



Optimization of Process Parameters for Adsorption of Phenol from Aqueous Solution Using Unripe Plantain Peels Activated Carbon

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

The study investigated the optimum conditions for the adsorption of phenol from aqueous solution using plantain peels activated carbon. Low-cost adsorbents were produced from unripe plantain peel by both physical and chemical activation processes at carbonization temperature of 400°C for 2 hrs. The chemical activated unwashed carbon (UPPAC) was activated with ZnCl₂ at impregnation ratio of 1:2 while the physical activated carbon (NAPPC) was not impregnated with any chemical. The produced carbons were characterized in terms of surface area, porosity, iodine number, ash content, carbon yield and pH. The result showed that the physicochemical properties of UPPAC were significantly higher than those of NAPPC having surface area of 957 m²/g, porosity of 32.2%, iodine number of 736 mg/g, ash content of 9.02% and carbon yield of 65%. The optimum conditions for the adsorption of phenol from the aqueous solution using UPPAC was based on three variables, contact time, adsorbate concentration and adsorbate pH. A total of 27 experimental runs were used to study the effects of these parameters using the response surface methodology (RSM) as the experimental design. The result of the batch adsorption was found to increase with initial adsorbate concentration and contact time but decreases with increase adsorbate pH. UPPAC achieved optimum percentage removal of 91% at initial phenol concentration of 21 mg/g and its removal was pH dependent (pH 2), better at acidic conditions. The amount adsorbed also increased with contact time until equilibrium was reached at 150 mins. Thus, chemically activated unripe plantain peel can be used for the removal of phenol from aqueous solution.

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1. INTRODUCTION

Phenolic contaminants are usually found from industrial effluents including pharmaceuticals, plastics, insecticides, paints, petrochemicals and many others [1]. Its presence in wastewater or drinking water even in low concentration, is a great concern due to its toxicity and carcinogenicity. Phenols impart taste and odour to water and are toxic to aquatic life even in very low concentrations [2]. The discharge of phenol and its derivative compounds to the environment without proper treatment may lead to serious health risks to human, animal and aquatic system [1]. Phenol has been designated as a priority pollutant by the US Environmental Protection Agency (EPA) and the National Pollutant Release Inventory (NPRI) of Canada [3,4,5]. According to world health organization the permissible limit of phenol in drinking water is 1 µg/l while Environmental Protection Agency (EPA) has set a limit of 0.1mg/l of phenol in wastewater [4]. Hence, it is essential to ensure that phenols in wastewater are treated to an acceptable limit before being discharged into water ways. Conventional methods for removal of phenol from water include distillation, adsorption, extraction, chemical oxidation, electro chemical oxidation and many others [5]. Among these methods, adsorption is worthy economical and effective [6]. Various adsorbents such as silica gel, alumina clay, synthetics polymer resins and carbonaceous materials are used in adsorption process but activated carbon is the major adsorbent used for adsorption [6].

Activated carbon is a form of carbon which is processed to have some pores that can increase the surface area available for adsorption or chemical reactions. They are composed of microporous, homogenous structure with high surface area and are used as adsorbents for separation and purification purposes [6]. Activated carbon have high degree of microporosity and the surface area may vary depending on the type of raw material and the conditions of carbonization during production [7]. Chemical or physical activation methods are the commonly used techniques for preparation of activated carbon and chemical treatments has been found to enhance the adsorption properties of activated carbon [8]. Activated carbon in the market are usually made from coal, lignite, peat, petroleum residue or wood which are expensive

and exhaustible. In recent years, low-cost adsorbents have been developed from food wastes, agricultural materials, industrial, municipal and bio-wastes. These bioresources are cheap, easily available, renewable and ecologically suitable [9]. Moreover, the prepared carbon material from these biomasses have shown excellent surface properties with high degree of porosity and high surface areas. Agricultural wastes such as palm shells, fruit shell, groundnut shell, coconut shell etc and the parts of the plant such as root, stem, bark, flower, leave, fruit peel, husk, shell and stone are included in the biowaste. Some agricultural waste /by products which have been used to produce activated carbon include corn cobs [10] and [11], palm kernel shells [12], mango seed [8], coconut shell [13], bamboo sticks [14], plantain peels [15,16,17,18,19] and many others. Selection of raw material depends on several criteria which include; high carbon content, low inorganic matter content for low ash result, high density and volatile matter content, abundance of the raw material, possibility of producing an activated carbon with high percent yield and low degradation rate upon storage. In real practice, it is not possible to have all of these features in a feedstock because most of the biomass may contains lower carbon contents than the coals, and gives lower yield. But due to the environmental concerns, high cost and non-renewability of commercial carbon, interest has been shifted to finding inexpensive and effective alternatives. Exploring effective and low-cost activated carbon may contribute to environmental sustainability and offer benefits for future commercial applications. Thus, this study investigated the production of activated carbon from unripe plantain peels and its optimum conditions for the removal of phenol from aqueous medium.

