Potential Small Scale Sea Water Reclamation from Plastic Waste Contamination

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Abstract. Plastics have become a potential source of contaminants in addition to being a universal environmental eyesore due to its global occurrence in every waste stream. Copper (Cu) adsorbed at high concentrations can be damaging to health. The optimum parameter conditions for the minimization of Cu from contaminated water due to plastic using coconut shell activated carbon were investigated. The influence of two experimental variables (adsorbent dosage and pH) were analyzed by the application of response surface methodology (RSM) and central composite design (CCD). Quadratic models were developed for efficiency improvement in treatment. The optimal removal settings attained were the adsorbent dosage of 26.58 g and 150rpm shaking speed, achieving 89.62% removal with a desirability value of 0.999. The predicted compared to the experimental data revealed that the experimental values are relatively in close agreement with the predicted results, which therefore define that the generated model has encapsulated the correlation between the adsorption variables and the response. The Langmuir model was best fitted to the experimental data.

1. Introduction
The increasing economic advancement is simultaneously accompanied by an increase in a waste generation which comprise among others synthetic polymers (plastics), which have become prevalent in all aspect of human activities, from coating and wiring, greenhouses, mulches, packaging, bags, kitchen utensils, films, covers, electric panels and containers. They constitute about 10% of the total waste generated around the world [1-3]. Most plastics are characteristically strong, durable, lightweight, and inexpensive. However, these plastic have some disposal issues, because they are not readily biodegradable hence pose inconvenience at sanitary landfills which generate leachates that constitutes of heavy metals and other pollutants [1,2,3,6,7]. Plastics also tend to leach some heavy metals with time into the environment. The mitigation of heavy metals has been of particular concern due to their toxicity and persistence, especially when in excess amounts in the environment[8-10]. The manufacture of the
plastic process is a source of contamination in the long run, for instance, heat stabilisers, plasticisers and slip agents comprise of trace metals, such as Lead, cadmium and zinc. Cadmium was an essential ingredient during polymer. These substances present a considerable risk to the aquatic environment when desorption occurs. Heavy metals such as Copper when adsorbed in excess amount has been reported to be a serious threat to life [4-5]. Similarly, Copper has been indicated to be released predominantly from plastics made from polyethylene and polystyrene and are found to be in excessive amounts compared to standards[6]. Desorption of metals by plastics portends another risk source to the environment. The plastics generally makeup approximately about 90% of the trash floating in the seas and is a potential hazard to organisms in these habitats which can act as well affect terrestrial life [3], as any negative impacts on the marine system invariably affect human life [11-14]. It is a common understanding that storm waters eventually end up in oceans, and as the storm flows it carries with it some debris and waste materials which often contain plastics because they are lightweight and easy to float in the runoff. Due to the rapidly increasing global plastic production and the consequential large plastic waste generation, Though the contamination impact on a larger scale is insignificant for now but could become a global threat to sustainability. Moreover, there are limited data on the effect of these anthropogenic physical and chemical waste material sources on marine fauna and flora. Different approaches exist for the treatment of contaminated water bodies, which comprise of physical methods, biological methods, chemical method and a combination of two or three of the mentioned methods to achieve an efficient treatment [15,18]. The physical-chemical methods have been renown in adsorption process for treatment of heavy metals by adsorbents. Adsorbents have been used worldwide in the form of zeolites and activated carbons which have waste biomass as a precursor for their production [10]. This study aims to investigate the potential application of adsorption process for a small scale treatment of saline water contaminated with heavy metals leached from plastics using coconut shell activated carbon (AC).

2. Materials and Methods
The AC was procured from Cabot Malaysia Sdn Bhd, Negeri Sembilan. The media was granular, and it was then washed clean with tap water and then rinsed several times with deionised water before drying in an oven for 24 hours at 105 °C. The dried sample was cooled to room temperature before being ground to a powder with the aid of mortar grinder (model Fritsch) and sieved using 75µm BS sieve. The seawater (synthetic) sample was prepared according to ASTM D1141-98 standard [19]. The available polymer plastics used were polyvinyl chloride (PVC), low-density polyethylene (LDPE), polystyrene (PS), polypropylene (PP), nylon, high-density polyethylene (HDPE) and polyethylene terephthalate (PET). The plastics were collected along the Straits of Malacca (1o41’1.82” N, 103o5’57.85”) and were shredded into particle sizes not more than 5mm. An equal proportion size of the plastics was taken and filled in a 4-litre capacity glass container up to about 3.5-litre mark, and then it was filled with the synthetic seawater and closed. The preparation was allowed to stand at ambient temperature for 90 days before testing. Concentrations measurement was done using atomic absorption spectrophotometer (AAS), model Perkin Elmer 800. Standard samples were used to calibrate the instrument before analysis.

