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Characterisation of Modified *Pinus sylvetris* Bark Activated Carbon for Adsorptive Capacity on Dye and Drug Industrial Wastewater

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Abstract

Water is an essential natural resources needed by all living nature but access to clean water has been a serious global problem courtesy industrial revolutions and developments involving generation of large amount of wastewaters containing toxic pollutants which find their ways into the various water sources and cause serious health and environmental challenges. In quest to proffer a solution, we prepared an alkaline modified *Pinus sylvetris* bark activated carbon (MPSBAC) to remove Congo red (CR) dye and tetracycline (TC) from aqueous solutions. MPSBAC was characterized by FESEM, FTIR and EDAX and the results revealed an irregular-scattered, porous and coarse morphology with the presence of several functional moieties and ionizable elements that are possibly responsible for removal of CR and TC from aqueous solutions through surface interactions. Adsorption capacity of the MPSBAC for removal of CR-dye and TC was also studied under different experimental conditions including pH, adsorbent dosage, contact time, temperature and initial concentration. The results showed optimal pH 2.0 and 8.0 for maximum adsorption of CR and TC respectively. Equilibrium adsorption capacity (q_e) decreased from 2038.45- 5.58 mg/g and 797.92- 0.25 mg/g for CR and TC respectively as adsorbent dosage increased from 1.00- 200.00 mg. The study of initial CR and TC concentrations showed increased adsorption capacities as the initial concentrations increased from 5 to 200 mg/L at 298 K, 308 K and 328 K. For CR and TC at 298 K, 313 K and 328 K, q_e increased from 18.07- 989.06 mg/L, 0.42- 671.04 mg/L; 19.84- 777.06 mg/L, 8.15-769.02 mg/L and 18.59- 988.02 mg/L, 14.87- 823.98 mg/L respectively. Contact time studies of adsorption of CR-dye and TC onto MPSBAC revealed that uptake of the dye and TC increased from 54.01- 99.22 % (135.05-244.95 mg/kg) and 96.45- 97.63 % (482.23- 487.98 mg/g) respectively as agitation time increased until equilibrium is reached after 180 minutes. The present study is of the opinion that MPSBAC could be a promising cheap adsorbent for the removal of dye and pharmaceutical products from aqueous solutions. It is therefore recommended that kinetics and thermodynamics studies should be carried out on the adsorbent to corroborate these findings.

Keywords: Characterisation, Adsorptive Capacity, Drug. Dye, MPSBAC, Wastewater

Introduction

Chemical industries are of immense importance in terms of their impacts on the environment [1]. Wastewaters from these industries generally contain dangerous and toxic organic and inorganic pollutants in varying degrees of concentration. Many materials in the chemical industry are hazardous and hardly biodegradable such that when present in soils and water bodies can enter the food chain and accumulate in living organisms [2]. Characteristics of chemical wastewater concentration, molecular size, solubility, toxicity and biodegradability of the pollutants determine the adequate treatment system [3,4].

Pine barks (PBs) are obtained from pine scot trees and their extracts have been reported to be good sources of some medicinal compounds capable of treating some diseases such as diabetics [5,6]. However, extraction of these compounds renders the remnant barks useless as wastes. These wastes can be processed for the removal of pollutants or toxicants from the environment by modifying cell walls of some plants. Modification of cell wall can alter the binding of contaminants as adsorption is mainly a cell surface phenomenon [7]. Surface modification is necessary, through physical treatments such as heating, boiling, freezing, thawing, drying, vacuum and freeze-drying, autoclaving, mechanical disruption and lyophilization or chemical treatment such as cross-linking with organic solvents and alkali or acid, to enhance the binding capacity of biomass and to elucidate the mechanism of adsorption [8]. Physical and chemical modifications have been used on the adsorbents to alter the surface characteristics either by removing or masking the functional groups or by exposing more binding sites [9,10].

Large amounts of waste are produced from agricultural based industries every year. Most of these wastes are released to the environment due to ineffective and improper disposal procedure and this leads to environmental pollution with a harmful effect on human and animal health [11]. Agricultural waste materials are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process. The functional groups present in biomass molecules include acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphydryl carboxyl groups, alcohols and esters [11,12,13].

Some active sites involved in the toxicants uptake are determined by using different techniques such as titration, infra-red (IR), Fourier transformed infrared spectroscopy (FTIR), Raman spectroscopy, electron dispersive spectroscopy (EDS), energy dispersive X-ray (EDAX), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), nuclear

magnetic resonance (NMR), X-ray diffraction analysis (XRD), X-ray absorption fine structure spectroscopy (XAFS), Electron spin resonance spectroscopy (ESR), X-ray absorption spectroscopy (XAS), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) and others [13,14,15,16].

