Eggshell Powder as an Adsorbent for Removal of Lead (II) in Panchor's River

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Abstract: Heavy metal such as lead has increase in the natural environment especially in the aqueous solution. Remediation method of adsorption offer a treatment for removing heavy metal in river. This experiment is to analyse and compare eggshell adsorbent of activated carbon in Panchor's river through its efficiency in removing heavy metal of Lead (II). Eggshell is designed as an activated carbon through physical and chemical activation in treating the water by undergoing adsorption process of few laboratory test. The efficiency of eggshell chemical activated carbon is high as the percentages removal of Pb is 48.21% compare to physical activated carbon with 32.14%. However, this study showed that both eggshell activated carbon is an effective adsorbent in removing Pb from aqueous solution of natural environment.

Keywords: Eggshell, activated carbon, heavy metal, chemical activation, physical activation, Lead (II), turbidity, pH

1. Introduction

The quality of water had always become the very importance and necessary component in our daily life to accomplish our task. The lack of clean water is a plague which affects billions of people every year. Heavy metals are harmful metals having density which are multiple times bigger than water. They are poisonous for every living being. It can enters human body through different ways like ingestion, retention and so on**.** They slowly grow over a long time in the body and toxic. Due to the anthropogenic activities, heavy metal pollution is a major environmental and medium-sized town concern[1]. Man-made activities may contribute to a great extent in their production for example are burning of fossil fuel, mining and utilization of numerous compound for crop development. Wastewater additionally contains heavy metal and when it is applied to crops it risks soil and plants development. The risks to human health of wastewater can be determined by various indices. Heavy metals cannot commonly be eliminated from the wastewater. This project was aiming to solve water problem such as water pollution with heavy metals beside maximise the usage of agricultural and food waste in better ways. The problem happens due to the poor sanitation and lack of waste treatment plant.

Panchor is one of the Muar's small town which is located next to Muar River. Panchor's river was once a clean river but due to food stalls activities around the river make the river become polluted. Before having a proper treatment of solid waste and sewage treatment facilities, most of the waste from the industrial estates and poultry farms are discharged directly into the river. In contrast to organic matter, mass pathogenic bacteria, parasitic larvae, and heavy metal are present in livestock and poultry manure. The act of releasing it directly into the water without adequate treatment had causes significant pollution of groundwater and surface water supplies [2]. As for the result, the rivers in Muar are no longer clean and it turn out to be brownish in colour. The improper activities had affect the ecological health of water bodies, the aquatic life and regular recreational activities.

Removal of heavy metals from wastewater has received a great deal of attention in recent years. Adsorbents like activated carbons prepared from some agricultural and food by products, some cellulosic waste and commercial activated carbons were used. Material to be used for removing heavy metal in wastewater must be cost effective material when using with large scale and also can be use in reducing environmental pollution. The search for an efficient way of resolving agricultural waste adequately will help protect the environment and the quality of health. Waste should be recycled, reused, and redirected towards the manufacture of value added goods for sustainable development. This is to preserve the environment on the one hand and to produce value-added goods on the other, while maintaining a zero waste policy.

In this research the process of adsorption was attempted using the eggshell of such a low-cost adsorbent. Eggshell is looks like such a largely crystalline calcium carbonate, physically [3]. These eggshells waste is suitable due to the high consumption of domestic egg and it contains high contents of calcium carbonate which is about (85 − 95%) [4]. Moreover, eggshells abundant were often produced daily as waste. Thus, eggshell is one of the major useful adsorbents for eliminating the heavy metals from the aqueous wastewater solution by the presence of calcium carbonate. Therefore, in this paper the study was conducted to evaluate the effectiveness of eggshells waste in removing heavy metals of lead (Pb^{2+}) ion from aqueous wastewater solutions.

1.1 Wastewater Treatment using Eggshell

Faced with ever more strict laws, heavy metals are today sources of pollution of environmental primary concern and are becoming one of the most serious environmental problems. Thus to protect humans and the environment, these toxic heavy metals should be eliminated from the wastewater [5]. Numerous approaches have been proposed and tested for the removal of toxic heavy metals from water supplies. Although chemical precipitation, coagulation, exchange of ions, extraction of solvents, filtration, evaporation, and membrane techniques have been used for this purpose, most methods have some weaknesses, such as requiring several pre - treatment and additional treatments [6].

