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ACID AND ALKALINE PRETREATMENT OF BIOCHAR AND THEIR EFFECT ON THE REMOVAL OF BISPHENOL A FROM AQUEOUS SOLUTION

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ABSTRACT

This work prepared and compared the efficacies of HNO_3 and NH_4OH pretreated sugarcane biochar (HNO_3-BC and NH_4OH-BC) and untreated sugarcane biochar (BC) for the removal of Bisphenol A from aqueous solution. The adsorbents were characterized using SEM and FTIR to observe their morphology and functional group. Further characterization was done for pore volume, bulk density, surface area, pH, moisture and ash contents. Adsorption studies was done by batch process to determine the effect of variation in contact time, adsorbent dosage, concentration, temperature and pH on the removal of bisphenol A by the adsorbents. Results from the analysis showed that adsorption was more favourable and efficient with NH_4OH-BC (which was able to remove about 98.30% of BPA at dosage of 0.10g, pH 6, concentration of 70mg/l, time 40 min and temperature of 25°C) than HNO_3-BC and BC. Chemically activated adsorbents are very efficient and can be used as an alternative to expensive adsorbents for the uptake of BPA from industrial effluents and other sources before they are discharged into the environment.

Key words: Acid pretreatment, alkaline pretreatment, biochar, bisphenol A, sugarcane bagasse, adsorption**.**

INTRODUCTION

Bisphenol A (BPA) is an industrial chemical widely used in the production of polycarbonate plastics and epoxy resins. Given its endocrine-disrupting properties and potential adverse health effects (tumors, obesity, heart diseases in humans, polycyclic ovarian syndrome, fatty liver disease, insulin resistance, bioaccumulation through food webs, neurological challenges, e.t.c [1, 2], the removal of BPA from wastewater has become an important environmental concern. Adsorption is a promising method for BPA removal, employing various materials as adsorbents [3-5].

The use of waste materials, different composite materials and natural substances as adsorbents have received great attention as effective adsorbents due to their reliable resources, low cost and environment friendly. Recent studies have shown variable results regarding the effectiveness of treated and untreated adsorbents for the adsorption of BPA from aqueous medium. Kamil *et al*., [6] studied the removal of BPA using novel palm kernel shell magnetically induced biochar (MBC) and non-magnetically induced biochar (NBC). Results showed that MBC demonstrated superior maximum removal efficiency of 94.2% over NBC. According to research conducted by Zhang *et al*. [7], alkaline-hydroxide-treated activated carbon demonstrated enhanced removal rates of BPA, achieving more than 90% efficiency. The study highlighted that the increased basic sites on the adsorbent surface promote interactions with BPA's phenolic hydroxyl group, significantly improving adsorption performance. Furthermore, it has been reported that alkaline-treated biochar exhibited considerably higher BPA adsorption than its untreated counterpart, due to the formation of additional hydroxyl and carbonyl groups on the surface during the treatment process [8]. It has also been demonstrated that sulfuric acid-activated carbon adsorbed up to 95% of BPA from aqueous solution under optimized conditions [9]. The high adsorption capacity was attributed to the increased surface area and enhanced active sites generated during acid treatment. The efficacy of acid-treated zeolites has been evaluated, noting the significant increase in BPA adsorption compared to untreated zeolites, largely due to increased ion-exchange capacity and surface reactivity [10].

The studies reviewed showed that the capacity of carbon to remove BPA depends on their chemical characteristics. This work compared the efficiency of acid, alkaline pretreated sugarcane bagasse biochar and untreated sugarcane bagasse biochar for their efficacy in removing BPA from aqueous solutions.

MATERIALS AND METHODS

Adsorbent preparation

Sugarcane bagasse (SB) obtained from Alausa sugarcane market dumpsite at Abakaliki, Ebonyi State was thoroughly washed with distilled water until a colourless filtrate was achieved, dried for 3 hours (to a constant weight) in an electric oven at 105^{o}C and carbonized by heating at 200^{o}C for 30 mins in a carbonizer. The char obtained was ground and sieved through a standard sieve to obtain particles in the range of 50-120µm. The SB biochar was divided into three parts, two pars differently activated by stirring with 0.5M NH_4OH (ratio 1:2) and 0.5M HNO_3 (ratio 1:2) for 6 hours at 250 ^{o}C to obtain NH_4OH-BC and HNO_3-BC respectively, the third part was unactivated (BC). The NH_4OH-BC and HNO_3-BC were washed with distilled water until neutral. The adsorbents were characterized using SEM and FTIR to observe their morphology and functional group. Further characterization was done as described by Eze *et al*., [11] and Onweukeme and Egemba [12] for pore volume, bulk density, surface area, pH, moisture and ash contents.

