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PLASTIC POLLUTION CONVERSION INTO ADSORBENTS FOR HEAVY METAL TREATMENT: OPTIMIZATION OF ISOTHERM METHODS AND ADSORPTION APPLICATIONS

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Abstract

Plastic waste in the ocean leaches chemicals, polluting marine environments. A recent study examined adsorption capacities of various media to address this concern. After a natural leaching process of three months, it was observed that activated carbon (AC) and a combination of activated carbon and zeolite (ZEO) demonstrated superior heavy metal removal efficiency. Specifically, 30g of activated carbon removed 91.72% of metals and a 10g mix of AC:ZEO achieved 90.38%. In contrast, 50g of zeolite removed 88.10%. Notably, the mixture of activated carbon and zeolite was especially efficient in removing copper. Additionally, the pH remained stable during these processes. The adsorption behavior was best described using the Langmuir isotherm model, outperforming the Freundlich model. This was evident from a higher correlation coefficient value for the Langmuir model across all tested media. The study emphasizes the potential of AC and AC:ZEO in addressing marine contamination from plastic waste.

***Keywords**: Adsorption; Heavy metals; Zeolite; Activated carbon; Sorption model; Plastic waste*

Introduction

Plastic is a human-made material that is produced from the factory basically in industry, the physical characteristic of plastic is strong, durable, lightweight, inexpensive and easy to produce due to the addition of additives in its production. The surrounding environment existing in the ocean attacks the plastic. Moreover, plastic is degraded when UV radiation is exposed either in seawater or under direct sunlight which makes the plastic become brittle and wrecked and become micro-plastic [1]. However, plastic degrades on beaches more quickly because of the high percentage of oxygen and direct sunlight exposure, which leads to structural integrity decline of the plastic [2, 3].

Generally, most heavy metals are not only dangerous to human beings but also for the environment. Mercury, copper, cadmium, zinc, lead, manganese, barium, arsenic and iron are metals that are common. In the samples from marine, these metals are often found in measurable levels [4]. Among pollutants, copper has attracted in this research because it is the most release in plastic made from polyethylene and polystyrene also exceeding the permissible value in Malaysia standard. There are several methods in the treatment of pollutants [5]. However, for lower heavy metal concentration and inexpensive process adsorption is more preferable technique and these composite media also have been widely used in treating a heavy

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metal. This research aims to study the removal of zinc, lead and copper from contaminated seawater with natural ZEO and commercial AC. The only copper exceeding above the permissible limit, thus a treatment process will be conducted to remove the heavy metal. However, there is less research in seawater treatment. These media which are activated carbon and zeolite have their classes either in hydrophobic or hydrophilic classes. Many of the techniques that can be done to determine this class include the angular contact experiments [6]. The solubility of a substance in water is significant: solubility in the sense of the chemical compatibility between the water and the solute. The more hydrophilic a substance the less likely it is to be adsorbed. Conversely, a hydrophobic substance will more likely be absorbed.

The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence [7]. Typically, zeolite attracts specific molecules and elements that fit their structure and to negative charges such as ammonium, potassium, calcium and magnesium. It is also found to be able to filter elements such as zinc, lead, copper and other heavy metals. Activated carbon from plant origin is porous, inexpensive and readily available for use as adsorbents, furnishing a large surface area to remove contaminants. Activated carbon is a widely used material for its wonderful adsorption capacities and properties in removing organic and heavy metal pollutants.

Adsorption is a preferable technique and has been widely used for treating industrial wastewater for heavy metals. But there is a lack of reference on seawater treatment. The increasing salt concentration yields an increase in adsorption capacity [8]. However, various previous studies have been proposed to interpret salt effects.

This research aims to study the removal of zinc, lead and copper from contaminated seawater with natural ZEO and commercial AC. The only copper exceeding above the permissible limit, thus a treatment process will be conducted to remove the heavy metal. However, there is less research in seawater treatment [9].

Experimental part

Materials

Leaching of heavy metal from plastic waste

Metal pollution is common in a marine system. It is found that the leaching of heavy metals such as zinc, nickel, copper, manganese, cadmium and lead from finished plastic products into the simulating solvents is hazardous to human health and can cause various health problems [5]. Table 1 shows the previous study that shows a certain type of plastic waste leach heavy metal [10].

