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Insight into Environmental Regeneration - Kinetics and Thermodynamics Adsorptive Evaluation of Modified *Pinussylvetris* Bark Activated Carbon on Textile and Pharmaceutical Effluents

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Abstract

The indiscriminate discharge of industrial effluents into the environment is currently one of the world's major ecological problems from the toxicological point of view and their bioaccumulation and exposure can create allergic problems. Acidic dye- Congo red (CR) and Tetracycline are water soluble contaminants and the quest to make water environment free from pollutants becomes necessary. Modified Pinus sylvetris bark activated carbon (MPSBAC) is an abundant, effective and environmentally friendly biosorptive material capable of removing dyes and tetracycline from wastewaters. Kinetic models at 25 °C showed that pseudo-second order best fitted the adsorption of CR dye and TC with R^2 values of 0.9714 and 1.000 respectively. Thermodynamics studies indicated that the adsorption reactions were spontaneous, endothermic and involve a high degree of molecular disorder at the surface interaction between the MPSBAC and the adsorbates. MPSBAC showed a good potentiality for pollutants removal from waste waters and is therefore recommended for use on a large scale.

Keywords: *Adsorption, MPSBAC, Congo red, Tetracycline, Kinetic models, Thermodynamics studies*

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Background to the Study

The quest for good quality living for flora, fauna and human beings has drawn researchers' enthusiasm in recent times to toxic effluents generated from global industrial activities. Various water sources contaminated by pollutants have become a serious environmental challenge (Babalola, Temitope, Elifsha, Nnenna, Abimbola & Martins, 2016a). Developments in industrial and agriculture sectors have resulted in generation of large amount of waste water containing toxic pollutants which must be removed and the water must be absolutely treated before discharge (Sivakumar & Palanisamy, 2008; Emin & Şükrü, 2008). The waste waters from these industries generally contain toxic organic and inorganic pollutants in varying degrees of concentration. Many materials in the chemical industry are toxic, mutagenic, carcinogenic or simply hardly biodegradable and when present in soils and water bodies, can enter the food chain and accumulate in living organisms.

Discharge of dye effluents and antibiotics into environment is currently one of the world's major environmental problems from both toxicological standpoint. A massive amount of dyes is discharged by textile and cosmetics industries just as huge amount of antibiotics is released from the pharmaceutical and agricultural industries through animal husbandry into the environment because of improper processing (Soumitra *et al*., 2013; Ke Li *et al*., 2013). The discharged dye and antibiotic effluents are highly toxic even at very low concentration and their existence in natural water bodies may pose serious threats to the ecosystem and human health. Hence removal from wastewaters before discharge into water bodies emerges as a major challenge from environmental point of view (Soumitra, Amit, Panda& Sagar, 2013; Zhehua, Ting, Bingdi, Tyler, Shuili & Yulin, 2015).

Dye is an easily recognized pollutant due to its colour. It is widely used in textile, paper, plastic, food and cosmetic industries (Sumanjit, Seema & Rakesh, 2012). Congo red (CR) dye, [1-napthalenesulfonic acid, 3,3-(4,4-biphenylenebis(azo)bis(4-amino-)disodiumsalt], is a benzidine-based anionic bisazo dye known to metabolize to benzidine, a known human carcinogenic and mutagenic compound, which is a potential danger. Exposure to CR dyeand its bioaccumulation can create allergic problems (Oladoja & Akinlabi, 2009; Soumitra *et al*., 2013). Effluents containing CR are generated from the textile, printing and dying, paper, rubber, and plastic industries (Oladoja & Akinlabi, 2009). CR dye has a complex chemical structure, difficult to biodegrade, stable towards light and soluble in aqueous solution (Soumitra *et al*., 2013). However, its removal from the aqueous solution is physicochemically or chemically possible (Oladoja & Akinlabi, 2009).

Pharmaceutical effluents as well as rural effluents and the drugs in animal manure for soil fertilization can find their way into the watercourses if not properly managed. Indiscriminate discharge of treated or untreated domestic sewage and improper disposal of expired or unwanted drugs can also endanger the aquatic ecosystem (Aga, 2008).

