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REMOVAL OF COD FROM PHARMACEUTICAL WASTEWATER USING SUGARCANE BAGASSE AND BETONITE CLAY

F. A. Aderibigbe [1,*], I. A. Mohammed [1], S.I. Mustapha [1], H.B Saka[2], M. K. Amosa[3], A. L. Adejumo [4], R. U. Owolabi[5] and A.B Shittu[1]

[1] Department of Chemical Engineering, University of Ilorin, Ilorin, Nigeria
[2]Quality Control Department, Segmax Oil Nigeria Limited, Kere-Aje, Ogbondoroko, Kwara State, Nigeria
[3] Waste Management Unit, HSE Division, Department of Petroleum Resources, 7, Sylvester Ugoh Crescent, Jabi, Abuja-FCT, Nigeria.
[4] Department of Chemical Engineering, Osun State University, Osogbo, Nigeria
[5]Department of Chemical Engineering, University of Lagos, Lagos, Nigeria.
* **Corresponding author:** Dr. Aderibigbe Fatai Alade, +2348033822123, aderibigbe.fa@unilorin.edu.ng

ABSTRACT

Water pollution is a major concern because of its negative effect on humans, plants and aquatic creatures. The concentration of COD in the wastewater is an indication of its impurity. Various pollutants impart COD to the water; hence, its removal is synergistically adequate for the removal of these impurities (organic and inorganic). The cost of adsorbents and the problems associated with their regeneration had led to the search for alternate low-cost adsorbents. This study involved the treatment of wastewater obtained from a pharmaceutical industry in Ilorin, Nigeria using sugar-cane bagasse and clay as adsorbents for the reduction of COD to a permissible level set by the World Health Organization for reuse as irrigation water for agricultural activities. For the treatment process, 27 experimental runs were designed, executed and analyzed to identify the best operating condition that brings about the lowest residual COD concentration. An optimum COD removal response of 97.8 % was obtained at adsorption conditions of adsorbent loading 0.75 g/mL, temperature 45 °C and retention time of 120 min. The developed composite adsorbent reduced the COD content to a permissible level.

Keywords: Adsorption, Pharmaceutical Wastewater, COD, Sugar Cane Bagasse, Clay

1.0 INTRODUCTION

Water pollution is one of the serious problems that the world is facing in this era. In Ilorin metropolis of Nigeria, the major problem leading to water pollution is the increasing population, industrialization and urbanization. Collection, treatment and disposal of domestic and industrial wastewater are serious issues to be handled to prevent environmental degradation. Industrial wastewater usually contains various compounds such as: phenol, chromium, suspended solids and dissolved organic compounds and these compounds present in water leads to an increase in the COD of that water body and it is necessary that it should be treated to an environmental permissible level Olafadehan and Aribike, (2000). It was reported by Ali, *et al.* (2020) that composite offers great potential as a low-cost and effective biocomposite material for the organic dyes removal and COD reduction from water/ wastewater. Removal of chemical oxygen demand (COD) from wastewater has been of considerable interest for several decades, but detailed mechanisms are poorly recognized Ziqi, *et al.* (2019)

With the rapid growth of pharmaceutical needs, large quantities of wastewater containing products, raw materials, solvents and detergents from complex manufacturing processes are generated. Martínez, (2017). Even conventional biological wastewater treatment facilities produce effluent organic matter with high chemical oxygen demand (COD), salinity, color, limited biodegradation, and toxicity, which increase the potential risk to receiving waters and human health. Kaya, (2017).

All the pharmaceutical industries produce large number of organic materials and antimicrobials in their wastewater, so it is important to treat the effluents to meet environmental standards before discharge. Adsorption is a wastewater purification technique for removing a wide range of compounds from industrial wastewater. Adsorption involves the ability of solid particles to attract to their surfaces gas molecules or solutions with which they are in contact Tilley, *et al*. (2014).