Adsorption studies

The adsorption studies were carried out as described by [12] & [13], with little modification. For time variation, each of the biochar 0.6g were transferred into 10ml of 70mg/l BPA solution, the mixture agitated at 150rpm for 20-120 minutes, (at intervals of 20 minutes) at pH 6 and temperature 25^{o}C. After agitation, the solution was filtered and the filtrate analyzed for residual dye concentration using UV/VIS spectrophotometer. For pH variation, pH was varied at 3,4,6,8,9,10 using 0.5M HCl and 0.5M KOH to adjust the pH while the other conditions were kept constant. Variation of adsorbent dosage was conducted by varying the adsorbent from 0.5-1g, at interval of 0.1g, while concentration was carried out using 10ml of BPA solution at various concentrations of 50, 60, 70, 90, 110, 130mg/l. The effect of temperature 25°C, 35°C,55°C was conducted in a water bath. All other conditions were kept constant as one is varied. The percentage of BPA removed was calculated using:

$$\text{Re}\ (\%) = \frac{\text{Co}-\text{Ce}}{\text{Co}} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots\ (1)$$

where Co and Ce are the initial and final BPA concentration in mg/l respectively. The adsorption experiments were performed in triplicates in order to minimize error and the accurate mean values for Re obtained.

RESULTS AND DISCUSSION

Physical properties

Table 1 showed the physical properties of the adsorbents (NH_4OH-BC, HNO_3-BC and BC).

Table 1: Physical properties of the adsorbents (NH_4OH-BC, HNO_3-BC and BC

Physical properties	**NH_4OH-BC**	**HNO_3-BC**	**BC**
pH	7.24	6.84	7.16
Average pore volume (cm^3/g)	0.640	0.750	0.132
Bulk density (g/ ml)	0.853	0.835	0.814
Surface area (cm^3)	6134	5841	384
Moisture content (%)	2.13	2.11	6.24
Ash content (%)	31.16	29.14	6.09

Chemical activation of the SB affected its physical properties as shown in Table 1. The moisture content, surface area, bulk density and pore volume of NH_4OH-BC and HNO_3-BC were enhanced, and hence, were positively affected by chemical activation, while the ash content was negatively affected. Activation increased the surface area of the NH_4OH-BC and HNO_3-BC, providing more active centers for adsorption of the adsorbate to take place. The low moisture content of the NH_4OH-BC and HNO_3-BC could increase the capacity of activated carbon.

Plate 1 showed the SEM images of the adsorbents

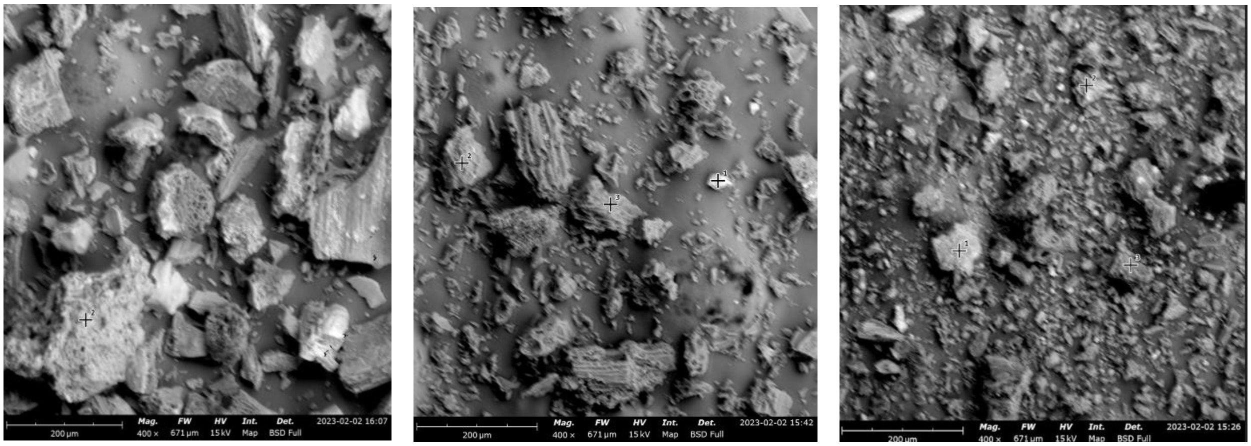

Plate 1: SEM (a) BC (b) HNO_3-BC (c) NH_4OH-BC

The SEM image of BC showed rough surface and irregular shapes, while the plates of HNO_3-BC, NH_4OH-BC revealed more porous and rough crystal mesophores which could enhance the surface area for adsorption. The increased roughness and porosity (of the HNO_3-BC and NH_4OH-BC) may be due to partial degradation of the biomass by the activators leading to more fragmented and modified structure.

Figure 1 represents the FTIR spectra of the adsorbents.