Large scale production of antibiotics began in the 1940s, when they were being extensively used in animal husbandry to reduce illness, increase feed efficiency, protect, promote growth, enhance productivity and to increase profit, and being used less for human beings

(human antibiotics) for bacterial infections (Wegner, 2003; Coghlan, 1996; Sarmah,Meyer & Boxall,2006; Bonner, 1997). Antibiotics are designed to mainly affect microorganisms butmany of them are poorly absorbed in the animal gut, resulting in about 30–90% of the antibiotics being excreted in their original form via faeces or urine into the environment. The excreted residual antibiotics are potential hazards to the organisms in the environment (Sarmah *et al.*, 2006). Among the numerous antibiotics available are tetracyclines and its derivatives.

Tetracyclines (TCs)are broad-spectrum antibiotics that are widely prescribed as therapeutic agents and growth promoters in humans and animal husbandry. They are poorly assimilated such that after intake by humans and animals, more than 70% of TCs leave the organism unmetabolized (Dzomba, Kugara & Zaranyika, 2015). TC residue in the environment will induce the occurrence of anti-tetracycline bacteria. According to Luo,Xu, Rysz, Wang, Zhang& Alvarez(2011), the diversity of TC resistance genes in sewage treatment plants, lagoons and groundwater has been discovered. TC antibacterials form complexes with metals and humic acid in sample matrix which makes their extraction very difficult (Dzomba*et al.*, 2015).

The best strategy to clean highly polluted wastewater is in general to treat them at the source and sometimes by applying onsite treatment within the production lines with recycling of treated effluent (Fayza, Hala, Hisham, Saber, 2004). Some conventional techniques involving physical, chemical and biological processes such as ion exchange, chemical co-precipitation, electrochemical precipitation, reverse osmosis, solvent extraction, solid phase extraction, evaporation, membrane filtration and adsorption, sonochemical degradation, chemical oxidation, flocculation, photocatalytic decomposition, electro-catalytic degradation and adsorption, aerobic and anaerobic degradation, enzymatic oxido-reduction have been utilized in quest for saving the environment from these harmful toxicants but each technique vary in their effectiveness, cost, simplicity and flexibility (Babalola *et al.*, 2016a; Ratna & Padhi, 2012).However, various research studies have shown that pollutants in aqueous solutions can be removed by adsorption/biosorption processin batch or continuous operation at laboratory scale, which can be considered to be ideal for industrial-scale treatment of effluents.

Many polymeric material based adsorbents have been developed for the treatment of polluted wastewater (Chatterjee, Lim, Woo, 2011; Zhu *et al.*, 2012). Now-a-days, modified and unmodified natural polymers are preferred because of their low cost, easy availability and biodegradable nature (Crini and Badot, 2008). Tree barks are one of the most abundant bioresources readily available. They are obtained after forestry operations and industrial processes (Sen, Pereira, Olivella, & Villaescusa, 2014). Among the numerous agrowaste barks is pine bark (PB). PB saregenerated from pine trees. They have been reported to contain some extracts that are antioxidants and anti-inflammant, with the capacity to improve diabetic microvascular damage and correct some other medical problems of the cells and eyes (Tsutomu, Mitsutaka, Daisuke, Masahito, Tomoyasu, Mayu, Rika, Kinya, Ken-ichi & Masaki, 2009). However, the bark remnants have not been reported to be useful and as such are being disposed of as a waste. Hence, its use as an adsorbent for the removal of CR dye and TCresidues from the environment.

Materials and Methods

The *Pinus sylvetris* bark used for this research was got in large quantity from the University of Ibadan Botanical Garden, Ibadan, Nigeria. The *Pinus sylvetris* bark was washed to remove impurities like sand and leaves, and the noven dried at 100 ºC for 72 hours. The dried sample was pulverized into particle size ≤ 300 µm.5 g powder was impregnated with 0.2 M, 1.1 M and 2.0 M KOH solutions. The KOH impregnated sample powder stood in a heating mantle at 30 °C for 24 hours and agitated at 250 rpm. This was done to homogenize the pine bark powder in the KOH solution. Thereafter, the slurry of the impregnated sample was placed in an oven at 100 °C overnight. The 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 being introduced into the microwave oven at different power ratings of 600-1080 W, with impregnation ratios of 0.2-2.0 for 10-30 min. The modified *Pinus sylvetris* bark activated carbon (MPSBAC) produced after the microwave irradiation was cooled in a desiccator to room temperature and thereafter subjected to mild washing with 0.1 M HCl and hot distilled water to remove impurities until the pH's were found to be 6.5 and 7.5.