Chemical oxygen demand (COD) is the amount of oxygen required for the chemical decomposition of organic matter and biological oxygen demand (BOD) is the amount of oxygen required for the biological decomposition. The COD concentration level of a wastewater is indicative of its purity. Various pollutants impart COD to the water. The treatment of this wastewater is for the ultimate goal of meeting the required standard set by the World Health Organization WHO for discharge into water bodies without harming the aquatic life Ayorinde, (2019). Chemicals are broken down using strong oxidizing agents and these chemical reactions create what is measured in the laboratory as the chemical oxygen demand (COD). The BOD test measures the oxygen demand of biodegradable pollutants whereas the COD test measures the oxygen demand of oxidizable pollutants.

An adsorbent made from the hybridization of Bagasse and Bentonite clay was used for the treatment of wastewater for the removal of pollutants present in the water, and dissolved organic substance which leads to the reduction of COD, color and Heavy metal contents. Clays are well known and familiar to mankind from the earliest days of civilization. Clays are not just relatively cheap and abundant, they possess high sorption properties and potential for ion-exchange, and are strong adsorbents Shichi and Takagi, (2000). Clays also have large surface areas ranging up to 800 m^2g^{-1}, which adds to their high adsorption capacity Okuda, *et al.* (2000). Bagasse is fiber remaining after the extraction of the sugar-bearing juice from sugarcane. Bagasse is also the fibrous residue left over after cane milling with 45-50 % moisture content consisting of a mixture of hard fiber, with soft and smooth parenchymatous (pith) tissue with high hygroscopic property. Bagasse contains mainly cellulose, hemi cellulose, pentosanes, lignin, Sugars, wax, and minerals Loh, *et al.* (2013). Hence, this study explored the potential of using sugarcane bagasse-clay composite as adsorbent in reducing the COD content of pharmaceutical wastewater.

2.0 MATERIALS AND METHODS

2.1 Samples Collection and Preservation

The sugar cane bagasse and bentonite clay used were collected within Ilorin in Kwara State of Nigeria. The wastewater from a pharmaceutical industry in Ilorin was used for general physicochemical characterization and was stored in the pre-washed 5 liters keg which was preserved in the refrigerator; samples for COD analysis were stored in the pre-washed 100 mL bottles. All samples were properly labeled and kept in ice chest cooler prior to their transportation to laboratory where further preservation in refrigerators continued before analyses.

2.1.1 Preparation of sugarcane bagasse

The *saccharum officinarum* (sugarcane) bagasse was collected from Ilorin market. The bagasse was washed with distilled water to remove dirt and surface impurities, and then oven-dried at 105 °C for 24 h. They were then cut into smaller pieces and placed in a miller which consists of a series of rollers that crushed them. They were then placed in separate crucibles and carbonized in a furnace at varying temperatures of 350, 425 and 500 °C. The furnace was allowed to cool for 24 h before the carbonized bagasse were removed and sieved to obtain 5-50 μm grain size for material that passes through sieve number 200. The sieved materials were then impregnated in phosphoric acid for 12- 18 h to become activated carbons. They were then washed with distilled water, spread on tray at room temperature to be drained. The product was then dried in an oven at a temperature of 105 °C for 3 h and kept in desiccators to cool.

2.1.2 Preparation of clay

The clay was put in separate crucibles and calcined in a furnace at varying temperatures of 700, 800 and 900 °C. The furnace was allowed to cool down for 24 h before the charred were removed. The charred clay was impregnated in phosphoric acid for 12-18 h to become activated carbons. They were then washed with distilled water, spread on trays at room temperature to be drained. The product was then dried in an oven at temperature of 105 °C for 3 h and kept in desiccators to cool down.