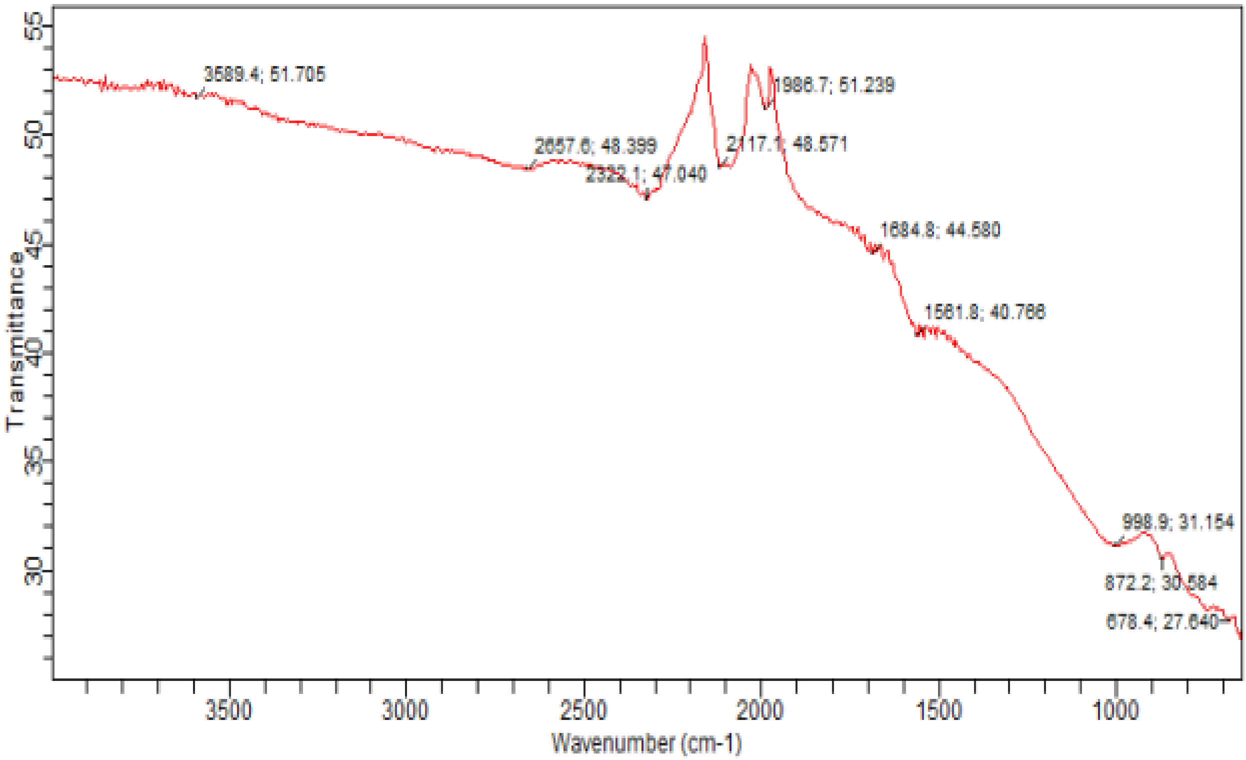

Figure 1a: FTIR spectra of BC

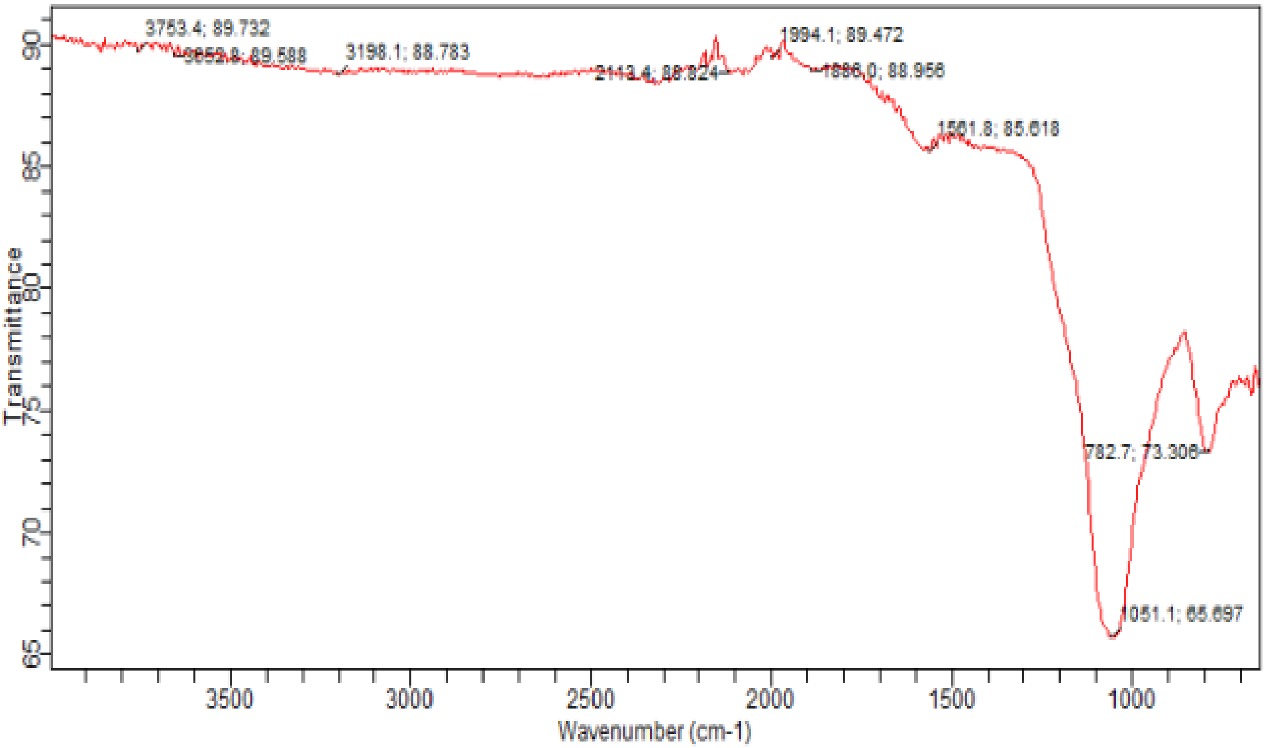