For the removal of toxic heavy metals, usually activated carbon, silica gel, activated alumina and ion exchange resin have greater ability. Nonetheless, due to the high installation and running costs, their use is not frequent and limited to special care [6]. There is a need to adopt cheaper and readily available materials due to the cost of the activation process which can be used economically on a large scale [4]. The eggshells from egg-breaking processes are considerable waste disposal problems for the food industry in this aspect, so the production of value-added by-products from this waste is to be encouraged [7].

Eggshell with strong adsorptive properties i.e., pore structure, $CaCO_3$ and protein acid mucopolysaccharide which may evolve into an adsorbent. Carboxyl, amine, and sulphate are important functional groups of protein acid mucopolysaccharides that can attach heavy metals to form ionic bonds. In addition, the shell of the eggs is a neutralizing agent, any aqueous solution combined with the shell of the eggs is more basic as then heavy metal can precipitate and settle on particles of the egg shell [8].

1.2 Adsorption

Adsorption derives from the unsaturated and unbalanced molecular forces present on any solid surface. Therefore, when a solid surface is placed in contact with a liquid or gas, there is a connection between the surface forces fields and the liquid or gas fields. The solid surface attempts to fulfil these residual forces by trapping the gas or liquid molecules, electrons, or ions and holding them on its surface [9]. Advantages of adsorption is it results in better concentration of gas or liquid in the near vicinity of the solid surface, given the existence of the gas or vapour, than in the process of bulk gas or vapour. The mechanism that causes the surface excess is called adsorption [9]. Adsorption has been considered one of the best methods for extracting organic and inorganic wastewater toxins and unnecessary chemical components from the agriculture and food industries [10].

Other than that, the efficiency of the adsorption process depends on what type of adsorbent, its physical characteristics, such as particle size and pore size, the stage it is in parameter such as temperature, initial concentration and dosing were carried and processed [11]. Thanks to their excellent ability to adsorb, activated carbons have been the most commonly used sorbents and have been taken from the agriculture and food industry for a variety of applications such as decolouration of sugar and vegetable oils, elimination of copper ions and unwanted organics in the distilled alcoholic beverage industry, and others [10].

Moreover, most of the adsorption process is using an eco-friendly items and natural sources such as agricultural and food waste like rice husk, eggshells, tamarinds peel and others. It is for ensuring the environmental will not be affected by these substances when they been used. Agricultural waste has a flexible, porous structure and includes carboxyl, hydroxyl and other reactive groups. In the field of reducing pollution, it can be used as a biomass adsorption medium that not only decreases the environmental burden but also has the benefit of waste treatment [2]. In addition, through this adsorption process the eggshell activated carbon can be analyse and compare in Panchor's river. Thus, it is also one of the efforts in aiming to minimise the problem towards the river.

2. Materials and Methods

2.1 Preparation for Eggshell as Adsorbent

In this research, chicken eggshells collected from cafeteria of Kolej Kediaman Pagoh in University Tun Hussein Onn Malaysia (UTHM), Pagoh campus. After washing and drying the raw material, 250g of the raw material is weighed and crushed and was placed in furnace for 4 hours at 200ºC [12]. Usually, the physical methods are thermal reactions at temperatures beyond 700 ºC [13]. In fractions of 600μm mesh size particles, the dried eggshells were grinded and well sieved and stored in sterilised containers for use as adsorbent in physical activation carbon [14]. Thus, it is called physical activated carbon.

Eggshell chemical activated carbon was produced by pouring 60g of the carbonised eggshell in a beaker. 50mL of H_2SO_4 was inserted and left for 24 hours on the stirrer. After that, by washing with deionized water, neutralisation was achieved. Thermal activation (600 °C, 1 hour) in the muffle furnace. Milling of the eggshell can cause decreased specific surface area, according to several research. The adsorbent was administered as a non-milled eggshell [12]. Fig. 1 below shows the preparation process of eggshell as adsorbent.
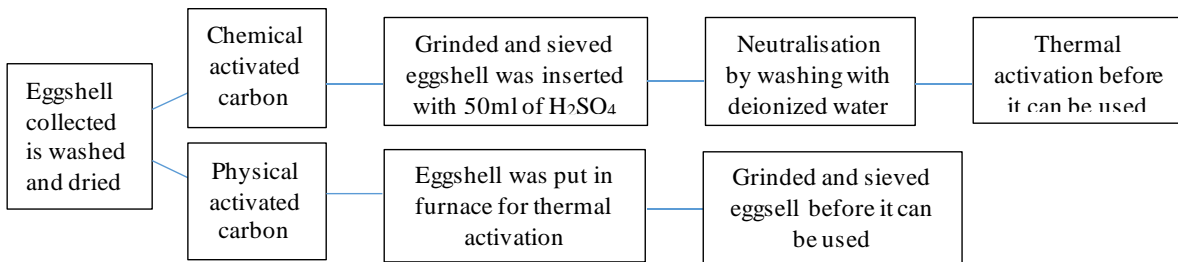