2.2 Adsorption Experiments

Due to use of two adsorbents (sugarcane bagasse and bentonite clay), ratios of 1:1, 1:2, 2:1 were varied in relation to the adsorbent loading of 1 g/100 mL of sample water. Both adsorbents were varied at temperatures of 350, 425 and 500 ℃ for sugarcane bagasse (SB) and 700, 800 and 900 ℃ for Bentonite clay (BC). The temperatures of each adsorbent were combined in the ratios above reaching a sum of 27 samples in a conical flask. The mixture of adsorbents and wastewater sample in the conical flask were agitated at 100 rpm with magnetic stirrer for 1 h to ensure equilibrium.

The combination was as thus, 350-900 ℃, 425-900 ℃, 500-900 ℃ of SB to BC respectively and at a ratio of 1:1 to give 0.5 g each for both materials (sugarcane bagasse and clay), 350-900 ℃, 425-900 ℃, 500-900 ℃ at a ratio of 1:2 to give a mass of 0.33 g for sugarcane bagasse (SB) and 0.67 g for Bentonite clay(BC) and 350-900 ℃, 425-900 ℃, 500-900 ℃ at a ratio of 2:1 to give a mass of 0.67 g for sugarcane bagasse (SB) and 0.33 g for Bentonite clay(BC) to give a total of 9 samples.

The next batch was then, 350-800 ℃, 425-800 ℃, 500-800 ℃ of SB to BC respectively and also a ratio of 1:1 to give 0.5 g SB and 0.5 g BC, 350-800 ℃, 425-800 ℃, 500-800 ℃ at a ratio of 1:2 to give a mass of 0.33 g SB and 0.67 g BC and 350-800 ℃, 425-800 ℃, 500-800 ℃ at a ratio of 2:1 to give 0.67 g BC and 0.33 g BC to give other sets of 9 samples.

And for the final batch, 350-700 ℃, 425-700 ℃, 500-700 ℃ of SB to BC respectively and at a ratio of 1:1 to give 0.5 g SB and 0.5 g BC, 350-700 ℃, 425-700 ℃, 500-700 ℃ at a ratio of 1:2 to give a mass of 0.33 g SB and 0.67 g BC and 350-700 ℃, 425-700 ℃, 500-700 ℃ at a ratio of 2:1 to give 0.67 g SB and 0.33 g BC to give other sets of 9 samples.

After this period of adsorption process, the filtrates gotten after the filtration were analyzed for residual COD and the removal percentages recorded. The conditions of the most efficient result from the adsorption process were planned to form the basic boundaries for optimization using Box- Behnken design.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of the Wastewater

The pharmaceutical industry wastewater was characterized of COD, Phenols and Heavy metals analysis and the results were compared with the concentration thresholds limits for irrigation water given by world health organization (WHO). It was observed that the results of the analysis were higher than the permissible limits proposed by World Health Organization (WHO) as shown in Table 1 and thus, the reason for this project, aimed at the removal of organic waste in water leading to the reduction of COD in the water sample using cheap composite adsorbent (sugarcane bagasse and bentonite clay).

Table 1. Raw Water Characterization

	Analysis results	WHO benchmark for irrigation water
COD	3926.4 mg/L	250 mg/L
Phenols	1.6123 g/mL	0.001 g/mL
Heavy metals- ZN	0.10	0.01
Fe	0.46	0.30
Pb	0.01	0.01

3.2 Batch Adsorption Results

A set of three batches was designed for the batch adsorption process to make a total number of 27 samples of which COD analyses was carried out on each sample. Table 2 shows the combination of the temperatures and mass ratios of the adsorbent (Sugarcane bagasse and Bentonite Clay) and the result of the COD analyses. After the adsorption process, the sample was taken to the laboratory for analysis and it was observed that there was a considerable concentration reduction of the COD from the initial value with the most efficient adsorbent being at operating conditions of 500-900 ℃ calcination temperature range, mass ratios of 1:2 as shown in Table 2 at constant adsorption temperature of 35 ℃ and agitation of 100 rpm. The condition of the best adsorbent was then used in the optimization studies as shown in Table 3. The COD analysis carried out after the optimization studies showed an optimum removal of 97.8 % at conditions of 45 ºC of temperature, 120 min of time and 0.75 g of adsorbent loading as shown in Table 3