2. MATERIALS AND METHODS

2.1 Preparation and Activation of Plantain Peel Carbon

Unripe plantain peels were collected from a food vendor making plantain chips who is based in Port Harcourt. They were cut into smaller pieces and thoroughly washed with distilled water to remove dirt's, sand and oil and then sun-dried until it was very dry. The samples were carbonized and activated according to the

method by [15] with little modifications. One portion (500 g) was carbonized in a muffle furnace at 400°C for 2hrs (physical activation method) and then cooled in a desiccator before ground into powder. The other portion (500g) was chemically activated with zinc chloride (ZnCl₂) and then dried before carbonizing at 400°C for 2hrs. The ZnCl₂ solution was prepared by dissolving 250 g of anhydrous zinc chloride in 1000ml of distilled water in a standard flask. The ZnCl₂ solution was added to the dried plantain peel samples in a conical flask and then heated on a hot plate to almost dryness. Mixing 250 g of ZnCl₂ with 500 g of plantain peel represents an impregnation weight ratio of 1:2. The carbonized samples were cooled in a desiccator and then ground into powder without washing off the activating chemical in order not to generate additional wastewater from the production of the activated carbon that would require treatment. The carbon sample prepared by physical activation method was named Non-Activated Unripe Plantain Peel Carbon (NAUPPC) while the chemically activated carbon sample was named Unripe Plantain Peel Activated Carbon (UPPAC).

2.2 Characterization of the Plantain Peel Carbon (NAUPPC and UPPAC)

Activated carbon is characterized by several physicochemical parameters which would influence the performance of the adsorbent. The characterization of the plantain peel carbon (NAUPPC and UPPAC) was based on determination of the surface area, porosity, carbon yield, moisture content, bulk density, ash content, pH and iodine number. The specific surface area of the activated carbon was measured using Brunauer-Emmet-Teller (BET) surface area analyzer using N₂ as adsorbate at the liquid nitrogen temperature of 77K. The moisture, ash content and carbon yield were determined using the standard test methods (ASTM D 5142, 2866-94 and 3175 respectively) [20]. The iodine number of the carbon samples was determined using the methods of ASTM D4607 which is based on three-point isotherm. The pH was determined by boiling 100 ml of distilled water in an Erlenmeyer flask containing 4 g of each carbon sample for 5 mins. The pH was measured after the supernatant liquid was poured off and cooled to room temperature. Porosity /void fraction is a measure of the void spaces in the activated carbon. It is a fraction of the volume of voids over the total volume. And it ranges between 0 and 1 or as a percentage

between 0% to 100 %. All these tests were done in duplicate and the average result taken. The bulk density and porosity were calculated from Equation 1 and 2.

$$\text{Bulk density} = \frac{\text{Mass of wet carbon Sample}}{\text{Mass of Volume}} \quad (1)$$

$$\text{Porosity } (\eta) = \frac{V_v}{V_t} \quad (2)$$

Where: V_t = Total volume = $\pi r^2 h$ (r = radius of cylinder and h = height of cylinder)

V_v = Volume of void = $V_t - V_s$

$$V_s = \frac{M_s}{G_s P_w}$$

G_s = specific gravity, P_w = density of water and M_s = mass of activated carbon.

2.3 Design of Experiment (DoE) for Process Parameter Optimization

A Response Surface Methodology (RSM), full factorial design with three levels, was used to design the adsorption process. The following parameters, initial concentration of adsorbate (IC), contact time (CT), and adsorbate pH, were considered in the DoE and this gave a total of 27 experimental runs. The percentage (%) adsorbed was taken as the response of this study while the initial concentration, pH, contact time and a fixed amount of adsorbent dose was taken as input parameters.