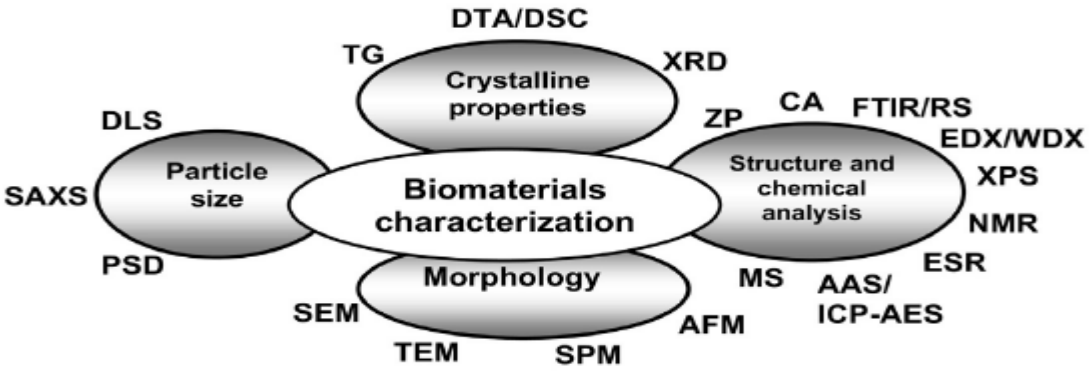


Figure 1: Physicochemical characterization of chemicals [17]

Materials and Methods

Stock solutions of 1000.00 mg/L each of tetracycline (TC) and congo red (CR) dye were separately prepared by dissolving 1.00 g in distilled water. Experimental solutions were prepared from the stock solutions by simple dilution.

Pinus sylvetris barks obtained in large quantity from the University of Ibadan Botanical Garden, Ibadan, Nigeria were washed and oven dried at 100 ^{o}C for 72 hours. The dried sample was pulverized into particle size $\leq$ 300 μm. 5.00 g powder was impregnated with 0.20 M, 1.10 M and 2.00 M NaOH solutions. The NaOH impregnated sample powder stood in a heating mantle at 30 ^{o}C for 24 hours and agitated at 200 rpm to homogenize the pine bark powder in the NaOH solution. Slurry obtained from the impregnated sample was placed in an oven at 100 ^{o}C overnight. Pyrolysis of the dried impregnated material took place in a Kelvinator microwave oven, KML62B Model, 230 V, 50 Hz, with a maximum power of 1200 W. The dried impregnated samples were initially subjected to nitrogen atmosphere, before introduction into the microwave oven at different power ratings of 600-1080 W, with impregnation ratios of 0.20-2.00 for 10-30 minutes. The modified *Pinus sylvetris* bark activated carbon (MPSBAC) produced after the microwave irradiation was cooled in a desiccator to room temperature and subjected to mild washing with 0.10 M HCl and hot distilled water to remove impurities until the pH was close to neutral.