Table 2 COD Result from Batch Adsorption Process

Mix Ratio	Calcination Temperature (°C)								
	350-900	425-900	500-900	350-800	425-800	500-800	350-700	425-700	500-700
1:1	381.6	401.8	386.4	401.1	396.2	421.8	352.7	382.3	421.2
1:2	327.8	423.6	326.4	397.8	388.0	401.3	335.6	352.8	389.7
2:1	350.1	489.6	402.4	421.6	381.4	426.4	350.1	398.7	378.2

Table 3 Adsorption Condition and COD Result from the Box- Behnken Design

Runs	Temperature (°C)	Time (min)	Adsorbent loading (g)	COD residual (mg/L)	Removal %
1	45	75	1	300.2	92.4
2	45	120	0.75	86.4	97.8
3	35	120	1	212.7	94.6
4	25	120	0.75	505.6	87.1
5	25	75	1	393.6	89.9
6	25	30	0.75	601.6	84.7
7	35	30	1	323.5	91.8
8	35	75	0.75	310.1	92.1
9	45	30	0.75	153.6	96.0
10	25	75	0.5	777.6	80.2
11	35	30	0.5	380.2	90.3
12	35	75	0.75	289.2	92.6
13	35	120	0.75	280.6	92.9
14	35	120	0.5	305.2	92.2
15	45	75	0.5	313.6	92.0
16	35	75	0.75	280.5	92.9
17	35	75	0.75	278.2	92.9

3.3 Response Surface Plot

As shown in Figure 1, it was observed that on moving from the least adsorbent loading of 0.5 g to 1.0 g, there was an increase up to 90 % COD removal at 25 ℃. Also, 95 % COD removal was achieved at 0.5 g and between 25 to 40 °C. Figure 2 compares the effect of time and temperature with COD percentage removal. At 30 min, between 25 to 40 ℃, the COD percentage removal increased from about 80 to 95 %. Also, at 120 min, the COD percentage removal increased from 80 to 98 % between 25 ℃ to 40 ℃. Figure 3 shows that at 1.0 g between 30 to 120 min, the COD percentage removal increased from 92 to 95 %.

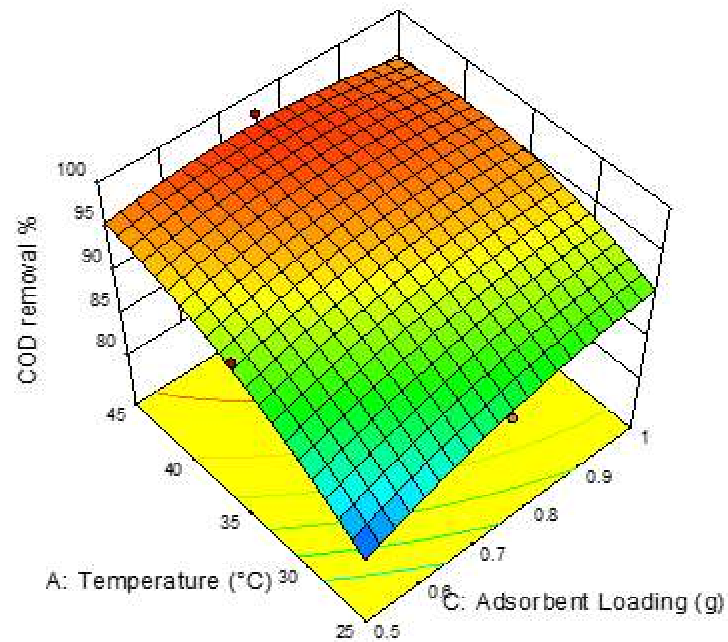

Figure 1: Response Surface Plot Showing the Effect of Temperature (°C) and Adsorbent Loading (g) On COD Removal% Using Sugarcane Bagasse and Clay Composite as adsorbent