Figure 1b: FTIR spectra of HNO_3-BC

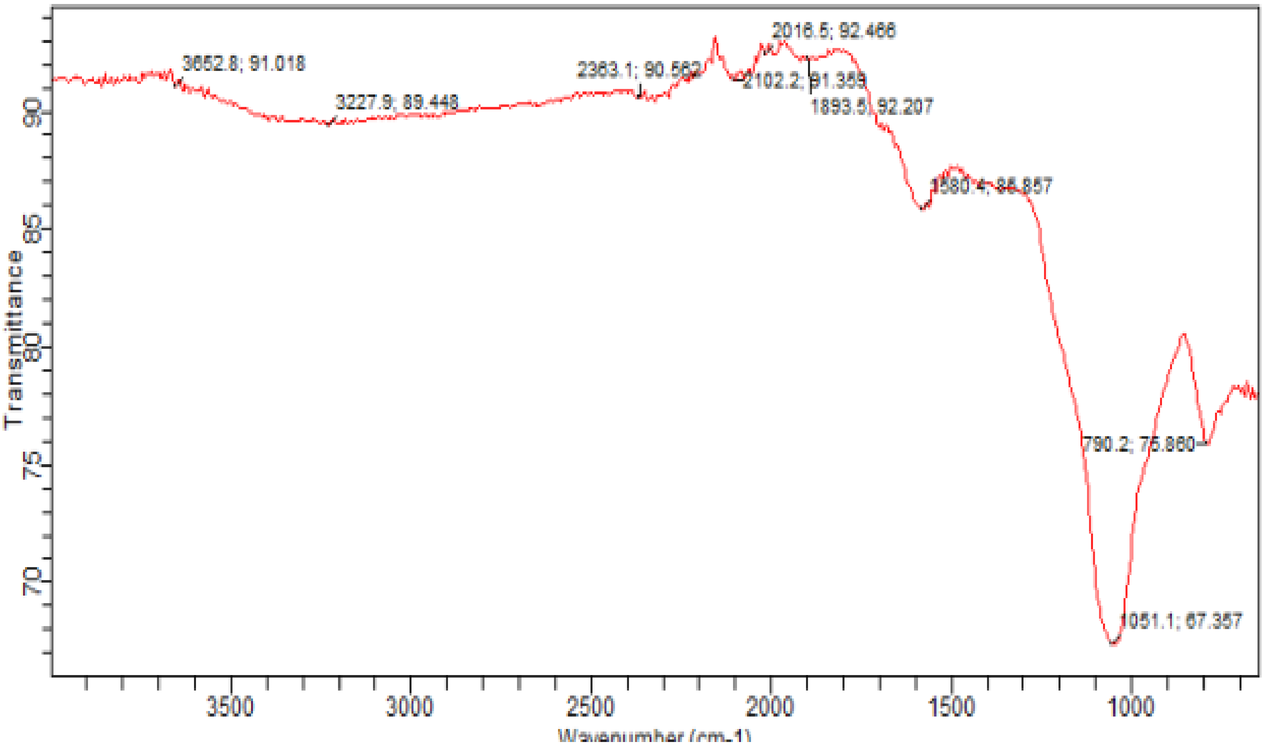

Figure 1c: FTIR spectra of NH_4OH-BC.