3. Results and Discussion
3.1. Contaminant analysis
Table 1 shows the concentration of the pollutants after the leaching period of 90 days. The results show that leaching of the contaminant had occurred and the Copper exhibited the higher value (609.00 mg/L) which is above the recommended limit of 50 mg/L compared to Lead (0.223 mg/L) and Zinc (6.02 mg/L) as shown in table1.
Table 1. Physico-chemical properties of seawater sample after leaching.

| Parameter | Value (mg/L) | Permissible Value (mg/L) | Reference |
|-----------|--------------|--------------------------|-----------|
| Time, (min) | RCO % | pH | 6.38 | 6.5 – 8.5 | EPA, 1986 |
| Lead, Pb208 | 0.225 | | 8.5 | | IMWQS* |
| Copper, Cu63 | 609.00 | | 2.9 | | IMWQS* |
| Zinc, Zn66 | 6.02 | | 50 | | IMWQS* |

* Malaysia Marine Water Quality Criteria and Standard

Due to such a high concentration of the Cu present in the leached sample, treatment options were explored experimentally to have insight into its efficiency for future applications.

3.2. Batch experiment

Batch experiment optimisation on the parameters that influence the treatment was conducted according to the RSM approach, and performed at ambient temperature by using 100 ml contaminated sample in a conical flasks, and placed on an orbital shaker (Model Deiki), and varying agitation speed and dosage according to CCD array (table 3) [10,11]. To evaluate equilibrium conditions, samples were withdrawn at the end of 120 mins and tested for residual concentration. The range of factors used in the design was summarized in table 2.

Table 2. Codes and ranges of factors for the RSM design.

| Factor | Code | Low | High |
|--------|------|-----|------|
| Agitation speed (rpm) | X1 | 50 | 200 |
| Dosage (mg/L) | X2 | 10 | 50 |

The Cu in mg/L was determined using AAS. And experimental results were calculated based on percentage removal, according to equation (1).

\[
\% \text{Removal} = \left[ \frac{(C_i - C_f)}{C_i} \right] \times 100
\]

(1)

Where \(C_i\) and \(C_f\) are the initial and final Cu (mg/L) concentration.

Based on table 3, the experiments were carried out using various combinations of the two parameters, and the assay outcome indicated that the two parameters have a significant effect the adsorption efficiency of adsorbent in the remediation of Cu from the seawater. The assay results are presented in table 3, which indicated that a reasonably close agreement exists between the actual and predicted adsorption efficiencies for the removal of Cu. These adjoining agreement of the actual and predicted adsorption efficiency confirms the reliability of the model in predicting the performance of the adsorbent. The model performance prediction can also be explained by the coefficient of determination value R2, whose reliability increases as the value approaches one (1). However, R2 is not an indication of goodness of fit, because the value increases as the variable are increased irrespective of whether they have significant influence or not. On the other hand, an adjusted R^2 provides an adjustment to the R^2, such that only variables that have significant impact to the data increase the value of adjusted R^2,
therefore, when there is a large difference between the $R^2$ value and $R^2_{adj}$, it implies that nonsignificant variable terms were contained in the model. The comparison of the $R^2$ (0.9895) and the adjusted $R^2$ (0.9791) shows that there is a reasonable agreement between the values (see table 4) as well as significant goodness of fit.

Table 3. Design order for the real and coded values with the predicted and experimental results for Cu removal.

| Std | Factor X1  | Factor X2  | Adsorption efficiency % |
|-----|------------|------------|-------------------------|
|     | Actual Value | Predicted Value |                      |
| 1   | 50 (-1)     | 10 (-1)    | 64.68                  | 63.83   |
| 2   | 200 (1)     | 10 (-1)    | 77.76                  | 78.65   |
| 3   | 50 (-1)     | 50 (1)     | 52.49                  | 51.03   |
| 4   | 200 (1)     | 50 (1)     | 70.66                  | 70.95   |
| 5   | 50 (-1)     | 30 (0)     | 68.86                  | 71.17   |
| 6   | 200 (1)     | 30 (0)     | 89.72                  | 88.54   |
| 7   | 125 (0)     | 10 (-1)    | 78.55                  | 78.51   |
| 8   | 125 (0)     | 50 (1)     | 67.09                  | 68.26   |
| 9   | 125 (0)     | 30 (0)     | 87.86                  | 87.14   |
| 10  | 125 (0)     | 30 (0)     | 86.21                  | 87.14   |
| 11  | 125 (0)     | 30 (0)     | 88.48                  | 87.14   |