Table 1. Type of plastic waste leach heavy metal

Types of waste	Cadmium	Copper	Zinc	Lead
PVC	0.42	3.81	4.3	2.67
PET	0.43	6.99	10.48	2.59

Adsorbent and chemical

Zeolite powder was formed after the grinding process. After the zeolite powder is grounded, the zeolite sample will be sifted to obtain a uniform size beyond 75 μm sieve size to obtain a uniform zeolite powder size. Then this absorbent material is dried in the oven at 110°C for 24 hours to remove the moisture content and cooled to room temperature before being stored. As for activated carbon that has been used in this study is the powder from the fraction of charcoal or normally known as PAC which means powdered activated carbon.

Methods

Batch adsorption experiments

Using 100mL of seawater sample and homogenized with 10, 20, 30 and 50g of single activated carbon, zeolite and combination of both adsorbent media. The initial and final concentrations were determined by inductively coupled plasma–mass spectrometry (ICP – MS). The glass bottles were sealed with Teflon and were mounted on a shaker. The shaker was placed at room temperature and 150rpm for a 1hour, 2hour and 3hour. The amount of metal adsorbed is calculated as follows as equation below:

$$q = \frac{C_i - C_f}{V_m} \quad (1)$$

Isotherms model

The approximation of the experimental data for metals adsorbed onto adsorbent media was done using by the isotherm's models of Freundlich model [11] and Langmuir model [12]. The following conditions are suggested by these models; Monolayer absorption is supposed by Langmuir model with a homogenous distribution of adsorption sites and sorption energies, with no interactions between the adsorbed ions or molecules. The equation of Langmuir has resulted as equation below:

$$q = \frac{qm \,.\, Kl \,.\, Ce}{1 + Kl \,.\, Ce} \quad (2)$$

By transforming the Langmuir equation (2) into a linear form, adsorption parameters were determined.

$$1q_e = 1Q_0 + 1Q_0 K_L C_e \quad (3)$$

The KL and qmax values were obtained from the intercept and slope of the Langmuir plot qe versus qe/Ce. The equilibrium parameter RL that is dimensionless can express the significant characteristics of the Langmuir isotherm. The equilibrium constant RL is constant and often referred to as equilibrium parameter or separation factor [9].

$$R_L = 11 + (1 + K_L C_0) \quad (4)$$

It is shown by the Freundlich model that lateral interactions between the energetic distribution of sites and adsorbed ions or molecules are heterogeneous. This is because there exists a diverse nature of the metal ions adsorbed: free, or hydrolyzed species and diversity of sorption sites. The equation of Freundlich is as below:

$$Q_e = K_f \, C_e^{1/n} \;, LogQ_e = logK_f \, logC_e \quad (5)$$

Results and discussion

Leaching of pollutant

After three months, the readings of lead and zinc was found to be 0.335 mg/L and 6.02 mg/L. Meanwhile, for copper, the value increases to 720 mg/L from 46 mg/L. It can be said that plastic waste contaminates the sample. However, only copper exceeding above the permissible limit, thus a treatment process will be conducted to remove the heavy metal. Table 2 shows the physiochemical properties of sea water sample.

Batch adsorption experiments

It is important to determine the optimum time for the removal of these media. As referring to Figure 1, it is experimented by keeping the dosage of adsorbent constant to 20g with the variation of contact time 60, 120 and 180 minutes. As to minimize the time, it takes 1 hour by considering other literature that most of the optimum adsorption time is 120 minutes. From, the result shows that 120 minutes is the optimum time for removal. After getting an optimum time removal, the batch adsorption process has been done. It is conducted by keeping the time constant to 120 minutes and increasing the dosage of the adsorbent media with 10, 20, 30 and 50g.

Table 2. Physiochemical properties of sea water sample after three months

Parameter	Value (mg/L)	Permissible value (mg/L)	Reference
pH	6.38	6.5 – 8.5	EPA, 1986
Lead, Pb208	0.335	8.5	Malaysia Marine Water Quality Criteria and Standard (IMWQS)
Copper, Cu63	720.00	2.9	Malaysia Marine Water Quality Criteria and Standard (IMWQS)
Zinc, Zn66	10.02	50	Malaysia Marine Water Quality Criteria and Standard (IMWQS)

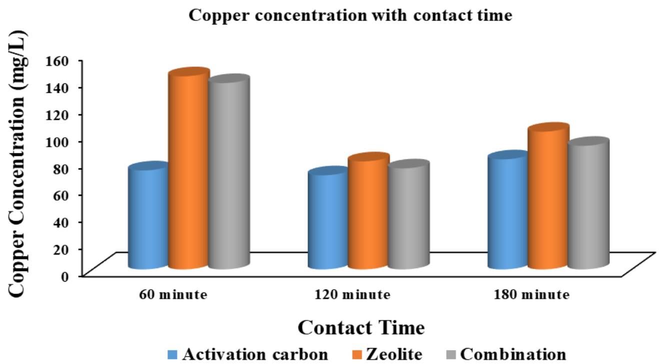

Fig. 1. Adsorption media in concentration of copper against contact time in three adsorbent media