2.4 Batch Adsorption Studies

The different combinations from the DoE were used to run batch adsorption studies to determine the optimum conditions for the removal of phenol from aqueous medium using the unripe plantain peel activated carbon (UPPAC). The initial adsorbate concentration used were 2, 16 and 30mg/l; the pH used were 2, 6.5 and 11 while the contact time used were 30, 105 and 180 mins. The pH medium was buffered. A fixed amount of adsorbent dose (5 g) was used for the study. A total of 27 experiments were run with all possible combinations of parameters to study the optimal conditions for the phenol adsorption. The phenol stock solution was diluted with distilled water to obtain the desired initial concentration. All the chemicals used were of analytical grade and all the experiments were done in duplicate. The adsorption efficiency was calculated from Equation 3, and this was used as criterion for determining optimum conditions for phenol removal.

$$\% R = \frac{C_i - C_e}{C_i} \times 100\% \quad (3)$$

Where: R= adsorption efficiency (%)

C_e = equilibrium concentration of the adsorbate (mg/l).

C_i = the initial conc. of adsorbate (mg/l).

3. RESULTS AND DISCUSSION

3.1 Characterization of the Unripe Plantain Peel Carbon (NAUPPC and UPPAC)

The results obtained from the characterization of NAUPPC and UPPAC are represented in Fig. 1. From the result, the surface area of NAUPPC was $731\text{m}^2\text{g}^{-1}$ while that of UPPAC was $957\text{m}^2\text{g}^{-1}$ after activating with ZnCl_2 at impregnation ratio of 1:2. The higher surface area observed in UPPAC may be attributed to the chemical activation process as observed by [21] which reported that chemical activation does not allow the char produced during carbonization to shrink but helps to dehydrate the raw materials resulting in char that has porous structure and an extended surface area. Also, UPPAC has a higher iodine number of 736mg g^{-1} while that of NAUPPC was 509mg g^{-1} . Note that, iodine

number is usually used to estimate the surface area of activated carbon at room temperature condition and as an indicator for the porosity of activated carbon. Furthermore, the UPPAC also has a higher porosity of 32.2% compared to 21.4% of NAUPPC indicating that UPPAC may be preferable for adsorption due to its higher porosity, higher surface area and higher iodine number. Also, the ash content of UPPAC (9.02%) was lower than that of NAUPPC (11.08%). [22] reported that ash content of carbon suitable for absorption should be within a range of 1 – 20%. Note that, ash content influences ignition points of carbon, which is a major consideration where adsorption of certain solvents is applied because it reduces the overall activity of activated carbon and the efficiency of reactivation. The lower the ash value, the better the activated carbon for use as adsorbent. Thus, UPPAC was adopted as the preferred adsorbent for further studies.

3.2 Results of Batch Adsorption Studies

The batch adsorption study to determine the optimum conditions for the removal of phenol from aqueous solution with UPPAC was based on the DoE and the results from the different experimental runs are shown on Table 1. The results of the optimum conditions necessary for adsorption are shown in Figs. 2 to 4.

