REMOVAL OF PHENOL FROM PHARMACEUTICAL EFFLUENTS USING LOCUST BEAN POD AND BENTONITE CLAY

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ABSTRACT

The pharmaceutical industry uses large volumes of fresh water in the process of producing pharmaceutical products and this leads to the generation of large volumes of wastewater. This wastewater is usually profiled for contaminants such as hydrocarbons, dissolved solids and aromatic alcohols such as phenolic compounds which are hazardous to humans. Previous investigations have revealed that the wastewater could be treated by either conventional treatment technologies or biomass treatment systems. However, most of these conventional treatment technologies have higher energy consumption and capital requirement compared to the use of biomass treatment systems. Hence, the current study has employed the use of adsorbents derived from the hybridization of locust bean pod represented as category A, and clay represented as category B for the reduction of phenol from pharmaceutical industry wastewater. The best adsorbent (A3:B3) combination in ratio 1:1, reduced the phenol content to a permissible concentration level of 0.2662 mg/L. This was subjected to an optimization process using Box-Behnken of RSM and lower phenolic concentration of 0.211 mg/L was attained at operating conditions of 45 ºC of temperature, 70 min of contact time, and adsorbent loading of 0.1 g. This study has established that the combination of locust bean pod and clay adsorbent is promising for pharmaceutical wastewater treatment.

Keywords: Adsorption, Wastewater, Phenol, Locust bean pod, Clay

1.0 INTRODUCTION

Currently, the world is facing many challenges that are answerable to the growing human population. As a consequence, several environmental issues have resulted in greenhouses gases emissions and huge wastes generation of various origin (i.e. animal, agricultural, industrial, municipal wastes) Akpenpuun *et al*. (2016). If these wastes are disposed of without treatment, they may contribute to environmental hazards and for this reason, several waste treatment technologies such as thermochemical and biological ones amongst others are continuously emerging Atieh, (2014).

Environmental pollution simply implies the unfavourable alteration of our surroundings (local or global) by human actions, which directly or indirectly cause changes in energy patterns, radiation levels, chemical and physical constitution of organisms. (Azad *et al.*, 2015; Ferrari *et al.,* 2010). Water pollution is one of the most undesirable environmental problems in the world and it requires solutions. Pharmaceutical industries generate a lot of wastewater characterized by a number of contaminants, including acidic or dissolved solids, organic pollutant, phenol, etc. many of these contaminants are carcinogenic, mutagenic, and toxic to human beings, plants, and aquatic animals. Hence, their removal from aquatic wastewater becomes environmentally important. The need to provide environmentally friendly and cost-efficient methods for wastewater treatment prior to its discharge into the water bodies cannot be over-emphasized.

Although the chemical methods of treating these effluents are useful but not preferred as they typically release further toxic compounds as by-products (Azad *et al.*, 2015; Gupta *et al.,* 2009). The biological degradation methods have also been studied; however, they are generally quite sensitive to temperature amongst other complexities. Of all these treatment technologies, adsorption is currently believed to be a simple and effective technique for water and wastewater treatment with the technique success largely depending on the development of an efficient adsorbent.

Dissolved phenolic compounds that are present in industrial wastewater cause pollution of groundwater and owing to their harmful effect these compounds generate a serious problem in this type of water resources. Exposure to this type of chemical reagents, once they enter into the human body can cause damage to the nervous and respiratory systems, kidney and blood system Mahugo-Santana, (2009). Phenolic compounds have been classified as the top 45th in the list of priority hazardous substances by the United States Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta, Georgia, which require immediate treatment before disposal into the environment Atieh, (2014). Consequently, removing these organic compounds or reducing their concentration level to meet the threshold levels set by various environmental standards represents a big challenge. This has led to the search for novel and cost-effective precursors as adsorbents for their removals.