Zeolite removal adsorption

Figure 2 shows that the percentage of the removal in 50g of zeolite adsorbent achieves the highest removal with 88.10% compared to other dosages. Meanwhile, the highest removal percentage for activated carbon is 91.72%. It is shown that the efficiency of the activated carbon to remove copper with only using 30g of adsorbent media. Also, the highest percentage of copper removal is 90.38% by using 10g of the combination of activated carbon and zeolite. It is shown that the combination of these two media can create a less adsorbent dosage with high removal efficiency.

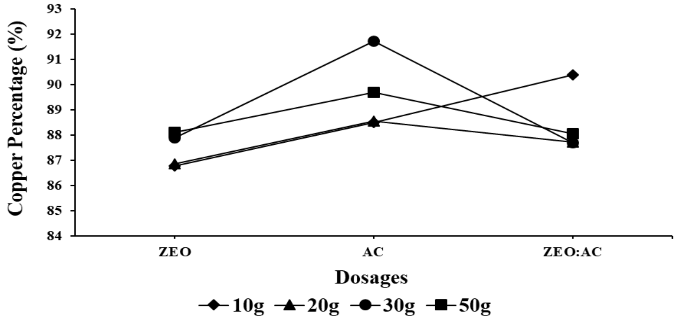

Fig. 2. Copper concentration against adsorbent media

Effect of pH

After performing the adsorption process for 120 minutes, the data of pH value was recorded. The initial pH of the raw seawater after soaking with plastic waste is 6.38. There is an increased value for all adsorbent media after the adsorption process. As for activation carbon the pH is 7.75. However, for zeolite and a combination of media, the pH value is higher than the activated carbon which is 7.81 and 7.80 respectively as illustrated in the Figure 3. This pH is within the range of permissible pH value in EPA, 1986 standard.

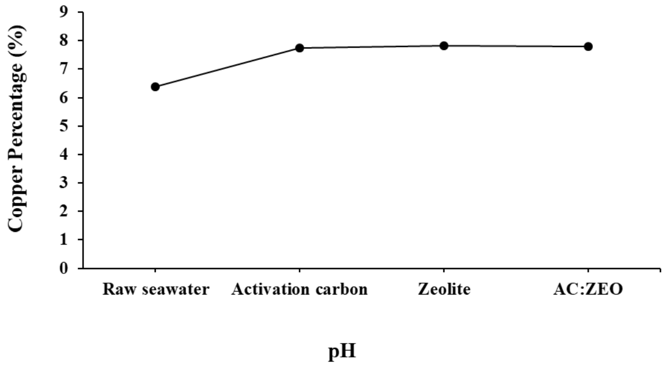

Fig. 3. Copper concentration against pH

Isotherm models

The data obtained during the experiments based on metal adsorption onto adsorbent media were used to determined by isotherms models of Freundlich (Freundlich 1906) and Langmuir (Langmuir 1916). Based on these two equations, the most appropriate correlation for the equilibrium curve has been established, it is important to show the design of the sorption system in the treatment process.

Langmuir and Freundlich model

Based on Figures 4 and 5 and Table 3. The coefficient of correlation value, R^2 is greater with the Langmuir than Freundlich. The model using Langmuir represented the best fitted of experiment data than the Freundlich isotherms, the R^2 value for zeolite, activated carbon and combination of both media is 0.9993, 0.9687 and 0.9901 respectively. It can be seen that the coefficient of correlation, R^2 for zeolite for the Langmuir model satisfactorily described the adsorption of copper onto the zeolite. Then, followed by activated carbon and a combination of both media Langmuir model satisfactorily describes the adsorption of copper onto zeolite. This indicates the monolayer coverage of copper on the surface of the zeolite.