The FTIR spectra of BC, HNO_3-BC and NH_4OH-BC shown in Fig 1a, b and c respectively were recorded at the region of 4000 cm^{-1}-400 cm^{-1} and interpreted by matching the spectra with Sigmaaldrich Merck IR spectra table and chart. BC FTIR spectrum showed a weak peak at 2000 cm^{-1}, implying a C-H bending vibrations. The HNO_3-BC and NH_4OH-BC FTIR showed frequencies in the finger print region, consisting of bending vibrations within the molecule.

HNO_3-BC has medium peak at 1100 cm^{-1}-1000 cm^{-1}, indicating the presence of C-O stretching vibrations of carboxylic acid which is associated with increased surface acidity and reactivity, implying a better adsorption capacity than BC. NH_4OH-BC also showed medium peak at 1050 cm^{-1}, indicating the presence of C-N stretching vibration of amine group. NH_4OH-BC may be more suitable for adsorbing acidic or anionic contaminants due to its basic surface properties [14]. The difference between BC and HNO_3-BC and NH_4OH-BC 950 cm^{-1}, an indication that complexation is highly evident in the impregnation of HNO_3-BC and NH_4OH-BCon the SB-BC [15].

Batch studies

Figures 2 revealed the effect of variation of dosage, pH, concentration, time and temperature respectively on the removal of BPA by the adsorbents (NH_4OH-BC, HNO_3-BC and BC).

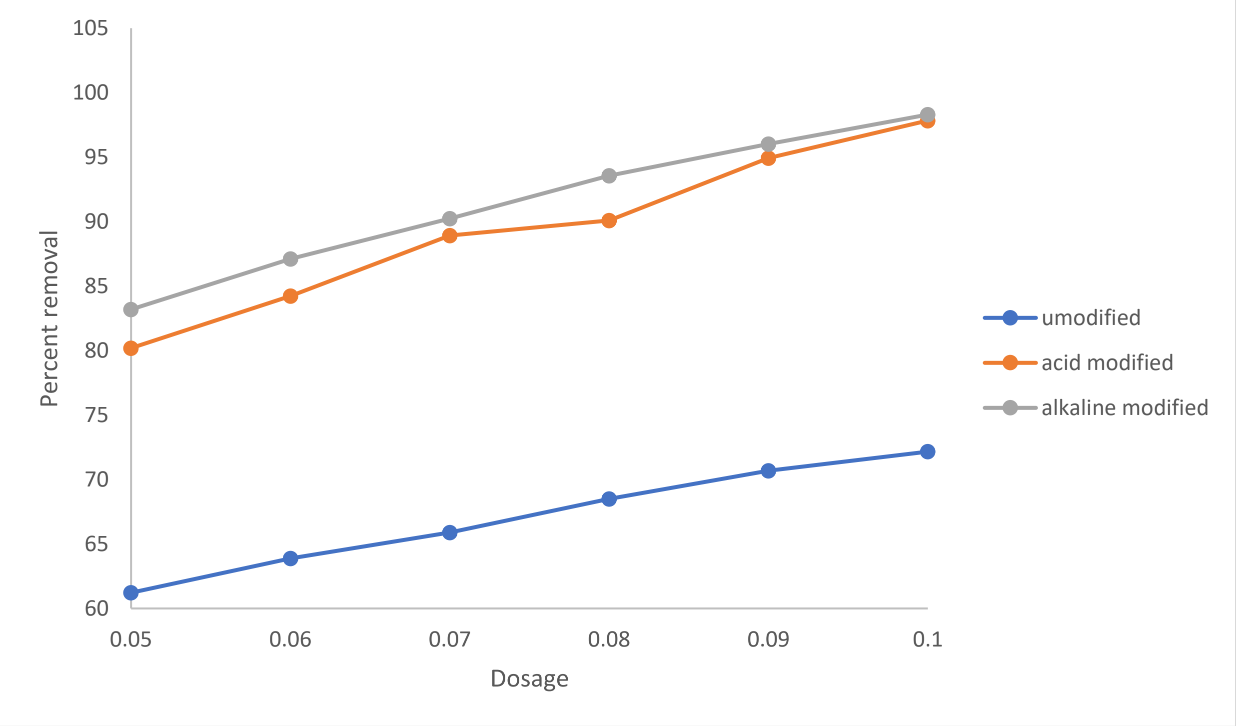

Fig 2a: Effect of variation in dosage on % removal.