Fig. 1 - Preparation process of eggshell as adsorbent

2.2 Adsorption Experiment and Analysis

Adsorbent is put in a 250 ml Erlenmeyer flask with 100 ml sample solution from Panchor's river (Fig. 2). The sample solution was taken using grab sampling method. A garb sample is any single sample that is obtained without combining or inserting other samples. The contents (adsorbent/100ml solution) were shaken for 1hour on an orbital shaker for continuous shaking (at 200 rpm). Then, the solid particles were separated by filtration. For analysis, the solutions were obtained and the concentration of sample solution was measured using a spectrophotometer.
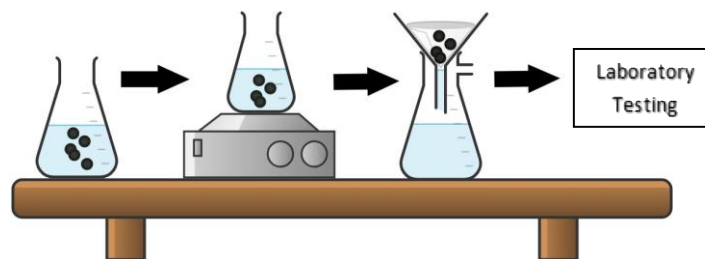

Fig. 2 - Adsorption experiment and analysis

2.3 Heavy Metal Analysis

Heavy metal analysis by Dithizone Method are for identify and measure the presence of heavy metal in water where it might cause diseases for living things when consumed[15]. Items needed in order to carry out heavy metal analysis are the DithiVer® Metals Reagent Powder Pillows, 10-mL[1], sample cells, beaker, stopper and DR6000 UV-VIS Spectrophotometer. The percentage removal (R) of Pb was calculated using equation below:

$$\% \text{ R} = \frac{C_o - C_e}{C_o} \times 100$$

(1)

C_o and C_e are the initial concentration of Pb in water sample and final concentration of Pb after adsorption and filtration respectively (mg/L).

3. Results and Discussion

3.1 pH

pH is a measure of water acidity which differ based on the geology of the catchment and flow of a river, and the release of waste water, normally it is in the range of 6. This hydrogen ion activity is affected by biological processes such as the absorption of carbon dioxide by plants during photosynthesis [16]. Table 1 below shows pH value for activated carbon by physical activation while Table 2 shows pH value for activated carbon by chemical activation.

Table 1 - pH value for activated carbon by physical activation

Adsorbent Dosages (g)	Initial pH	Final pH
0.6	6.00	7.34
1.2	6.00	7.76
1.8	6.00	7.91
2.4	6.00	7.58
3.0	6.00	7.48

Table 2 - pH value for activated carbon by chemical activation

Adsorbent Dosages (g)	Initial pH	Final pH
0.6	6.00	7.20
1.2	6.00	7.29
1.8	6.00	7.32
2.4	6.00	7.30
3.0	6.00	7.01

Based on Table 1 and Table 2 above, initial pH value are in the range of 6. The results are more acidic than the final value of pH which are in the range of 7. A pH scale of 0–14 with a pH value of 7 as the midpoint is standard practice, pH values below 7 gradually indicate more acidic reactions, and pH values above 7 generally mean simpler or alkaline reacts. However, at a temperature of 25°C, the pH of pure water is 7. For lower temperature, the pH of pure water is above 7 while for the higher temperature the pH of pure water is below 7 [17]. In-situ temperature is higher than temperature after adsorption and filtration thus it proved the pH to become more alkaline when the temperature decline. Initial pH value might be lower and acidic because of the presence concentration of lead (Pb) in the river. Both final pH for physical activation carbon and chemical activation carbon have increases in pH where the nearest pH value towards neutral for physical activation is at 0.6g. However, chemical activation have the nearest pH towards neutral at 3.0g with the value of 7.01. The greater efficacy of adsorption in the near neutral can be due to the absence of repulsive forces between the adsorbent surface and the Pb^{2+} species [18]. This happen because adsorbent in chemical activation undergo more process in the preparation stage such as neutralization after mixed it with acid.