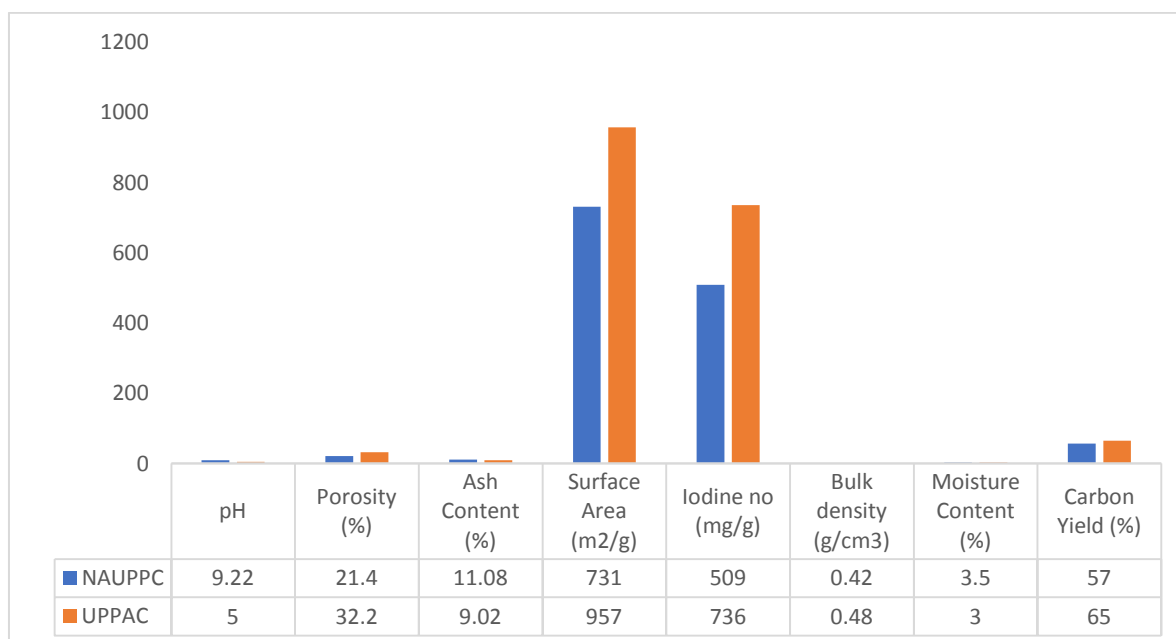


Fig. 1. Characterization of NAUPPC and UPPAC

Table 1. Results of optimum conditions for adsorption of phenol unto UPPAC

Observation	Sort order	Run order	Repetition	Initial Conc	Time	pH	% Absorbed
Obs1	1	1	1	2	30	2	70
Obs2	2	2	1	16	30	2	70.9
Obs3	3	3	1	30	30	2	69
Obs4	4	4	1	2	105	2	89
Obs5	5	5	1	16	105	2	88
Obs6	6	6	1	30	105	2	95
Obs7	7	7	1	2	180	2	91
Obs8	8	8	1	16	180	2	96.9
Obs9	9	9	1	30	180	2	97
Obs10	10	10	1	2	30	6.5	56
Obs11	11	11	1	16	30	6.5	58
Obs12	12	12	1	30	30	6.5	56
Obs13	13	13	1	2	105	6.5	89.5
Obs14	14	14	1	16	105	6.5	91
Obs15	15	15	1	30	105	6.5	86
Obs16	16	16	1	2	180	6.5	83
Obs17	17	17	1	16	180	6.5	93.2
Obs18	18	18	1	30	180	6.5	89
Obs19	19	19	1	2	30	11	4
Obs20	20	20	1	16	30	11	42.9
Obs21	21	21	1	30	30	11	49
Obs22	22	22	1	2	105	11	74
Obs23	23	23	1	16	105	11	82
Obs24	24	24	1	30	105	11	69
Obs25	25	25	1	2	180	11	78
Obs26	26	26	1	16	180	11	81
Obs27	27	27	1	30	180	11	83