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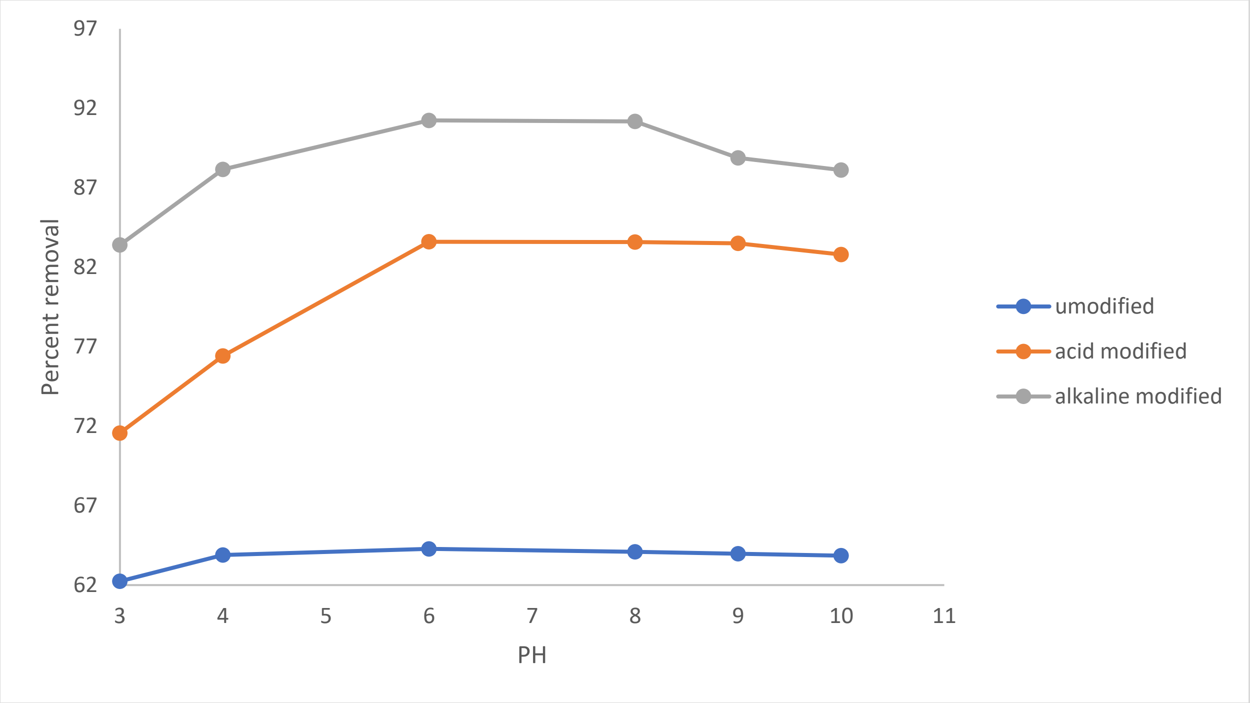

Fig 2b: Effect of variation in pH on % removal.