Clays are well known and familiar to mankind from the earliest days of civilization. Clay being readily available with low or no costs has a universal abundance alongside excellent sorption properties and potential for ion-exchanging capacities. This material is a strong candidate as an adsorbent and applies to several processes (Pollard *et al.,* 1992: Tilley *et al.,* 2014). Clays have been characterized by surface areas as high as 800 m^2g^{-1} leading to high adsorption capacities. The use of modified clays for adsorption capacity of phenolic compounds, aromatic compounds, pesticides and herbicides, and other organic contaminants have been comprehensively reviewed (Abdelrahman *et al.* 2019; Younes *et al.,* 2020).

On other hand, the African locust bean tree (*Parkia biglobosa*) is a vascular and hardwood perennial tree legume, belonging to the sub-family Mimosoideae and family Leguminosae. The pods commonly referred to as the locust bean pod are pink at the initial stage of development but become dark brown when matured. The pods are about 30 to 40 cm in length and usually contain about 30 seeds. Investigations on the pod have revealed that their activated forms have found excellent applications in several wastewater treatment processes such as drinking water clarification, and the removal of nitrogen and phosphorus (Mohapatra, *et al.* 2010; Nizami, *et al.,* 2017).

This study focuses on the use of locust bean (*Parkia biglobosa*) pods (LBP) and clay as adsorbent for the removal of phenol from pharmaceutical wastewater.

2.0 MATERIALS AND METHODS

2.1 Samples Collection and Preservation

The locust bean pods and bentonite clay used were collected within the University of Ilorin, Nigeria premises. The wastewater from a pharmaceutical industry in Ilorin was used for general physicochemical parameters and was stored in a pre-washed 5 L container preserved under a temperature condition of 4 ºC to guide against biological degradation of the sample. Samples for phenol analysis were stored in the pre-washed 100 mL bottles. All samples were properly labelled and kept under the temperature condition of 4 ºC prior to their transportation to the laboratory where further preservation in refrigerator continued before analyses.

2.1.1 Waste water analysis

0.5 mL of the wastewater sample was measured in a test tube using a micropipette, 2.5 mL of folin-C was added and 2.5 mL of Na_2CO_3, after which it was allowed a resident time of 30 min, then the absorbance of the mixture was determined by transferring the mixture from the test tube into a cuvette which was then placed in an already blanked spectrophotometer. The absorbance value was taken and the phenol concentration was obtained as 1.6123 mg/L. This value is higher than the permissible standards (i.e 0.2 mg/L for water fit for irrigation) and thus necessitating the need to treat the wastewater before discharge.

2.1.2 Preparation of locust bean pods

The locust bean pods were firstly separated from the seeds, then the pods were washed properly with distilled water to remove dirt and surface impurities, after which, it was oven-dried at 105 °C for 24 h, then it was cut into smaller pieces before being crushed in a grinder to powdery form, then it was sieved to remove oversized products. The weight before and after crushing gave the weight loss of the sample.

2.1.3 Preparation of bentonite clay

The bentonite clay was manually pulverized into little pieces. The crushed bentonite clay was washed with distilled water. Then the fine powder was dried in an oven at 105 ℃ for 4 h to remove moisture content and then sieved. It was calcined at temperatures; 700 , 800 and 900 ℃ for 2 h in a muffle furnace. The calcined samples were stored in airtight plastic bottles before adsorption experiments.

2.2 Adsorption Experiments

The batch adsorption process was carried out by introducing the adsorbent prepared at different conditions into a 250 mL conical flask containing 100 mL of the wastewater at different ratios. This process was repeated for all adsorbents. Thereafter, these set of flasks were placed in a thermostatic water bath shaker operating at a constant temperature of 35 ℃ and agitation of 120 rpm until the adsorption process attained an equilibrium contact time of 60 min. At the end of the adsorption experiment, the mixture was rapidly separated using filtration, then the phenolic content of each sample was checked using the same procedure reported earlier in section 2.1.1. Thereafter, an optimization study was carried out using Response surface methodology (RSM) in Design-Expert Software (version 10.0.1). Based on the initial preliminary experiment the following independent variables values were selected: 0.05, 0.1, and 0.15 g adsorbent loading, 25 , 35 , 45 ℃ temperature and 30, 50, 70 min contact time and fixed agitation of 120 rpm were used all through the experiments.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of the Wastewater

As shown in Table 1, water characterization was done on the wastewater collected i.e. phenol analysis. The phenolic content was found to be very high, which is the focus of this work. The results were compared with the limits for water disposed into a water body, given by the Nigerian standard.