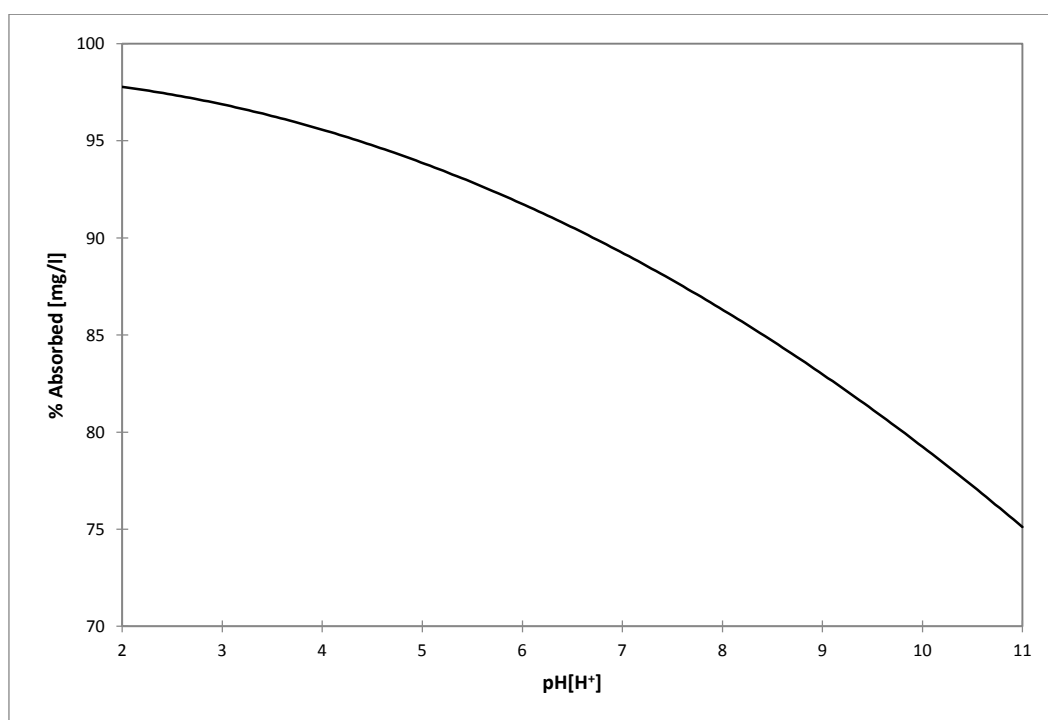


Fig. 2. Phenol adsorption onto UPPAC as a function of adsorbate pH

3.2.1 Effect of Adsorbate pH

Results on the effects of adsorbate pH on the removal of phenol onto UPPAC is shown in Fig. 2. It was observed that the percentage of phenol adsorbed decreased at a steady rate as the adsorbate pH increased from 2 to 11. A maximum adsorption of 97% was recorded at pH 2 indicating that phenol removal was pH dependent and was better at acidic conditions. This implies that pH affects the degree of ionization of phenol on the surface properties of unripe plantain peel activated carbon and phenol, being a weak acid, partially ionizes in solution. Similar trend was reported by [23] in which it was observed that at low pH, the surface of the adsorbent would be protonated, and this would result in a stronger attraction for the negatively charged phenolate ion. These negatively charged ions would be directly attracted to the protonated surface of the unripe plantain peel activated carbon by electro-static force while the unionized phenol molecules would also be attracted by physical force. Thus, at high pH, the hydroxyl OH^- ions would compete with the phenol molecules for adsorption sites thereby resulting in decrease of adsorption.

3.2.2 Effects of contact time

The adsorption of phenol onto UPPAC at different contact time was studied to find the equilibrium time required for maximum adsorption. The results as presented in Fig. 3 showed that the adsorption of phenol increased with increase in contact time until equilibrium was reached within 145 to 160 mins and thereafter, the adsorption rate started decreasing with time. The increased adsorption may be due to increased number of available vacant site on the adsorbent at the initial stage of adsorption process which resulted in an increased concentration gradient between the solute in solution and the solute on the adsorbent surface. Thus, the increased concentration gradient increased the rate at which phenol particles is adsorbed at the initial stage of adsorption, since adsorption kinetics depends on the surface area of the adsorbents. However, as contact time preceded, adsorption rate reduced due to accumulation of phenol particles on the vacant sites leading to a decrease in adsorption rate. Thus, maximum adsorption of about 95.89% was achieved at 150 mins. Similar trends were reported by [24,25,19,26] and [27] in which they attributed it to increased number of available vacant site on the adsorbent at the initial stage of adsorption.