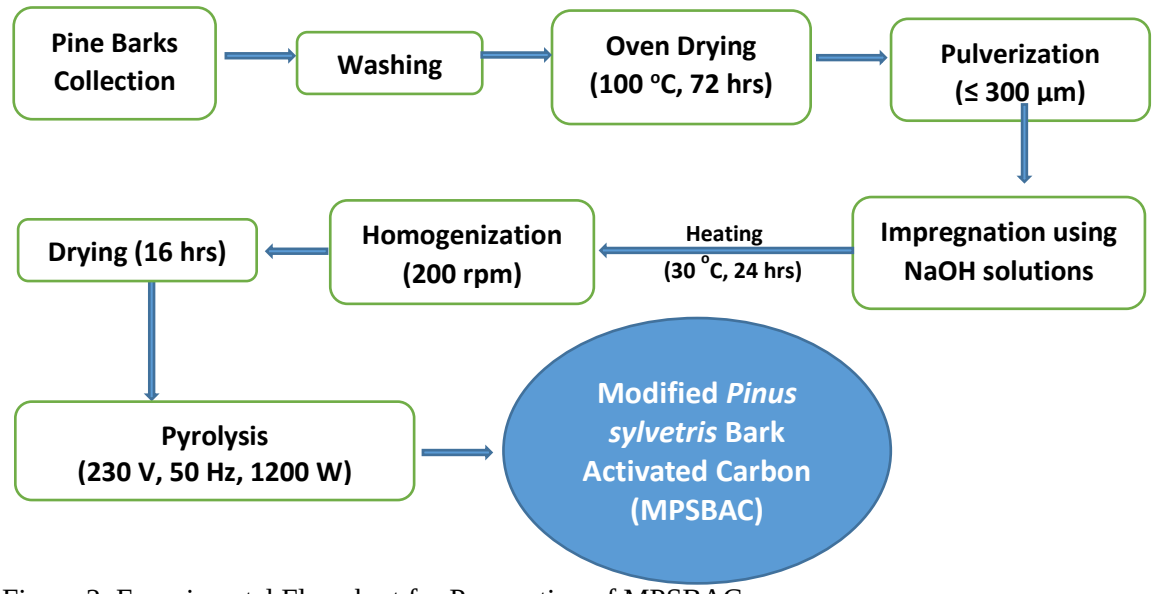


Figure 2: Experimental Flowchart for Preparation of MPSBAC

Surface Characterisation

Dried MPSBAC was characterised using FESEM, FTIR and EDAX for surface morphology, microstructures and micro-area compositions; obtaining information about the functional groups present and; for elemental characterization respectively. These would enable the understanding of MPSBAC pores structure and morphologies which play significant roles in adsorption process; prediction of possible interactions that may occur at the surface between the functional groups and those of CR dye and TC for their uptake and; revelation of various forms of elements present in MPSBAC at different proportions respectively.

Adsorption Studies of MPSBAC on CR and TC

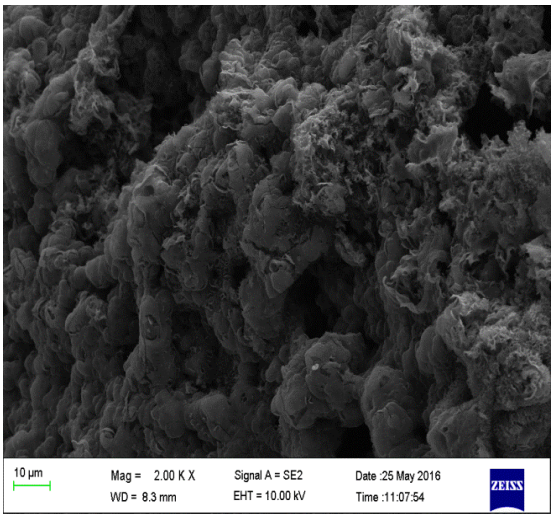
Adsorption studies were done by the optimization of various experimental variables such as pH, adsorbent dose, initial CR and TC concentrations, agitation time, and temperature. For the pH studies of CR and TC, 5 mg of MPSBAC was added to 100 mL plastic bottles containing 25 mL of 100 mg/L CR and TC solutions, which were adjusted with 0.1 M HCl or 0.1 M NaOH to obtain desirable pH (2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 respectively). For the adsorbent dose studies of TC and CR, 5–200 mg of MPSBAC were added to 100 mL plastic bottles containing 25 mL of 100 mg/L CR and TC solutions, which were adjusted to the pH of maximum adsorption (pH 2 and 8 respectively). Adsorption equilibria (experiments for initial CR and TC concentrations) of CR and TC were done by adding 5 mg of MPSBAC to 100 mL plastic bottles containing 25 mL of 5-200 mg/L CR and TC solutions, which were adjusted to the pH of maximum adsorption. Adsorption kinetics (agitation time experiments) of CR and TC were

done by adding 5 mg of MPSBAC to 100 mL plastic bottles containing 25 mL of 100 mg/L CR and TC solutions already adjusted to the pH of maximum adsorption and then agitated for 0.5–180 min. The above experiments were carried out at 298 K

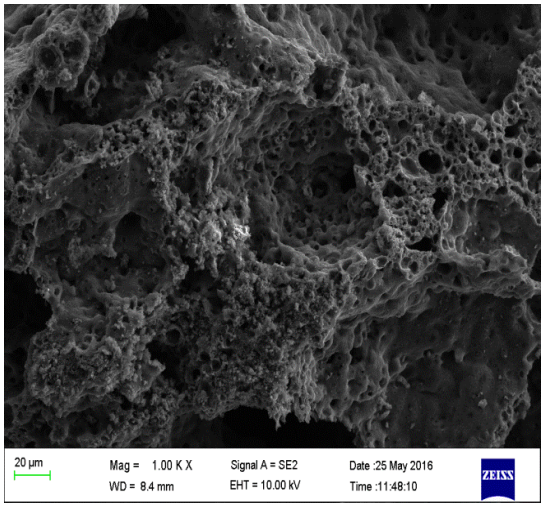
Results and Discussion

Surface Micro-Structural and Micro-Area Compositional Analysis of MPSBAC

Pores structures and morphologies play significant roles in the adsorption process. Figures 3 (a), (b), (c) and (d) show the FESEM images of MPSBAC at 10 µm, 20 µm and 100 µm.