Field emission scanning electron microscopy (FESEM), Carl Zeiss, Sigma model was used to study the surface microstructures of the MPSBAC. The surface area and pore structure of the MPSBAC were studied using Tristar II nitrogen sorptometer, 3020 V1.02 model. Samples were outgassed at 10-20 Torr vacuum, at 150 °C for 24 hours before the N_2 adsorption by multipoint technique at 77 K, between 10^{-3} and 10^{0} atmospheric pressures.

Stock solutions of 1000 mg/L each for tetracycline hydrochloride (TC) and congo red(CR) were prepared by dissolving accurately weighed amounts of TC and CR in distilled water. Experimental solutions were prepared from the stock solutions by simple dilution. Adsorption studies were done by the optimization of various experimental variables.

The pH studies of CR and TC were carried out using 5 mg of MPSBAC weighed into 100 mL plastic container containing 25 mL of 100 mg/L CR and TC solutions. 0.1M HCl or 0.1 M NaOH was used drop-wise to adjust the pH of the adsorbate to different pH (2, 4, 6, 8, 10 and 12). The mixtures were agitated in a temperature controlled shaker for 180 minutes at 298K and a revolution of 200 rpm. The MPSBAC was separated from the CR and TC by centrifugation. The supernatant CR and TC concentrations at equilibrium were then analyzed using UV/ Visible spectrophotometer at maximum wavelength of absorption (498 nm for CR and 356 nm for TC). The adsorption

kinetics of CR and TC was carried out batch wise at various agitation time intervals of 0.5-240 minutes at 298 K in a thermostat shaker. 25 mL of 100 mg/L of CR dye and TC solutions were adjusted to their optimum pH and contacted with 5 mg of the MPSBAC. The MPSBAC was separated from the CR and TC by centrifugation. The supernatant CR and TC concentrations were then analyzed using UV/Visible Spectrophotometer at maximum wavelength of absorption (498 nm for CR and 356nm for TC). The adsorption thermodynamics experiment of CR and TC was carried out at various CR dye and TC

concentrations (5, 10, 20, 50, 100, 200 mg/L). 5 mg of MPSBAC was weighed into 100 mL plastic containers containing 25 mL CR dye and TC solutions of different concentrations. The pH of each was adjusted to their optimum pH. Agitation was done in a thermostatic water bath shaker for 180 minutes at 298K, 313K, and 328K. The supernatant CR and TC concentrations were then analyzed using UV/Visible Spectrophotometer at maximum wavelength of absorption (498 nm for CR and 356nm for TC).

The Microsoft office excel 2007 (Solver add-in package) and the Microcal origin 8.0 software, Origin Lab corporation 2007 were used to plot the experimental data. The experimental data obtained from kinetic and thermodynamic studies were modeled with mathematical equations, which are given as;

$$q_t = q_e(1 - e^{-k_1 t}) \quad \text{Pseudo first order model (Lagergren, 1898)} \quad (1)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad \text{Pseudo second order model (Ho and Mc Kay, 1999)} \quad (2)$$

$$\ln(1 - F) = -k_{fd} t \quad \text{Intra particle diffusion model (Oladoja } et\ al.\text{, 2008a)} \quad (3)$$