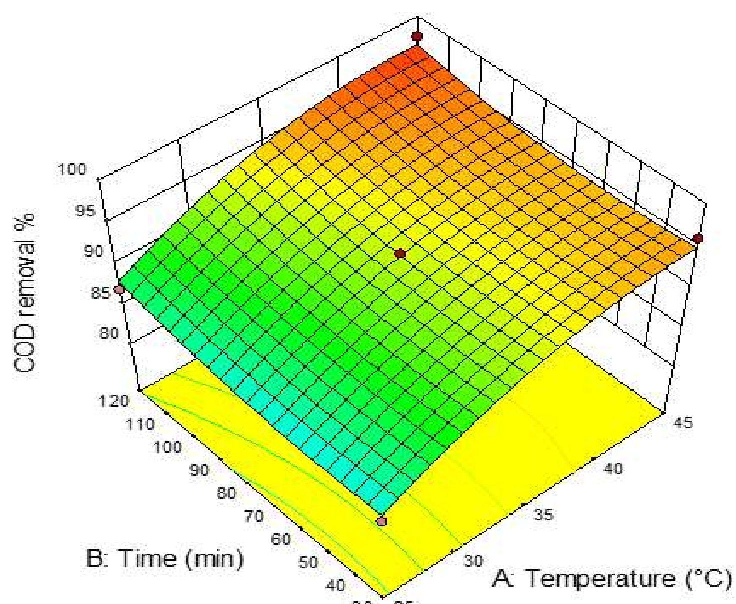

Figure 2: Response Surface Plot Showing the Effect of Temperature (℃) and Time (min) on COD Removal% using Sugarcane Bagasse and Clay Composite as Adsorbent.