(a)



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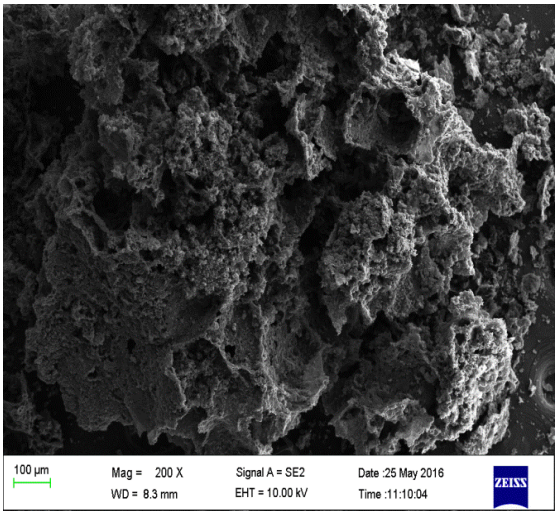
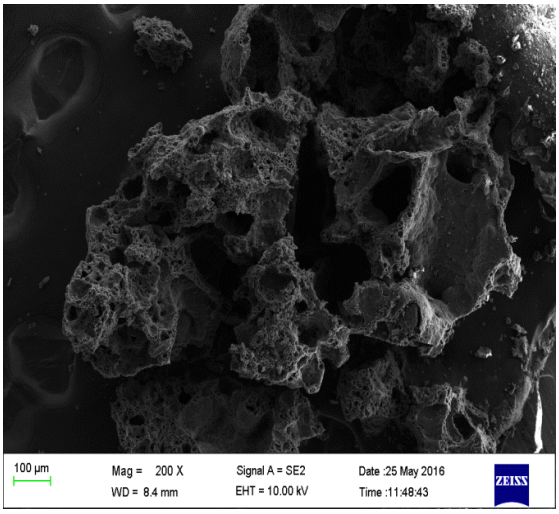


(c)



(d)

Figure 3: FESEM Images of MPSBAC at (a) 10 µm (b) 20 µm (c) 100 µm: WD = 8.3 mm and (d) 100 µm: WD = 8.4 mm.

From Figures 3 (a), (b), (c) and (d), MPSBAC has rough, scanty and scattered pores of various lump sizes that are irregularly shaped on their surfaces. This suggests increased surface area which can lead to higher adsorption capacities, improved adsorption rates due to high availability of adsorption sites, enhanced mechanical stability which reduces mechanical breakdown, increased surface-surface interactions with the adsorbates (CR dye/TC). Conversely, a rough and scanty surface could enhance diffusion resistance, creating a mass transfer resistance which could potentially slow down adsorption process and hinder regeneration of the adsorbent. These observations are in sharp contrast with the results obtained by Omorogie *et al.* [14] probably due to difference in the nature of the adsorbents used.

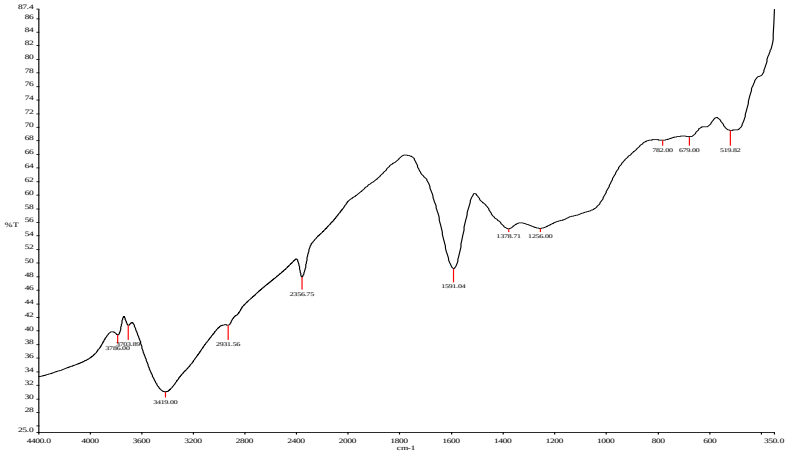


Figure 4: FTIR Spectra of MPSBAC

FTIR analysis of the dried MPSBAC showed the IR spectra pattern in Figure 4.