Table 1: Preliminary Analysis of Wastewater

	Analysis Result	Nigerian Standard (for water fit for irrigation)
Phenol Concentration	1.6123 mg/L	0.2 mg/L

3.2.1 Preliminary adsorption experiments

After the initial analysis was carried out and the result known, the adsorption process was carried out and the filtrate was analyzed for the phenolic content. Table 2 illustrates the result for phenol analysis 1. The most efficient adsorbent was observed to be A3:B3 at a ratio of 1:1.

Table 2: Phenol Concentration after Preliminary Adsorption Experiments

LBP:Clay	A1:B1	A1:B2	A1:B3	A2:B1	A2:B2	A2:B3	A3:B1	A3:B2	A3:B3
1:1(mg/L)	0.8090	0.9840	0.7014	0.3045	0.3203	0.7694	1.3140	1.1893	0.2662
1:2(mg/L)	1.1285	1.3713	0.5707	1.2292	0.1195	1.1970	1.4100	1.1025	1.0284
2:1(mg/L)	0.7331	1.0156	1.0411	1.0591	1.1960	1.2639	1.1658	0.9470	0.7617

3.3 Optimization Studies

As shown in Table 3, a temperature range of 25 - 45 ºC, contact time of 30 – 70 min and adsorbent dosage of 0.05 – 0.15 g were imputed into Box-Behnken design, which provided the best likely combinations of variables. The adsorption process was carried out again based on the conditions provided by the Box-Behnken design. The most efficient adsorbent which reduced the phenolic content to a concentration of 0.211 mg/L from 1.6123 mg/L after the runs as suggested by the Box-Behnken design was found to be at the following operating conditions: temperature of 45 ºC, time of 70 min and adsorbent loading of 0.1 g.

Table 3: Results of the Optimization Studies using Box-Behnken Design

Runs	Temperature (◦C)	Time (min)	Adsorbent loading (g)	Phenol Concentration Remaining (mg/L)	% Removal of Phenol
1	25	30	0.1	0.768	52.37
2	25	70	0.1	0.642	60.18
3	35	50	0.1	0.261	83.84
4	35	50	0.1	0.251	84.43

5	25	50	0.05	0.812	49.64
6	35	50	0.1	0.321	80.09
7	35	70	0.05	0.391	75.75
8	35	30	0.15	0.312	80.65
9	45	50	0.05	0.237	85.30
10	35	50	0.1	0.250	84.49
11	45	70	0.1	0.211	86.91
12	35	50	0.1	0.247	84.68
13	25	50	0.15	0.612	62.04
14	35	70	0.15	0.242	84.99
15	45	30	0.1	0.250	84.49
16	35	30	0.05	0.332	79.41
17	45	30	0.15	0.231	85.67

3.3.1 Effect of adsorption parameters

Based on the Box-Behnken design, the phenol efficiency was affected by variations in temperature, time and adsorbent loading. The effect of these parameters was investigated using the Box-Behnken design of experiments. The experimental conditions for the experiments were adsorbent loading of 0.05, 0.1 and 0.15 g, contact time of 30, 50 and 70 min, and temperature of 25, 35 and 45 ºC in 100 mL of wastewater.

3.3.2 Effect of contact time

Figure 1 illustrates the effect of contact time on percentage phenol removal. It was observed that at 50 min, there was an optimal phenol removal of 70 % which decreased to 68 % as the contact time was increased to 70 min.