3.2 Turbidity

Turbidity in water happens due to the suspended solids and colloidal matter. It can also occur from degraded soil caused by dredging or the development of micro-organisms. Strong turbidity makes it difficult to filtrate. If there are solids in the water, pathogens might be escape the effects of chlorine during disinfection. While high turbidity is often a result of poor water quality and land management, crystal-clear water doesn't always ensure safe water. Fig. 3 below shows the graph of turbidity removal efficiency against adsorbent dosage.
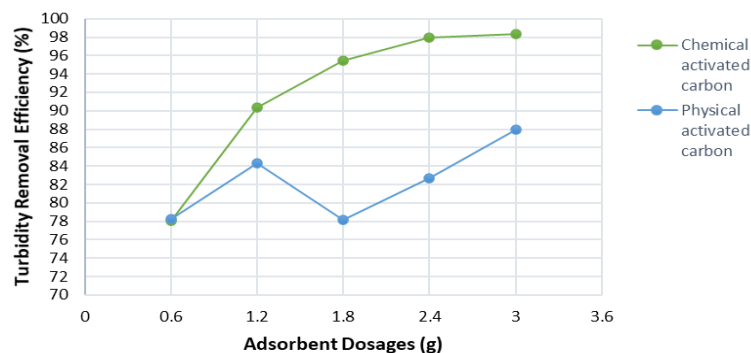
Fig. 3 - Graph turbidity removal efficiency against adsorbent dosage

Based on the result in Fig. 3 above, the highest turbidity removal efficiency was on 3.0g of adsorbent dosages for both chemical and physical activated carbon. The lowest turbidity removal efficiency were at 0.6g of adsorbent dosages with 78.09% and 78.21% for chemical and physical activated carbon respectively. The initial turbidity value was too high started from 67 NTU to 92 NTU. This happen regarding to huge amount of waste on a dumpsite near the river. Moreover, it was a tidal river water condition due to the uncertain weather. When there was heavy rainfall, the river contains high amount of silt and leachate as all the waste were dragged into the water body. These were the factors of Panchor River having high value of turbidity. After the sample of water was taken for adsorption and filtration process, the final value of turbidity having a declination of 17.0 NTU to 1.22 NTU. This prove both types of activated carbons works well in removing the pollutants that contaminate the water. The highest turbidity removal efficiency is 98.37% by chemical activation carbon on dosage of 3.0g. Chemical activated carbon shows an increasing value of graph than physical activated carbon. It was because chemical activation carbon has create porosity structure and improve the porous carbon yield when it is mixed with active agent [19]. In the meanwhile, physical activation carbon was typically a thermal activation process carried below 700°C thus it has lower turbidity removal efficiency [13]. The brownish colour of water samples turn into a clear water when using the chemical activated carbon than physical activated carbon. The yellowish colour blends well as all the samples were shaken for 1 hour on the orbital shaker.

3.3 Efficiency of Adsorbents

The effectiveness of adsorbent dosages for removing Pb was studied. There were 5 adsorbent dosages started with 0.6g, 1.2g, 1.8g, 2.4g and 3.0g were measured. This dosage is basis on the amount of sample solution, thus it can react well when experiment was carried out. Other than that, adsorbent types of physical activated carbon and chemical activated carbon were analyses. All of the dosages were used for both types of activated carbon. After adsorption and filtration process were carried out, it can be concluded that higher adsorbent dosage from chemical activated carbon produce higher percentage removal of Pb. The adsorption method basically relies on the particle size of the adsorbent, the greater surface area of the fine particle size, the adsorption capacity increases. This pattern is primarily due to a rise in the sorption surface area and the existence of more active sites of adsorption [14]. The effectiveness of adsorbent dosages was carried out by contacting eggshell powder activated carbon with 100ml sample of water from Panchor River.