Figure 4 showed spectra pattern of distinct absorption peaks at 3419 cm^{-1}, 2931.56 cm^{-1}, 2356.75 cm^{-1}, 1591.04 cm^{-1}, 1378.71 cm^{-1}, 1256 cm^{-1} and 519.82 cm^{-1} indicative of the presence of free O-H and N-H stretch for aliphatic compounds, C-H stretch of CH_2 and CH_3, C=O stretch of alcohol, aldehyde, ester or carboxylic acids, C=C stretch of alkenes, C-H bending vibrations of CH_2 and CH_3, C-O stretch of esters, ethers or phenols and out of plane bending vibrations. Some of these peaks shifted slightly from the peaks 3418.32 cm^{-1}, 2929.34 cm^{-1}, 1590.00 cm^{-1}, 1378.12 cm^{-1} observed for unmodified *P. sylvetris* activated carbon (AC) which did not show C=O and C-O absorption peaks. This could imply that the appearance of N–H stretch, C–O bend, and C–H stretch and bend in MPSBAC was as a result of the interaction between carbon skeleton of unmodified *P. sylvetris* AC and the hydroxides of sodium. This result is closely similar to that reported by Omorogie *et al.* [14] who cited disappearance of C-H stretch and N-H/C-O bend after modification of AC with Fenton reagent. EDAX analysis of MPSBAC is shown in Figure 5.

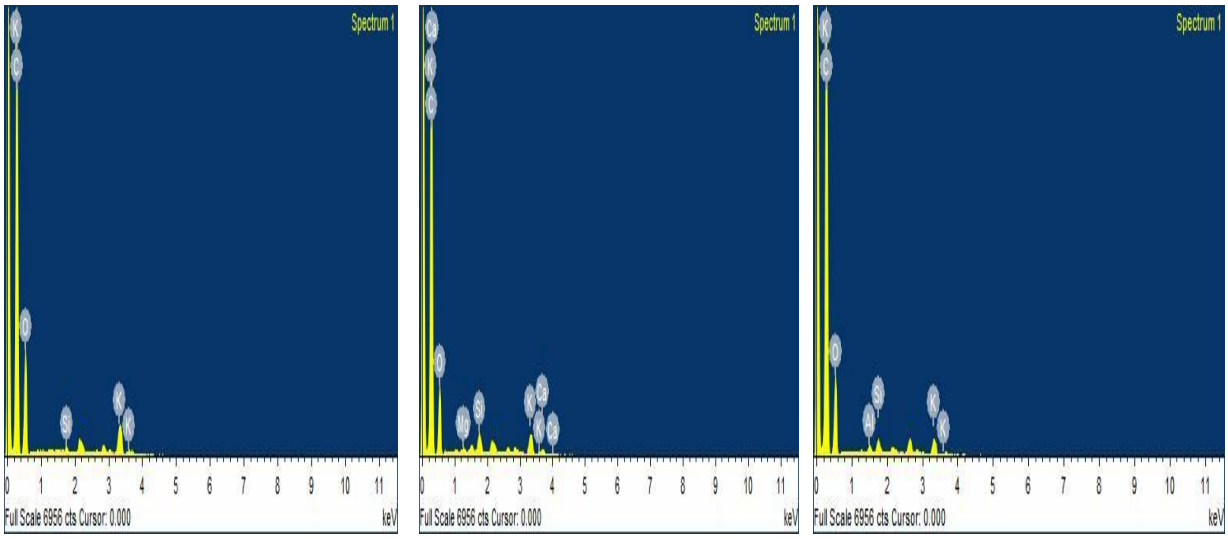


Figure 5: Energy Dispersive X-Ray (EDAX) of MPSBAC

The analysis revealed the presence of potassium, carbon, oxygen, calcium, magnesium, silicon, and aluminum in varied proportions. These elements play a major role in the binding of the CR and TC onto the surface of MPSBAC. They provide electrostatic surface on the MPSBAC for easy attraction of the counterpart ions in the aqueous solutions of CR and TC.

Effects of pH on Uptake of CR and TC

From this study, it was observed that the adsorption of CR onto the adsorbent increased as pH of the aqueous solutions increased from 2.0 to 12.0. The maximum amount of CR adsorbed by MPSBAC was observed at pH 2.0. This shows that below the PZC of the adsorbents, the uptake of CR was at its optimum. The possible adsorption mechanisms could be that at pH 2.0, the aqueous solution being acidic, offered large density of protons on the surfaces of the adsorbents and bound to the overall negative charge of the acid dye (CR) by electrostatic attraction. CR possesses π-electrons, which create electron-rich reactive centers conferring the need for reactive interactions [14] between it and MPSBAC.