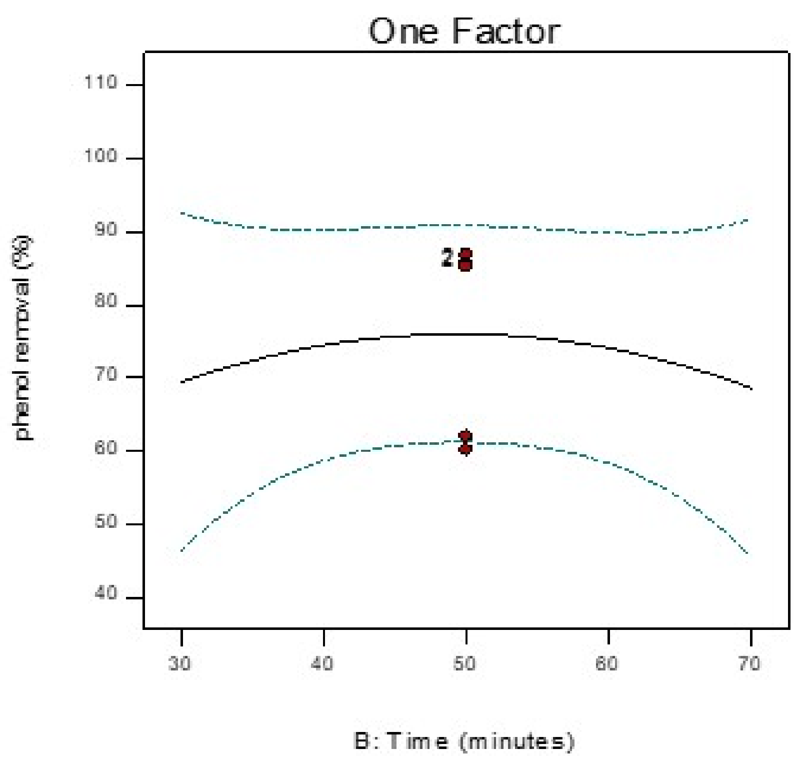

Figure 1: Effect of Time on Phenol Adsorption

3.3.3 Effect of temperature

Figure 2 shows the effect of temperature on phenol adsorption. It was observed that the optimal phenol removal of 90 % was achieved at a temperature of 25 ºC, but reduced to 80 % as the temperature was increased to 35 ºC. Further increase in temperature to 45 ºC increased the percentage removal of phenol to 90 %.

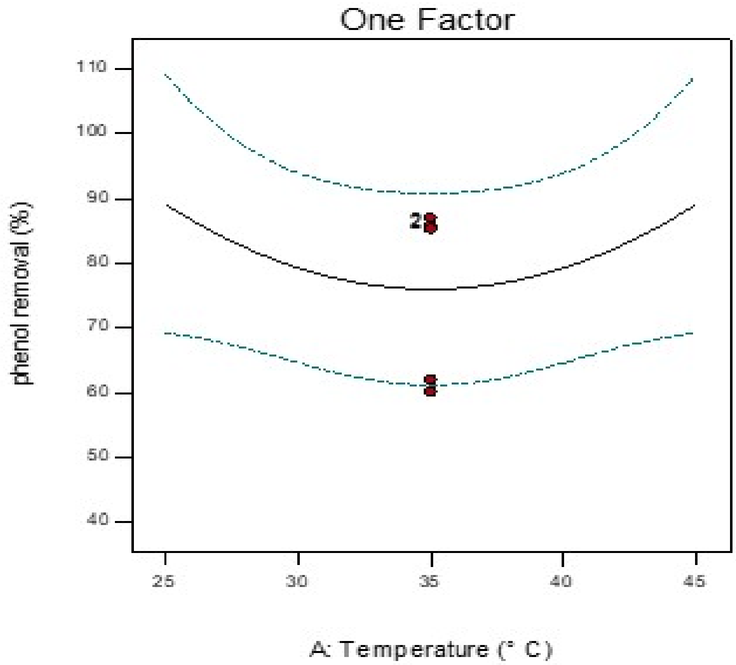

Figure 2: Effect of Temperature on Phenol Adsorption.