The adsorption process were accomplished by shaking for 1 hour of contact time at a room temperature of 26±0.5 °C and a shaking speed of 200 rpm. The sample of water then was brought for testing using all the parameter stated. Based on data collected before, an increasing amount in adsorbent dosages gives an increasing amount of turbidity removal, concentration of dissolved oxygen and a most nearest pH value to neutral. Thus, for the heavy metal test only the highest adsorbent dosage was test. Heavy metal test for initial concentration of Pb was taken before the adsorption process accomplished. The calculation of the percentage removal (R) of Pb is 48.21%.

The initial concentration of Pb was 0.056 mg/L. The concentration of Pb might be affected by the waste from nearby dumpsite and from the industrial estates and poultry farms around Panchor. Moreover, galvanized pipe and iron supports on the bridge near the collected point could became one of the cause in presence of Pb in water sample of Panchor's river. After adsorption and filtration process, the water sample with 3.0g of adsorbent dosages from chemical activated carbon was taken for heavy metal test and the concentration of Pb decreased to 0.029mg/L. The percentage removal (R) of Pb from the sample of water was 48.21%. Adsorbent dosages of 3.0g from physical activated carbon was test for heavy metal and the concentration of Pb decreased was 0.038mg/L. In consequence, percentage removal (R) of Pb was resulted for 32.14%. Activated carbon with chemical activation was chosen for it abilities in improving water quality.

3.4 Characteristics of Eggshell as Adsorbent

Spectroscopy of the FTIR difference in choose vibrations that lead to single chemical groups that are involved in a particular reaction. The molecular movements are measured by infrared spectroscopy. Functional groups may be associated with characteristic infrared absorption bands that relate to the functional groups' fundamental motions. Thus, functional group of eggshells activated carbon after adsorption process can be determined from Fourier Transform Infrared (FTIR) spectroscopy. The result of FTIR analysis after adsorption and filtration process was shown in Fig. 4.

Based on figure above, there are two types of eggshells activated carbon which are physical activated carbon in the black line and chemical activated carbon in the red line. Peaks shown in Fig. 4 represent the characteristics of eggshell activated carbon. The peaks for chemical activation carbon were located at 872, 1398, 1815, 2829 and 3724 cm^{-1}. As for the result, it is clearly shown that there is a C-H group that is typically specific and unique in the IR spectrum of chemical activated carbon. The presence of spectra 1398 cm^{-1} in between frequencies of 600 - 1500 cm^{-1} indicates the group. The peaks at 872 cm^{-1} might be indicates the out-plane deformation modes in the presence of calcium carbonate [7]. There are also C=C group and –OH group for peaks at 1815 cm^{-1} and 3724 cm^{-1} respectively. There is a small peak at 3724 cm^{-1} which indicates –OH group which must be resulted from hydroxyl group from the eggshell sample. For another activated carbon that represented by black colour line, there are a C-H bending group where peak 708cm^{-1} is located. Peak 1651 cm^{-1} represent the amides or carboxylate functional group, C=O stretching with a double bond

region. 2527 cm^{-1} peaks might be assigned to acidic hydrogen group (-OH) stretching. Peaks 3302 cm^{-1} and 3958 cm^{-1} respectively small peaks that indicates the carboxylic acid compound class and it was in –OH group of single bond.
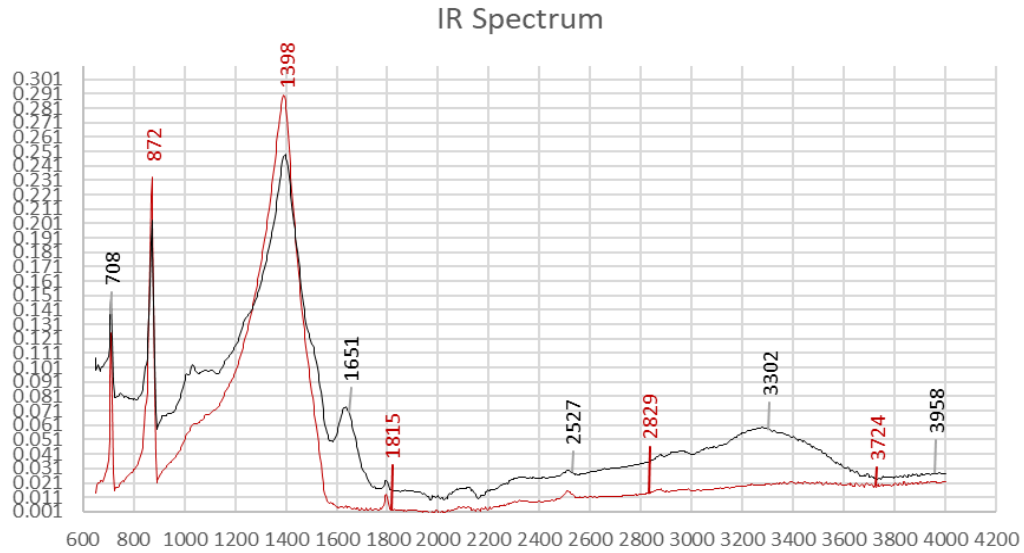
Fig. 4 - FTIR spectrum of eggshell activated carbon after adsorption process