Adsorption of TC onto adsorbents can be explained by its ionizability in aqua media into functional moieties; aromatic dimethylammonium, diphenolic ketone and tricarbonyl which ionize in solution to the isoelectric (zwitterionic), cationic and anionic forms [14]. Therefore, the adsorption mechanisms of TC onto MPSBAC is possibly due to electrostatic attraction, possession of $\pi - \pi$ electrons in the aromatic rings of TC through $\pi - \pi$ stacking interactions [14,18]. According to Omorogie *et al*. [14], the probable adsorption mechanism proposed for CR may not significantly hold for TC because its π-electrons were far less than those in CR, which possesses more aromatic rings than TC.

3.3 Adsorption Equilibrium Capacity against Dosage of MPSBAC for CR and TC

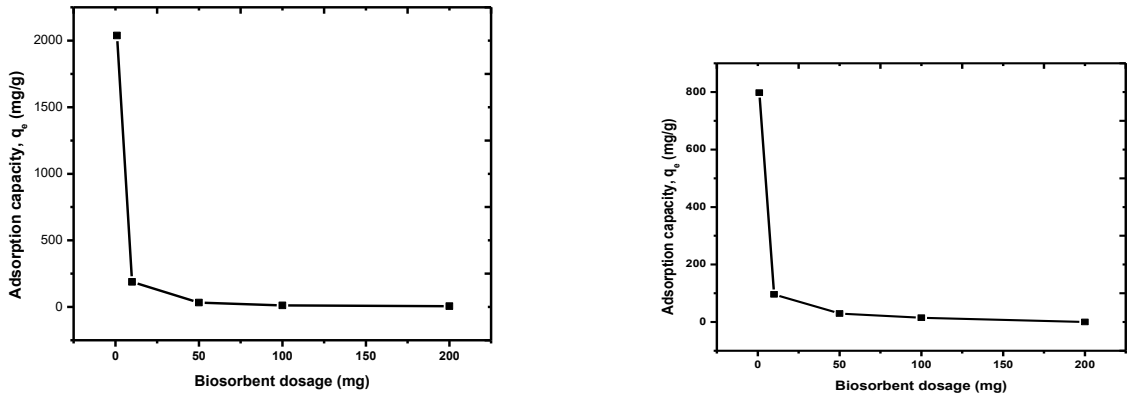
The adsorption equilibrium capacity against biosorbent dosage of MPSBAC for CR and TC is presented in Tables 1 and 2, and Figures 6 (a) and (b)

Table 1: Adsorption Equilibrium Capacity and MPSBAC Dosage for CR

Dosage(mg)	q_e (mg/g)	C_e (mg/L)	% Uptake
1	2038.4495	18.4620	81.54
10	188.1696	24.7321	75.27
50	32.2346	35.5307	64.47
100	11.9372	52.2510	47.75
200	5.5767	55.3861	44.61

Table 2: Adsorption Equilibrium Capacity and MPSBAC Dosage for TC

Dosage(mg)	q_e (mg/g)	C_e (mg/L)	% Uptake
1	797.9195	68.0832	31.92
10	96.3976	61.4409	38.56
50	29.2429	41.5142	58.49
100	14.6215	41.5142	58.49
200	0.2533	97.9734	2.03



(a) **(b)**

Figure 6: Plots of Adsorption Equilibrium Capacity against MPSBSC Dosage for the Adsorption of (a) CR dye (b) TC. (Initial Dye Concentration = 100 mg/L; Temperature = 298 K; Agitation Time = 180 minutes; Agitation Speed = 200 rpm).

The plots of q_e (mg/g) against MPSBAC dosage (mg) for CR and TC as shown in Figures 6 (a) and (b) respectively indicated a decrease in the adsorption capacity at equilibrium (q_e) as the adsorbent dosage increases. For CR and TC, q_e decreased from 2038.45- 5.58 mg/g and 797.92-0.25 mg/g respectively as adsorbent dosage is increased from 1-200 mg. Similar trend was reported by Kong *et al.* [19]. This may be attributed to a decrease in specific surface area due to the agglomeration of adsorbent particles, which causes reduction in the surface active sites and increase in diffusion path lengths. This aggregation becomes increasingly significant as the weight of the adsorbent increases [20,21]. Increase in adsorbent dosage as reported by Babalola *et al.* [22] also decreases mass transfer resistance.