3.3.4 Effect of adsorbent loading on phenol adsorption

Figure 3 illustrates the effect of Adsorbent loading on phenol adsorption. It was observed that phenol removal increased as the adsorbent loading increases and Optimum removal of 75 % was achieved using an adsorbent dosage of 0.074 g.

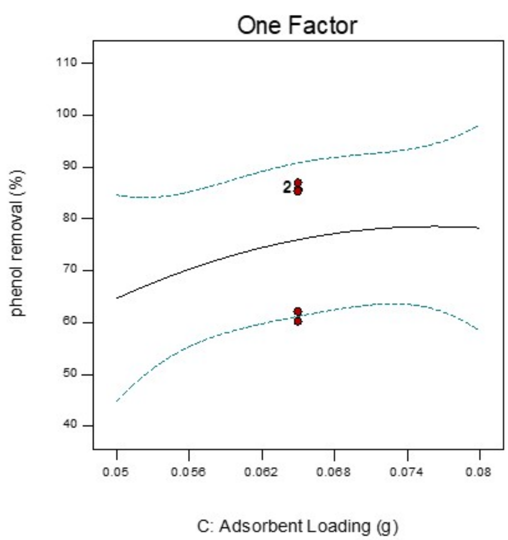

Figure 3: Effect of Adsorbent Loading on Phenol Adsorption

3.4 Response Surface Plot for Phenol Adsorption

Response surface plots of a combination of the factors were also generated to elucidate any combinatorial effects of the factors on the amount of phenol removed by adsorption. The plots re-emphasize the information on the one-factor plots. As shown in Figure 4, at 25℃, between adsorbent loading of 0.05 g and 0.08 g, the phenol removal % increases significantly to 90 %, however, at adsorbent loading of 0.08 g the phenol removal % decreases to about 75 % and rises again at 39 ℃ attaining more than it initial maximum value. As illustrated in Figure 5, between adsorbent loading of 0.05 g and 0.08 g and contact time of 30 min, the phenol removal % increased. However, at adsorbent loading of 0.08 g, the percentage phenol removal decreases as contact time was increased from 30 to 50 min. Also shown in Figure 6, at 25℃, between contact time of 30 to 70 min, the percentage phenol removal increases significantly to 80 %, however, at a contact time of 70 min, the percentage phenol removal decreases significantly to about 69 % at 35 ºC and further increases slightly with an increase in temperature from 35 to 45 ℃.

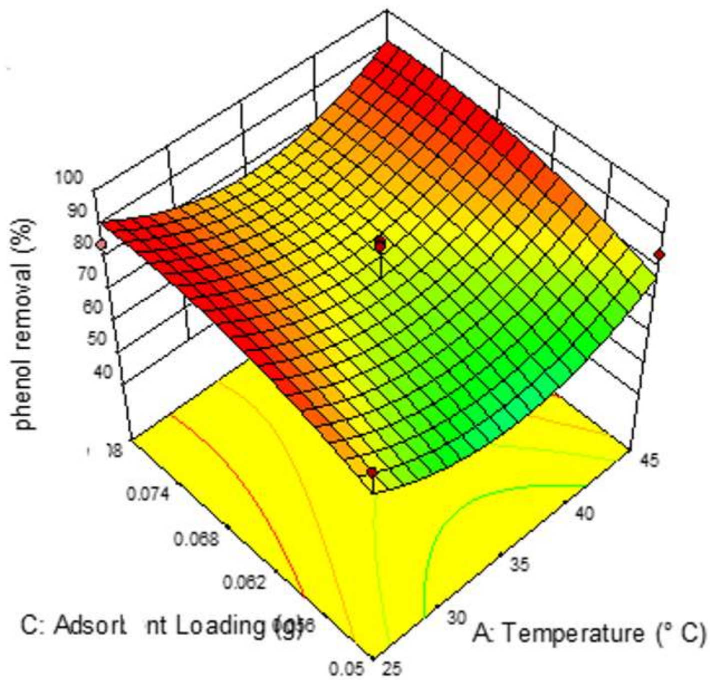

Figure 4: Response Surface Plot for the Effect of Temperature and Adsorbent Loading (g) on Phenol Removal (%) Using Locust Bean Pod and Bentonite Clay Composite as Adsorbent