From the SEM images, the textural structure study of eggshell particles can be seen. The eggshell particle's crystalline structure showed an angular fracture pattern as shown in Fig. 5 (a) [20]. As shown in Fig. 5 (a) and (b), the morphology of the chicken eggshell displayed fragments of rough, irregularly structured and spongy particles, aggregated along with microspores scattered on the sample surface. High specific surface areas could be given by the small size of the grains and aggregates, because the particle size can react directly to the surface region [21]. Generally, its pore diameter would be no more than a few microns. By electron microscope scanning, the pores on the eggshell surface can be classified into three categories: balanced pores, gradient pores, and mixed pores. The pore structure will obtain the full space under the same conditions relative to other structures [22].
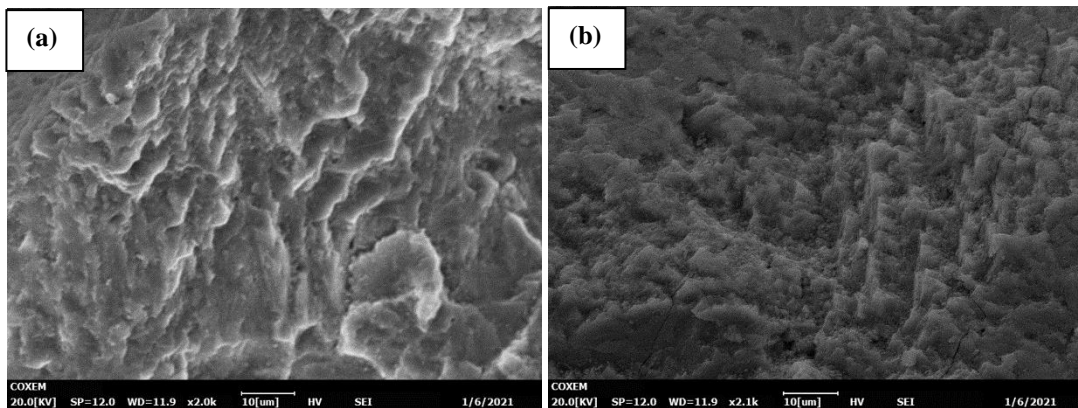
Fig. 5 - (a); (b) SEM images of eggshell activated carbon after adsorption with 2000x and 2100x magnification respectively

4. Conclusion

In conclusion, it is proven that eggshells can be used in improving water quality and it has a high efficiency to treat and remove Lead (Pb) river water. Both physical and chemical activated carbon have it owns advantages and disadvantages in treating water quality. Based on result obtained, the percentages removal of Pb by chemical activated carbon is 48.21%. It is higher compared to the percentages removal of Pb by physical activated carbon which remove 32.14%. Other parameter such as turbidity and pH also showed increasing adsorbent dosages from chemical activation carbon can produce a better result performance. This due to the chemical activated carbon that binds well with the pollutant. In consequence, filtration process using filtration vacuum pump has improved the water quality after adsorption. The turbidity removal efficiency shows an increasement data value especially for chemical activation carbon. It has the highest turbidity removal efficiency of 98.37% compare to the physical activation carbon. After

filtration, pH value and dissolved oxygen level increases to the normal range of 6.5 ~ 8.5 and above 5.0mg/L respectively. Several recommendation for better improvement are make the adsorbent as a recycle adsorbent and could be put in a pouch when used as it will be easier for handling especially if it is applied in a huge area.

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