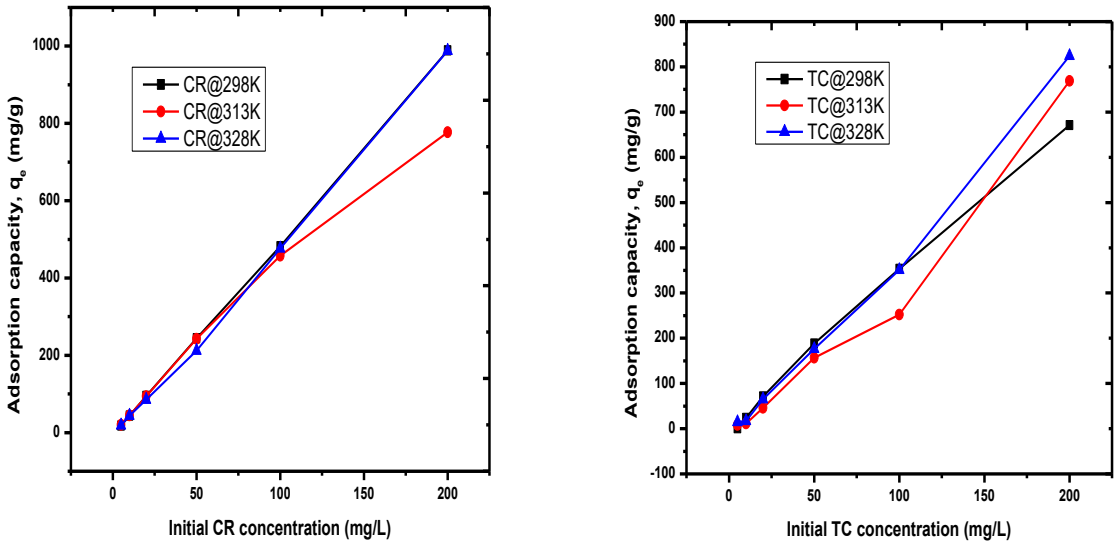
Comparison of adsorption capacities of various adsorbents for CR and TC from the literatures are shown in Table 4.

Table 4: Comparison of the Adsorption Capacities of various Materials in Literature for CR and TC

Adsorbents	**pH**	**Initial Concentration (mg/L)**	**q_e (mg/g)**	**Reference**
CR				
Terminalia ivorensis seed waste	2.00	100.00	85.47	[23]
Parkia biglobosa waste	2.00	150.00	266.67	[24]
Parkia biglobosa cellulose extract	2.00	150.00	288.18	[24]
C/NiO–ZnO fibers	6.50	100.00	613.00	[25]
Dialdehyde cellulose-crosslinked cellulose-chitosan foam	5.00	4000.00	1548.20	[26]
Pine AC	2.00	100.00	70.20	[14]
MPSBAC	2.00	100.00	164.66	This study
TC				
Cu-immobilized alginate	3.00	90.00	53.26	[27]
MWCNT functionalized MIL-53(Fe)	7.00	200.00	364.37	[28]
Graphene oxide/calcium alginate	6.00	60.00	65.40	[29]
NaY zeolite	12.00	120.00	201.77	[30]
CoO/CuFe2O4 composite	6.00	200.00	138.60	[31]
Fenton-functionalized pine ACMO	8.00	100.00	141.02	[14]
MPSBAC	8.00	100.00	248.72	This study

Effect of Initial CR and TC Concentrations

The effect of initial CR and TC concentrations was experimented on the adsorption capacity of MPSBAC. Figures 7 (a) and (b) depicts its response to the initial CR and TC concentrations from 5 to 200 mg/L at 298 K, 308 K and 328 K.



(a) (b)

Figure 7: Variation in the Adsorption Capacity against Initial (a) CR Concentrations (b) TC Concentrations (Biosorbent Dose = 100 mg; Temperature = 298 K, 313 K and 328 K; Agitation Time = 180 minutes; Agitation Speed = 150 rpm).

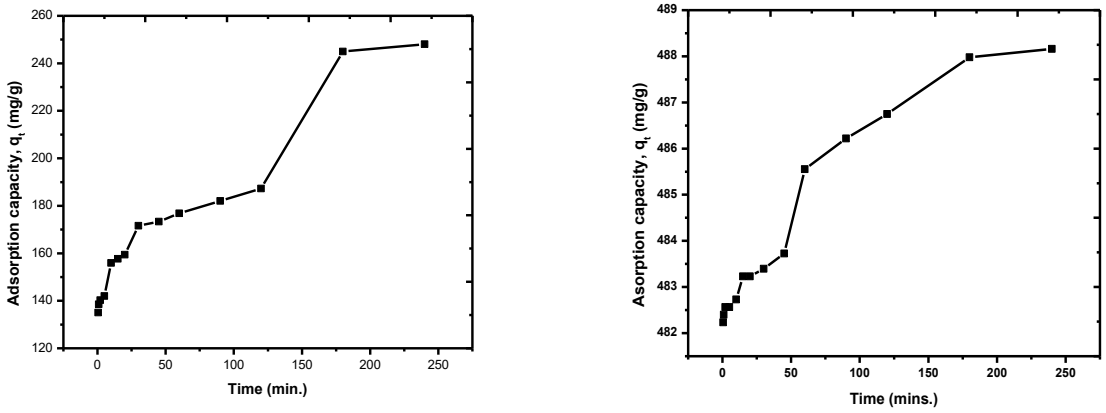
The result showed that adsorption capacities increased as the initial CR and TC concentrations increased. For CR and TC at 298 K, 313 K and 328 K, q_e increased from 18.07- 989.06 mg/L, 0.42-671.04 mg/L; 19.84- 777.06 mg/L, 8.15-769.02 mg/L and 18.59- 988.02 mg/L, 14.87- 823.98 mg/L respectively. According to Jabbar and Simaa [32], as initial concentration increases, the time required to reach saturation decreases. Increase in initial concentration increases the mass transfer of solute to attach free sites on the adsorbent. However, the result obtained in this work contradicts the view of Olasehinde and Abegunde [10] who reported decrease in adsorption capacity as initial concentrations of adsorbates increase. According to Olasehinde and Abegunde [10], the initial vacant sites on adsorbent were completely filled with molecules of adsorbate as the initial concentration increased.

