of the solution is adjusted by using 2% nitric acid and 1M sodium hydroxide (NaOH). The mixture was shakento obtain a homogenous mixture at 175rpm for 2 hours by using thermostatic shaker. Solutions were filtered and analyzed by using AAS.

Copper Percentage Removal (Qe)

The percentage of removal (Qe) of copper was calculated using equation 1.

$$\text{Removal percentage, } Qe = \frac{(Wa - Wi)}{Wa} \times 100 \qquad (1)$$

where W_i = initial concentration of Cu(II) and W_a = final concentration of Cu(II).

FINDINGS AND DISCUSSION

Effect of Initial pH

The effect of initial pH on the removal of copper ions, using untreated AGD and treated AGD coir has been studied by varying the range of pH from 1 to 6. The copper concentration in all samples with different pH range was analyzed and measured usingAAS.Table 1 and Table 2 illustrated the pH value on the removal of Cu^{2+} ions.

Table 1: pHvalue on the removal of Cu^{2+} using untreated AGD sample

pH	InitialConcentration	Final Concentration	Qe (%)
1	53.858	44.542	17.29
3	53.858	21.158	60.70
5	53.858	18.892	64.92
6	53.858	14.475	73.12

Table 2: pHvalue on the removal of Cu^{2+} using treated AGDsample

pH	Initial Concentration	Final Concentration	Qe (%)
1	53.858	36.942	31.41
3	53.858	0.942	98.25
5	53.858	0.333	99.38
6	53.858	0.000	100.00

From the results, pH 1 showed the copper percentage removal is approximately 17.29% for the untreated AGD and 31.41% for the treated AGD. The percentage of copper removal for untreated AGD and treated AGD samples at pH 3 were 60.70% and 98.25% respectively, and increased with increased of initial pH solution for treated AGD at pH 5 and pH 6, i.e. 99.38% and 100% respectively. This is due to the competition between protons and metal cations for the same functional groups and decrease in the positive surface charge resulting in lower electrostatic repulsion between the surface and metal ions [3]. Based on these results, treated AGD sample shows a good copper ions absorption capability compared to untreated AGD sample. However, at a low pH value of 1, both samples show fewer percentage of copper removal which is 17.29% for untreated AGD and 31.41% for treated AGD. According to [8], at low pH values, the concentration of hydrogen proton in the solution far exceeds the copper ions. Hence, the protons compete with copper ions in forming a bond with active site (the functional groups) on the surface of the absorbent, leaving the metal ions free in solution. This bonded active site thereafter became saturated and was inaccessible to other cations resulting in low adsorption capacity. This result shows a good agreement with previous study conducted by [8] where at low pH values, copper ion's absorption capacity is low.

Effect of Initial Concentration of Adsorbate

The effect of initial concentration of adsorbate on the removal of Cu^{2+} ions from untreated AGD and treated AGD sample were carried out by varying the concentration dosage of adsorbate (21.633ppm, 45.647ppm and 58.233ppm). The concentration of copper in the samples wasmeasured using AASand equation 1 is used for copper percentage removal calculation. Table 3 and Table 4 illustrated the concentration of adsorbate on the removal of Cu2+ ions.

Table 3: Concentration of adsorbate on the removal of Cu^{2+} using untreated AGDsample

pH	Initial Concentration	Final Concentration	Qe (%)
5	21.663	7.080	67.32
5	45.647	18.053	60.45
5	58.233	25.633	55.98

Table 4: Concentration of adsorbate on the removal of Cu^{2+} using treated AGDsample

pH	Initial concentration	Final concentration	Qe (%)
5	21.663	0.553	97.45
5	45.647	2.487	94.55
5	58.233	5.350	90.81

From this study, initial concentration of 21.663 ppm shows that the percentage of copper ion removal for both untreated AGD and treated AGD were 67.32% and 97.45% respectively. According to [3], at low concentrations, metals are absorbed by specific sites while with increasing metal concentrations the specific sited are saturated and the exchange sites are filled. The percentage of Cu^{2+} ion removal decreased for both samples as of initial concentration of adsorbate increased as tabulated in Table 3 and Table 4. Similar results were demonstrated by [13] for the adsorption of Cu^{2+} ions at 20 ppm, 40 ppm and 50 ppm. They found that as the adsorbate concentration increased, the higher energy sites are saturated and adsorption begins on lower sites, which resulting in a decrease of the adsorption efficiency.

Previous studies showed that the heavy metal ion sorption by absorbent followed by a two-step mechanism where the metal ions were physically or chemically uptake onto the surface of the absorbent before being taken up biologically into the cell [4]. The first step known as a passive transport occurs rapidly while the biological step or active transport, could take much longer time to be accomplished. In this study, the aromatic green dwaft coconut coir was dried and its biological functions were no longer active. Therefore, only the sorption could take place on the surface of the cell.

The untreated AGD and treated AGD has been examined as biosorbent for Cu^{2+} ions from aqueous solution. Based on the result, the treated AGDhas a higher percentage of removal compare to untreated AGD. The highest percentage of treated coir was 100%, while the highest percentage of untreated coir was 73.12%. This can be explained by comparing the structure of AGD coir. In [12] stated that certain cell wall components, especially lignin and pectin assumed to be connected with the sorption of metal ions.

The AGDis a pure material that not be added to any acid or base for the treatment, where the percentage of lignin in coir was still higher. Without any modification, the capacity adsorption of coir was lower because the lignin fills the space in the cell wall between cellulose, hemicelluloses and pectin components.This characteristic makes the capacity sorption lower as the space of sorption is limited. While, the AGDis treated as to modify the structure of the AGD. The results show that the sorption capacity for treated AGD is improved, since the treatment increased cellulose content in AGD.In [11] in their studies, about the composition of aromatic green dwarf coir fibers states that after the coir is treated with NaOH solution, the impurities and wax cuticle layers of the fiber's surface were removed. The fibrils were starting to separate from each other because the lignin and the cementing component had been removed by the action of alkaline solution, which leading to an increase of the surface area and potentially improving the fibers-matrix adhesion in composition. The cleaning treatment also produces changes to hydrogen bonding interactions of hydroxyl groups of cellulose, which resulting in the deformation of individual microfibrils. The alkaline treatment removing impurities from the fiber's surface, as well as lignin and hemicelluloses also reduced the fiber diameter.

CONCLUSION AND RECOMMENDATIONS

The aromatic green dwarf waste available in abundantmay create diverse environmentalissuesin Malaysia. Therefore, a step of converting this waste into a useful product is a must. This research had found that the suitability of aromatic green dwarf waste as biosorbent for the removal of copper in wastewateris proven effective. Wastewater treatment can be more economical and effective and dependence on the highly cost absorbent may be reduced. The biosorption capacity of the coir depends on the initial pH of the solution and the initial concentration.

Previous studies show that the research area mostly focused on the shell, coir and pith of the coconut but not the aromatic green dwarf coconut. In this research, the scope of study is focused on the aromatic green dwarf coir only.Aromatic green dwarf coir is very efficient biosorbent for the copper removal from aqueous solution as the adsorption capacity is higher for the both untreated and treated AGD. The results show that the 100% and 73.12% of copper is being absorbed by treated and untreated AGD respectively. As the adsorption of Cu (II) ions into biosorbent is affected by the initial pH and initial concentration, the objective is achieved. The result shows that the uptake of copper by biosorbent increases when the pH value is increasing, as the highest percentage of removal is recorded at pH 6. This shows the absorption can be applied to the most dilute aqueous solution. In other words, shifting to more cost effective material for heavy metals removal in wastewater is achievable.

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