Table 4. Analysis of variance (ANOVA) results for response parameters.

| Final equations with coded factors | $R^2$ | $R^2_{adj}$ | Predicted $R^2$ | Adequate precision | Coefficient of variation |
|-----------------------------------|-------|-------------|-----------------|---------------------|--------------------------|
| $Y_{Cu} = +87.14 + 8.69*\chi_1 - 5.12*\chi_2 + 1.27*\chi_1*\chi_2 - 7.28*\chi_12 - 13.75*\chi_22$ | 0.9895 | 0.9791      | 0.9113           | 63.83                | 29.285                   |

Figure 1 presents a 3D response surface plot for the remediation of Cu response parameter due to the interaction of speed and dosage by the RSM. It can be discerned that all the parametric quantities exhibit the highest level towards the middle region, implying a significant interaction between the factors.

Figure 2 exhibits the chart of the predicted experimental values besides the actual experimental values, the predicted results were closely distributed to the actual responses, indicating that the generated regression model can adequately describe the correlation between the independent variables and their responses for the pollutant removal. The consistent straight-line distribution of data indicates that the error is insignificant within the confines of the operative parameters.
Figure 1. Response surface plot for Cu removal.

Figure 2. Predicted vs. Experimental values for Cu removal.

Figure 3 shows the numerical optimised data by the RSM using CCD. The optimum conditions of the parameter in the adsorption system for the removal of Cu was evaluated as 150 rpm of shaking speed and 26.58 g/L of the adsorbent dosage.

3.3. Adsorption equilibrium

The equilibrium information was determined by using a pair of isotherm models, Langmuir [20] and Freundlich isotherm models [21]. The response is exhibited in figure 4 and figure 5, respectively, which illustrates that the Cu adsorption was on the increase with increasing adsorbent concentration. The coefficients of determination and the isotherm factors are encapsulated in table 5. Based on the coefficient of determinations relatively close value’s and the solution depicted in figures 4 and 5, both models can positively interpret the experimental data. However the Langmuir model fitted reasonably better with the data of Cu adsorption onto the adsorbent, similar behaviour has been reported by many authors [10]. Hence, the adsorption phenomena are not confined to a monolayer coverage solely, but Cu ions are adsorbed heterogeneously as well onto the adsorbent surface by the Freundlich isotherm theory.
The constants in the Langmuir isotherm can be determined by plotting 1/qe versus 1/Ce. The constant KL in the Langmuir isotherm signifies the extent of interaction between adsorbate and the adsorbent surface. RL represents the separation factor, such that if 0<RL<1, then it is indicative that the adsorption process is favourable, and unfavourable if RL> 1, the system will be irreversible if the RL= 0, and it will also be linear if the RL= 1. Furthermore, the constants Kf and n of the Freundlich model are calculated respectively from the intercept and slope of the linear plot of log qe versus log Ce. The Kf stands for the Freundlich coefficient indicating the magnitude of adsorbed Cu ions per unit equilibrium concentration. The Freundlich constant 1/n provides information about adsorption intensity or surface heterogeneity. The calculated value of 1/n, as presented in table 5, suggest favourable adsorption of Cu onto the adsorbent.

The heterogeneous surface is formed of locations on the sorbent having different binding energies. When the concentration of adsorbent is lower in quantity in the bulk fluid, all of the viable sites are susceptible to adsorption process so that that sorbent surface will be saturated at a faster time scale. At the same time, at the higher adsorbent dose, the sorption declines due to the limited accessibility to higher energy sites as the lower energy sites have significantly been occupied.

| Isotherm models | Langmuir | Freundlich |
|-----------------|----------|------------|
| R² RL KL qm     | R² Kf n  |
| 0.9964 0.0481 0.0325 17.86 | 0.9804 94.973 0.30 |

4. Conclusions
The outcome of analysis using batch adsorption study by RSM and CCD, show that the optimal condition for shaking speed was 150rpm and dosage 28.67 yielding the treatment efficiency 99.76% of Copper removal. The predicted response was in close agreement to the experimental response. Hence the derived quadratic model encapsulates the interaction of the parameters and their responses. The Langmuir isotherm model fitted the experimental data better. The study forms part of ongoing research of contaminant effect of plastics to the environment.
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