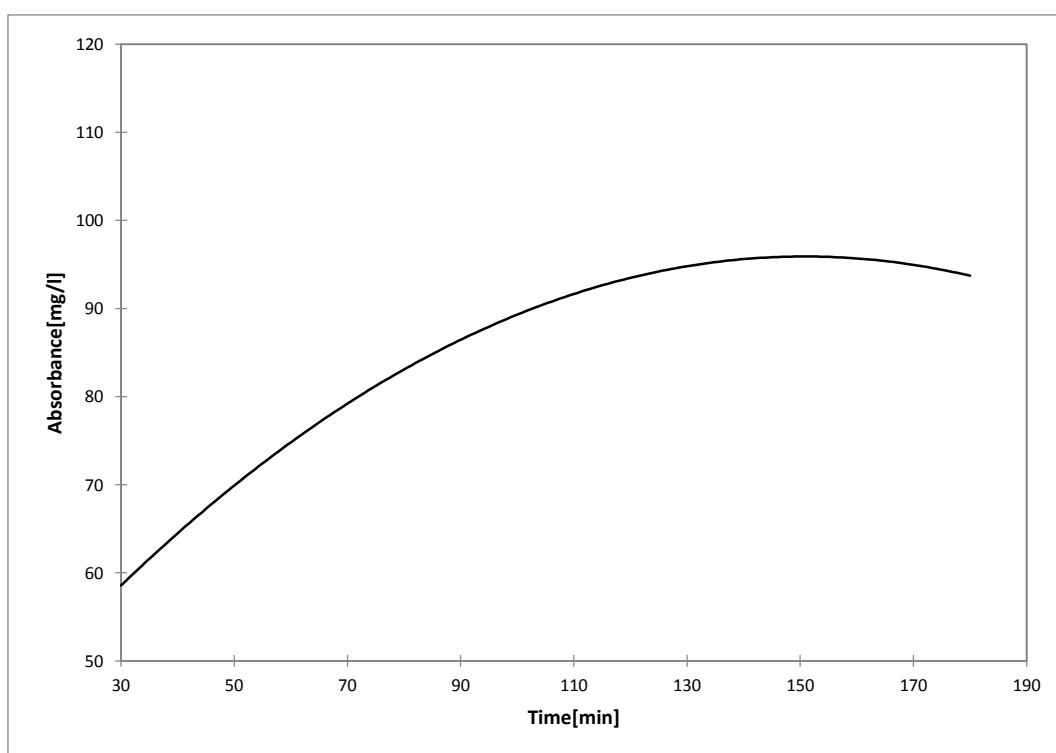


Fig. 3. Phenol adsorption onto UPPAC as a function of contact time

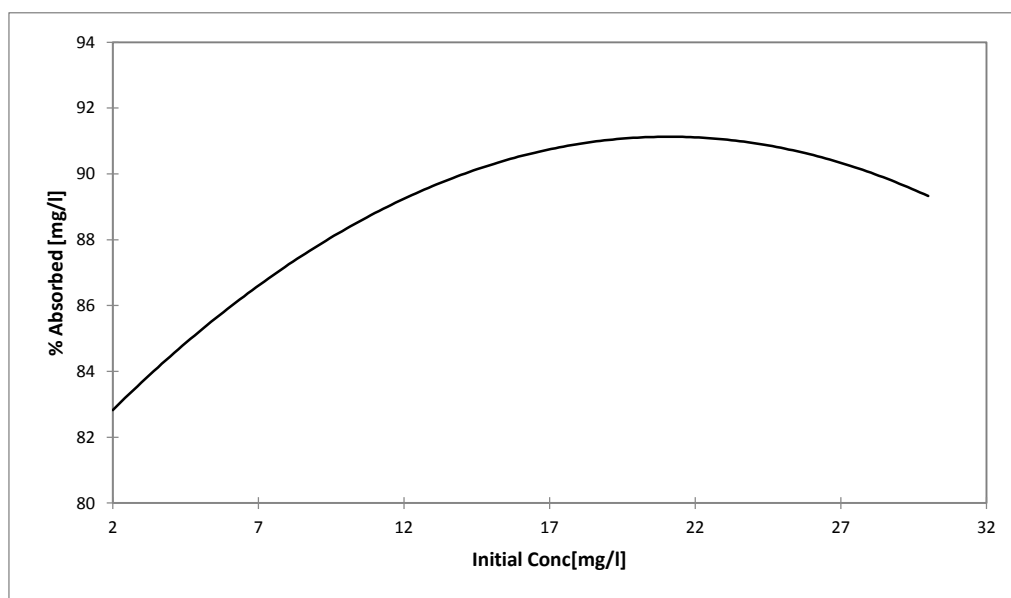


Fig. 4. Phenol adsorption as a function of adsorbate concentration

3.2.3 Effects of initial adsorbate concentrations

The effects of adsorption on different initial phenol concentrations are presented in Fig. 4. It was observed that the percentage removal of phenol increased at a steady rate as initial concentration increased up to 21 mg/l, attaining a maximum removal efficiency of 91%, after which further increase in initial concentration of phenol resulted in a decrease in its removal. This indicates that less favorable sites became involved in the process with increasing concentration. Similar trend was reported by [28] in which the percentage of phenol adsorbed increased as concentration increased and after attaining maximum removal efficiency, the percentage adsorbed decreases as the concentration of phenol increases.

4. CONCLUSIONS

The study investigated the production, characterization and optimum conditions for the adsorption of phenol from aqueous solution using unripe plantain peel activated carbon. The result shows that UPPAC sample, activated with $ZnCl_2$ at impregnation ratio of 1:2 gave a higher surface area, porosity, carbon yield and iodine number of 957 m^2/g , 32.2%, 65% and 736 mg/g respectively. The batch adsorption of phenol unto UPPAC was found to increase with initial adsorbate concentration and contact time while it decreases with increase adsorbate pH. UPPAC

achieved optimum percentage removal of 91% at initial phenol concentration of 21 mg/g and its removal was pH dependent (pH 2), better at acidic conditions. The amount adsorbed also increased with contact time until equilibrium was reached at 150 mins. Thus, chemically activated unripe plantain peel can effectively remove phenol from aqueous solution and the optimum conditions for the adsorption process are at pH 2, initial adsorbate concentration of 21 mg/l and contact time of 150mins.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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