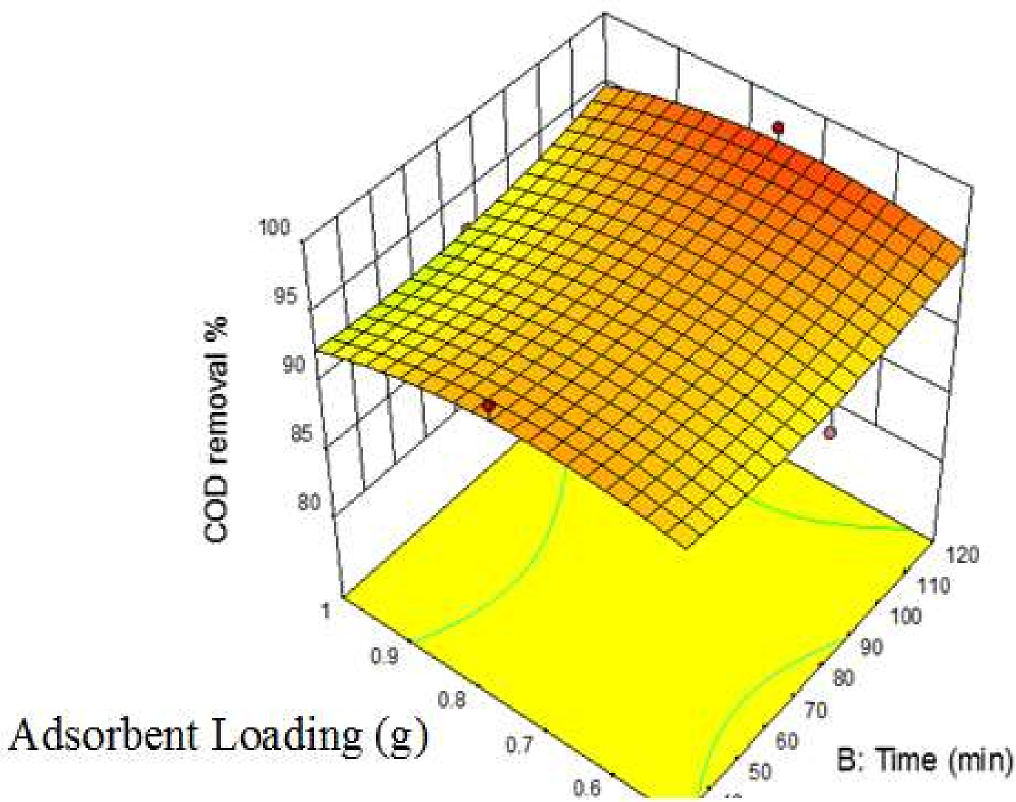

Figure 3: Response Surface Plot Showing the Effect of Time (min) and Adsorbent Loading (g) On COD Removal% Using Sugarcane Bagasse and Clay Composite as Adsorbent.

3.4 Effects of Each Variable on COD Removal

Temperature, time and adsorbent loading were plotted against COD removal % in order to find out the relationship and effect of each factor on the efficiency of COD removal. Figure 4 shows the graph of time (min) plotted against COD percentage removal in order to evaluate their relationship, and it was observed that there was only a little increase in COD percentage removal with increase in time from 30 to 120 min. In this study, varying temperatures of 25, 35 and 45 ℃ was used and the graph shows the point of peak temperature of 45 ℃ as well as the least temperature of 25 ℃ and it was shown that there is a significant increase in COD percentage removal as the temperature increases as shown in Figure 5. The effect of adsorbent loading showed that the only noticeable increase in COD percentage removal was observed at 0.75 g as shown in Figure 6.