Contact Time of Adsorption of CR and TC onto MPSBAC

Contact time of adsorption of CR and TC onto MPSBAC are as represented in Tables 3 and Figures 7 (a) and (b) respectively.

Table 3: Contact Time of Adsorption for CR and TC onto MPSBAC at 298 K

Time (minutes)	q_t (mg/g)	t/qt	C_t (mg/L)	% Uptake	q_t (mg/g)	t/qt	C_t (mg/L)	% Uptake
	CR				**TC**			
0.5	135.0478	0.0037	45.9809	54.01	482.2319	0.0010	3.5536	96.45
1	138.5312	0.0072	44.5875	55.41	482.3980	0.0021	3.5204	96.48
2	140.2729	0.0143	43.8908	56.11	482.5641	0.0041	3.4872	96.51
5	142.0146	0.0352	43.1942	56.81	482.5641	0.0104	3.4872	96.51
10	155.9482	0.0641	37.6207	62.38	482.7301	0.0207	3.4539	96.55
15	157.6899	0.0951	36.9240	63.08	483.2283	0.0310	3.3543	96.65
20	159.4316	0.1254	36.2274	63.77	483.2283	0.0414	3.3543	96.65
30	171.6235	0.1748	31.3506	68.65	483.3943	0.0621	3.3211	96.68
45	173.3652	0.2596	30.6539	69.35	483.7265	0.0930	3.2547	96.75
60	176.8486	0.3393	29.2606	70.74	485.5531	0.1236	2.8894	97.11
90	182.0737	0.4943	27.1705	72.83	486.2173	0.1851	2.7565	97.24
120	187.2988	0.6407	25.0804	74.92	486.7487	0.2465	2.6503	97.35
180	244.9491	0.7348	2.02037	97.98	487.9775	0.3689	2.4045	97.59



(a) (b)

Figure 7: Plots of q_t against Time (Contact Time Effect) on the Adsorption of (a) CR onto MPSBAC and (b) TC onto MPSBAC. (Initial Dye Concentration = 100 mg/L; Temperature = 298 K; Agitation Time = 180 minutes; Agitation Speed = 200 rpm).

Contact time studies of adsorption of CR-dye and TC onto MPSBAC revealed that uptake of the dye and TC increased from 54.01- 99.22 % (135.05-244.95 mg/kg) and 96.45- 97.63 % (482.23- 487.98 mg/g) respectively as agitation time increased until equilibrium is reached after 180 minutes. After 180 minutes, further increase in contact time showed no effects on the uptake of CR and TC probably due to the deposition of MPSBAC on the available adsorption sites. The amount of CR and TC adsorbed at the equilibrium time is a reflection of the maximum adsorption capacity (q_e) of the MPSBAC. Namasivayam & Kavitha [33] and Kim *et al.* [34] reported similar trend for CR and TC.

4. Conclusion

This research prepared an alkaline modified activated carbon from *P. sylvetris* bark. The results of FESEM, FTIR and EDAX analysis revealed that the activated carbon possesses the potentiality of effectively removing CR-dye and Tetracycline from their aqueous solutions. The results from selected adsorption studies carried out also showed that MPSBAC has a good adsorptive capacity to remove CR dye and TC-drugs from wastewaters containing them. The adsorption performance of the adsorbent showed that it could be applied for future treatment of water and wastewaters contaminated with industrial dyes and pharmaceutical products. It could therefore, be utilized for onsite treatment of wastewaters generated in these industries before discharging them into the environment.

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