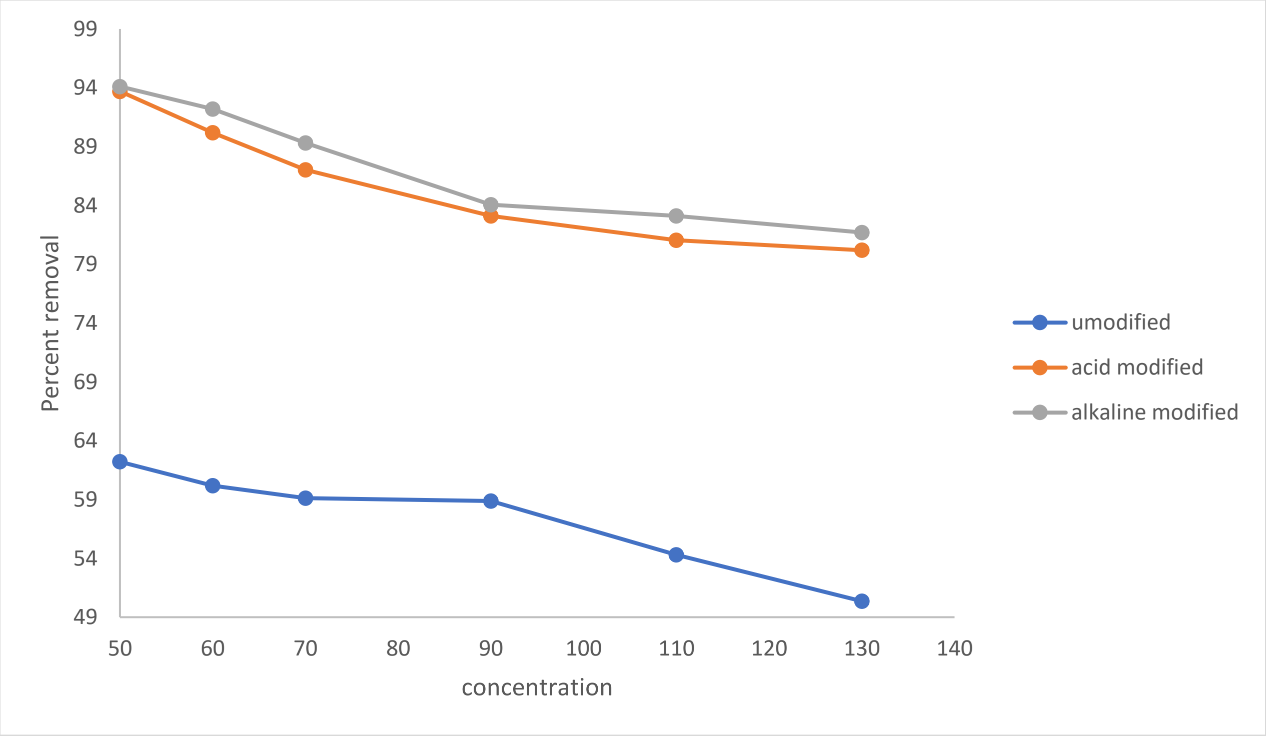

Fig 2c:Effect of variation in conc on % removal

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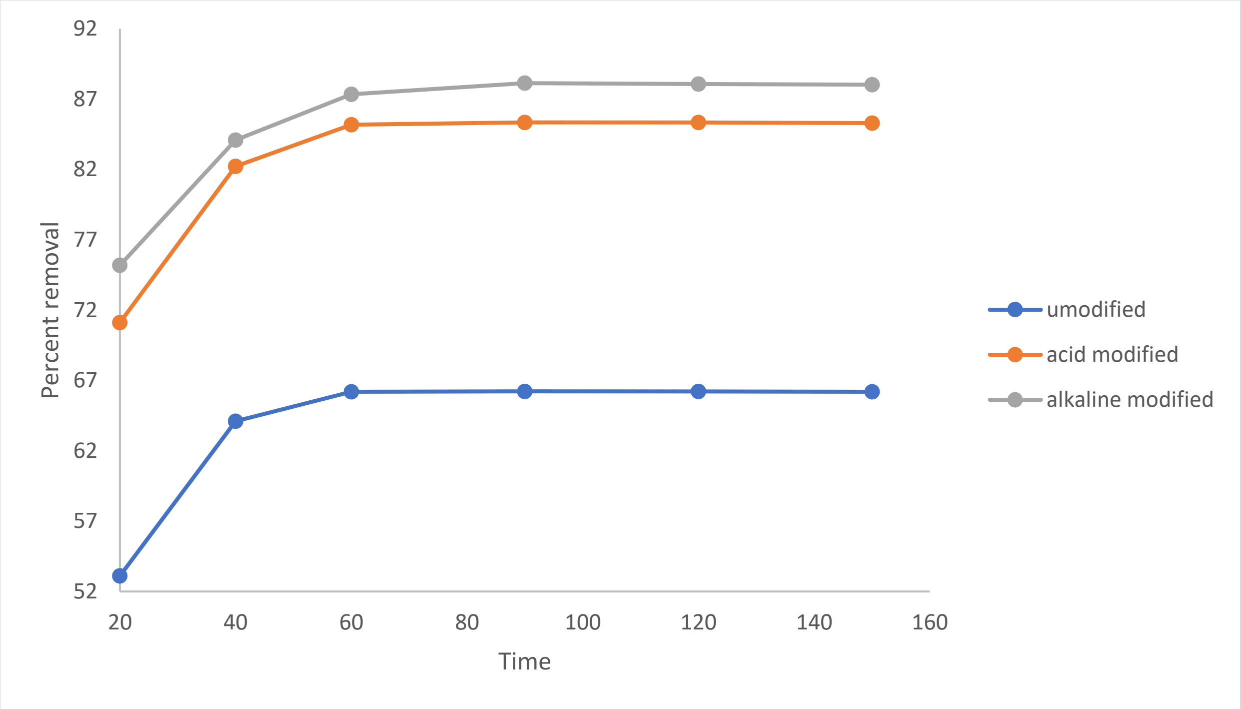