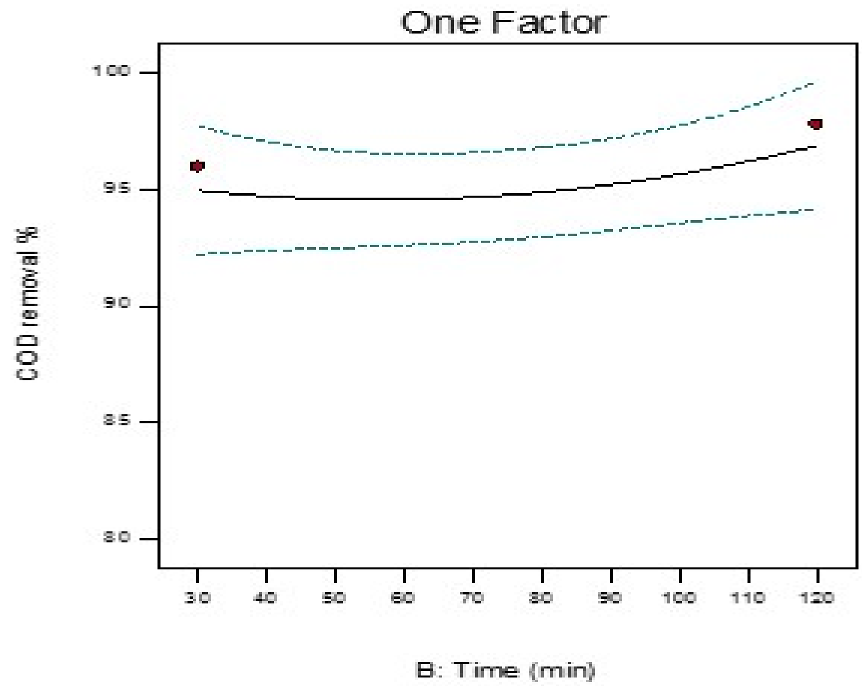

Figure 4: Effect of Time (min) on Percentage COD Removal **(%)**

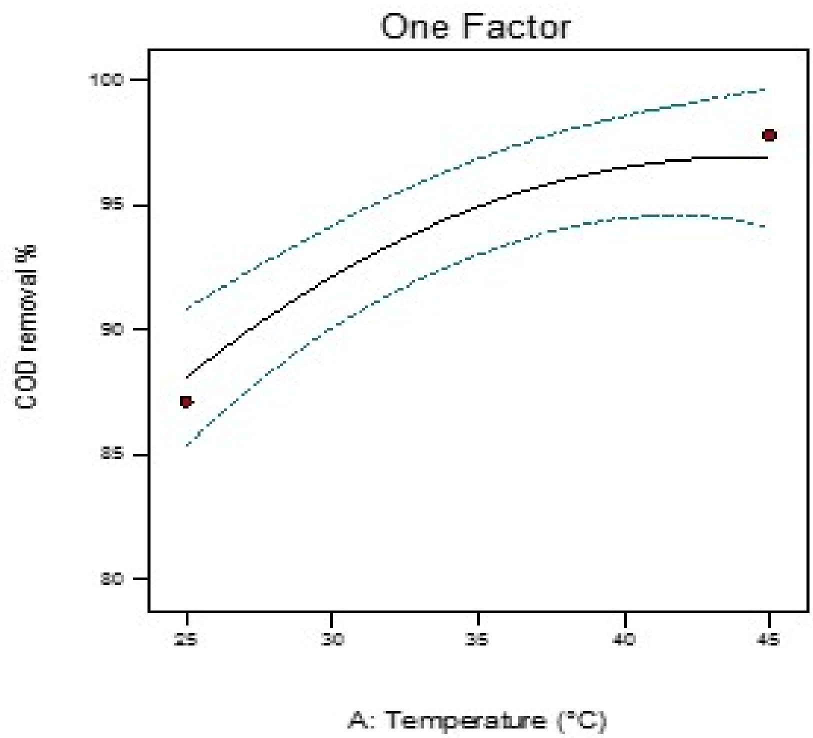

Figure 5: Effect of Temperature (°C) on Percentage COD Removal (%)

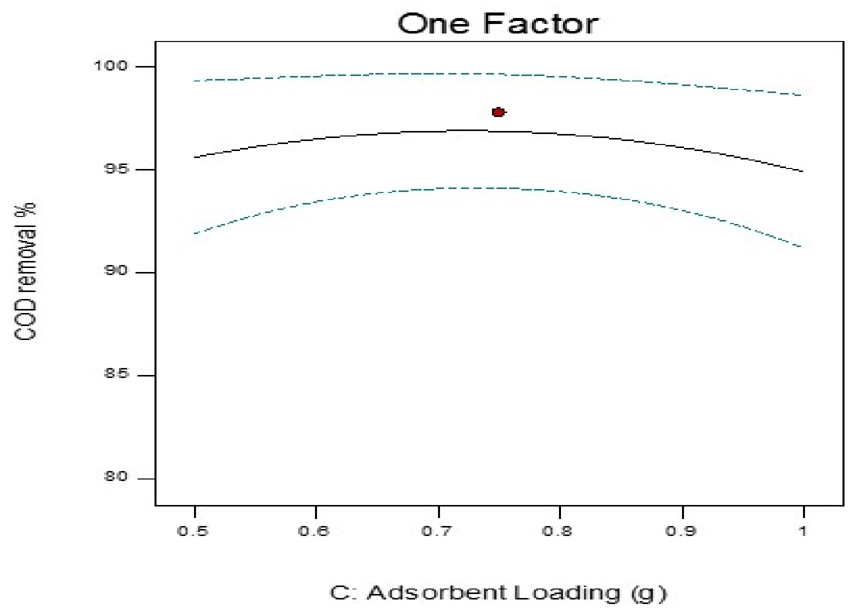

Figure 6: Effect of Adsorbent Loading (g) on Percentage COD Removal (%)

4.0 CONCLUSION

This study showed that hybridized sugarcane bagasse and bentonite clay are potential adsorbent materials that have the capacity to effectively reduce chemical oxygen demand (COD) concentrations in aqueous solutions, and the materials can be used as substitute to other expensive adsorbents. An optimum percentage removal (97.8%) of COD was achieved using Box-Behnken design method.

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