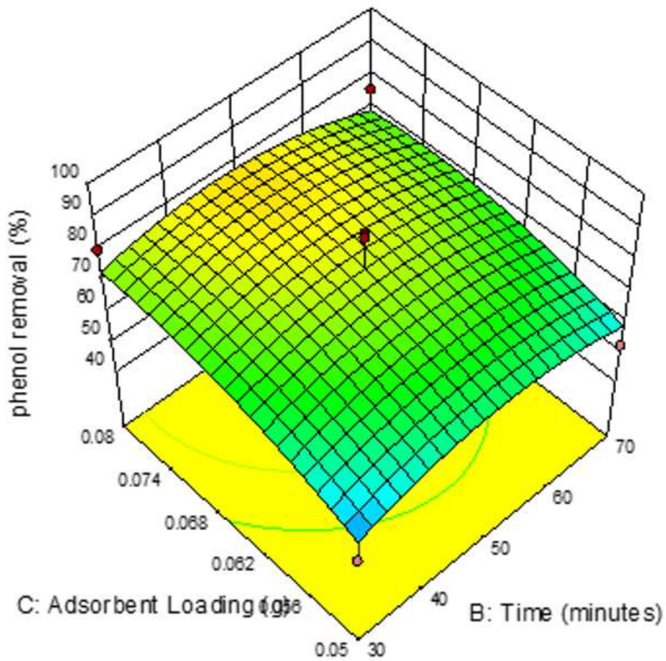

Figure 5: Response Surface Plot for the Effect of Adsorbent Loading (g) and Time (min) on Phenol Removal (%) Using Locust Bean Pod and Bentonite Clay Composite as Adsorbent

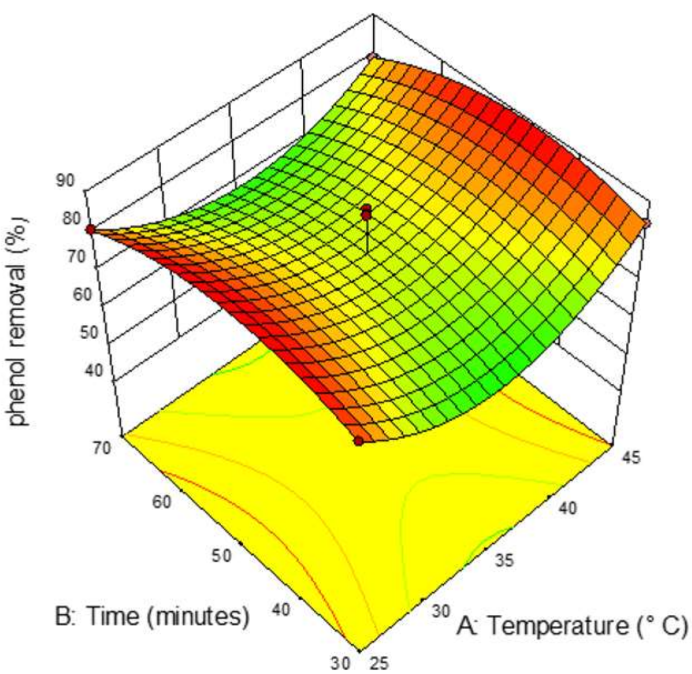

Figure 6: Response Surface Plot for the Effect of Time (min) And Temperature (℃) on Phenol Removal (%) Using Locust Bean Pod and Bentonite Clay as adsorbent

4.0 CONCLUSION

This study showed that locust bean pod and clay composite adsorbent has the potential to effectively remove phenol with an efficiency of 86.91 % from aqueous solutions and can be used as a substitute for other expensive adsorbents. The phenol content in the wastewater was reduced to the permissible level fit for irrigation reuse.

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