Fig 2d: Effect of variation in time on % removal

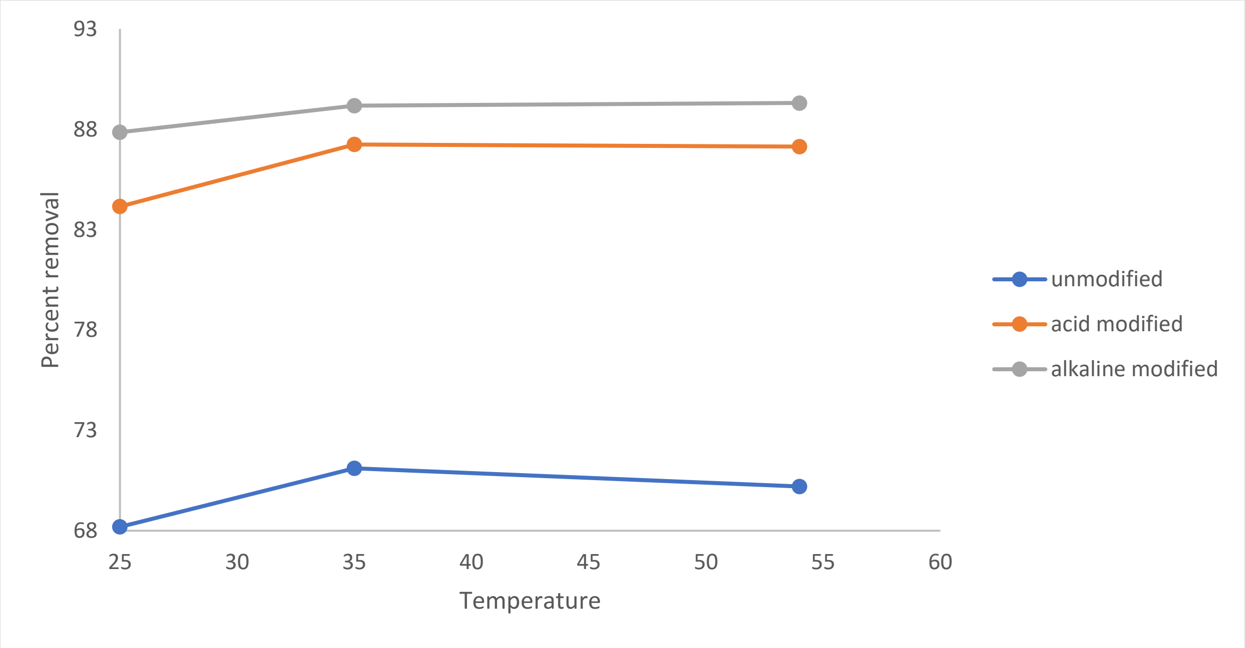

Fig 2e: Effect of variation in temperature on % removal

From Fig 2a, with increase in adsorbent dosage from 0.05-0.10g, the % removal of the BPA increased from 61.22-72.16% for BC, 80.19 to 97.84% for HNO_3-BC and 83.19 to 98.30% for NH_4OH-BC. This is because of the greater availability of the active sites and more surface area for adsorption as the adsorbent dosage increased [11, 12, 16].

For variation in pH (Fig 2b), the % removal increased with increase in pH up to the pH of 8 (for the three adsorbents) and then decreased. This may be attributed to electrostatic repulsion forces between the BPA and the biosorbents. Also, at pH 5-9, BPA existed in neutral form, with its N- containing surface functional group deprotonated, resulting to reduced adsorption capacity, thus the decrease in %removal as pH increased. The maximum % removal obtained was 91.24% (at pH= 6, NH_4OH-AC). NH_4OH-BC has the highest % adsorption, followed by HNO_3BC, and then BC. This trend was also observed by Timbo *et al.*,[16].

The uptake of BPA (% removal) decreased as the initial BPA concentration was increased from 50 to 130mg/l, as shown in Fig 2c, because the active sites are saturated and the exchanged sites are filled [17]. The uptake of BPA favoured NH_4OH-BC more than HNO_3-BC and the BC for variation in initial concentration.

Fig 2d showed that the % removal also increased rapidly as contact time is increased from 20-60 minutes, with maximum adsorption of 88-14% (NH_4OH-BC), and then declined (on reaching equilibrium). This may be due to saturation of the active sites of the adsorbents. The % removal of the NH_4OH-BC was higher than the HNO_3-BC and the BC. This trend is due to high ratio of available surface at low concentrations and low ratio of available surface area caused by saturation at high concentration of the absorbate [16].

The % removal of BPA by the adsorbents increased with increase in temperature (from 25 ºC -35ºC) in Fig 2e, and then declined on further increase in temperature (to 55 ºC), showing that adsorption mechanism is by chemisorption. The decline, can also be as a result of breaking of bonds. Among the adsorbents, NH_4OH-BC has higher % removal, followed by HNO_3-BC, and then BC.

CONCLUSION

The adsorption studies showed that the adsorption was more favourable and efficient with NH_4OH-BC (which was able to remove about 98.30% of BPA at dosage of 0.10g, pH 6, concentration of 70mg/l, time 40 min and temperature of 25ºC) than HNO_3-BC. Extant literatures supporting this finding are [14, 18-19]. The uptake of the BPA was more for the chemically activated adsorbents (NH_4OH-BC and HNO_3-BC) than the BC. Therefore, the chemically activated adsorbents are very efficient and can be used as an alternative to expensive adsorbents for the uptake of BPA from industrial effluents and other sources before they are discharged into the environment.

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