Table 3. Parameter of linear representation of Langmuir and Freundlich for copper adsorption

Adsorbent	**Langmuir**				**Freundlich**	
	qm	K_L	R^2	R_L	n	R^2
Zeolite	1.716	0.012	0.9993	0.12	0.1	0.8305
Activated carbon	4.847	0.0135	0.9687	0.11	0.46	0.2555
Zeolite and activated carbon(combination)	4.527	0.018	0.9901	0.08	0.219	0.6093

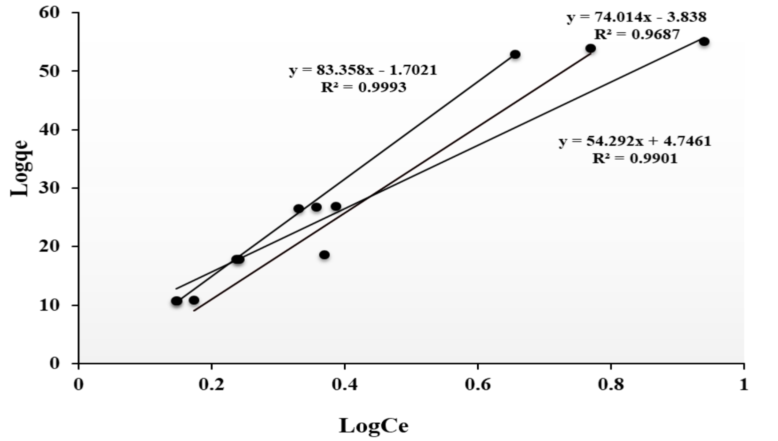

Fig. 4. Isotherm adsorption of copper for combination media with Langmuir curve fitted

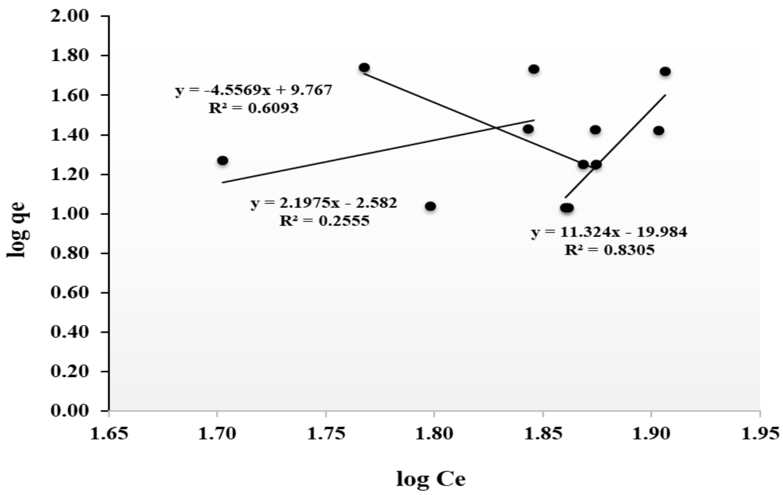

Fig. 5. Isotherm adsorption of copper in Freundlich curve fitted

The value of Langmuir equilibrium parameter RL for the combination of adsorbent was found to be 0.12, 0.11 and 0.08 respectively for zeolite, activated carbon and combination of both media. This value is within the range for favourable adsorption (0 < RL < 1) [9]. It is also can be seen that the Freundlich R^2 value from activated carbon was found to be 0.8305, 0.2555 and 0.6093 for zeolite, activated carbon and a combination of both media. It is indicated by this that the adsorption data was not adequately described by the Freundlich isotherm model.

Conclusions

The AC and mixture of these two materials (ZEO:AC) are more efficient at removal of heavy metals. By using a plastic-type of Polyethylene (PE) from mineral bottle waste and Polystyrene (PS) from food packaging the concentration of leaching heavy metal. From the result, the copper concentration was above the permissible limit, so the adsorption treatment is best to remove copper in the seawater solution. After the determination of heavy metal concentration, the parameter to be taken into account to determine the characteristics of the sample is pH. Meanwhile, the analysis of the selected heavy metal which is copper was conducted using an Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). The obtained adsorption results show that ability of removing heavy metal by activated carbon (AC) and combined media is higher than zeolite (ZEO) with a percentage of removal 91.72% in 30g AC and 90.38% in 10g of combination media. In contrast, the ZEO removal percentage was 88.10% in 50g. Hence, AC and a combination of these two media result in higher efficiency of copper removal. In addition, there are no changes in pH during these processes. To show an adsorption system’s design in removing copper, the establishment of the appopriate correlation is essential for the equillibirum curve. Freundlich and Langmuir isotherm models were used in fitting with the experimental data. The correlation coefficient is greater in case of the Langmuir model for AC, ZEO and combination of both media than Freundlich. Thus, the Langmuir was approptiate to describing these adsorptions.

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