The standard free energy (ΔG^o) can be determined from the following equation:

$$\Delta G^o = -RT\ln K_e \quad (4)$$

and,

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (5)$$

Therefore, $-RT\ln K_e = \Delta H^o - T\Delta S^o$

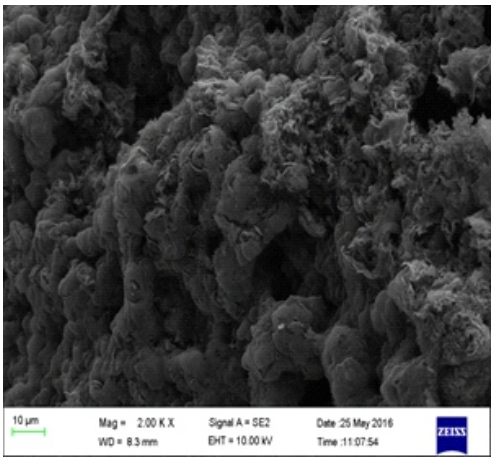
$$\ln K_e = \frac{\Delta G^\circ}{R} - \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) \quad \text{(Van't Hoff equation)} \quad (6)$$

The q_t is the amount of CR and TC adsorbed at time t (mg/g), q_e is the adsorption capacity of CR and TC at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (min^{-1}), t is the contact time (min), k_2 is the pseudo-second-order rate constant (g/mg/min), F is the fractional attainment of equilibrium, $F = q_t / q_e$ and k_{fd} is the intra particle adsorption rate constant.

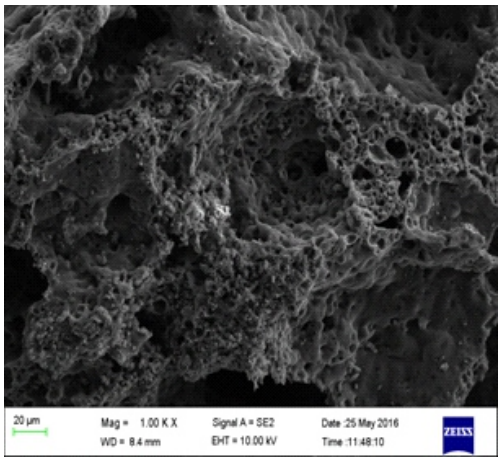
Results and Discussion

Surface Micro structural and Micro-area compositional analysis of MPSBAC

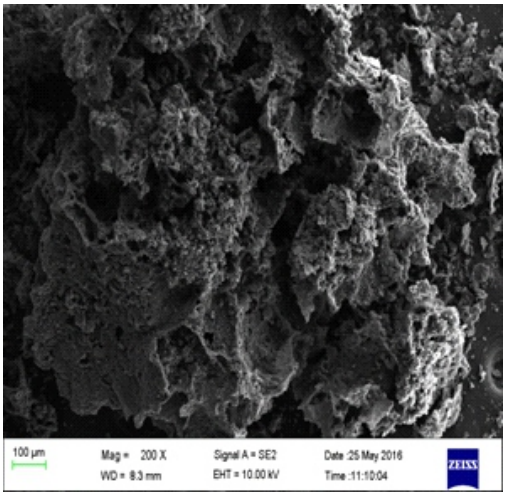
To understand their pores structures and morphologies which play significant roles in the adsorption process. Figures1.0 (a), (b), (c) and (d)show the FESEM images of the MPSBAC at 10 µm, 20 µm and 100 µm. These images revealed that MPSBAC has its morphologies with scanty and scattered pores of various lump sizes that are irregularly shaped on their surfaces.



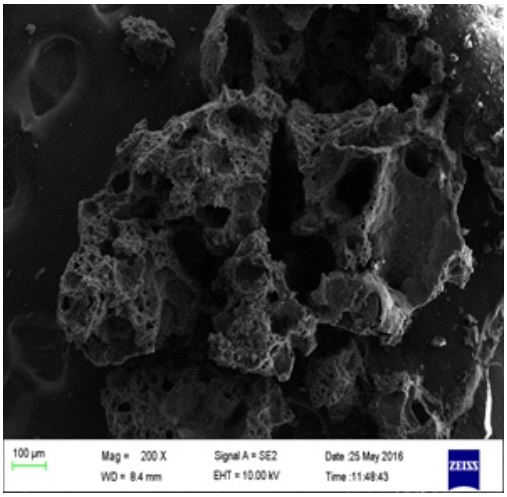
(a)



(b)



(c)



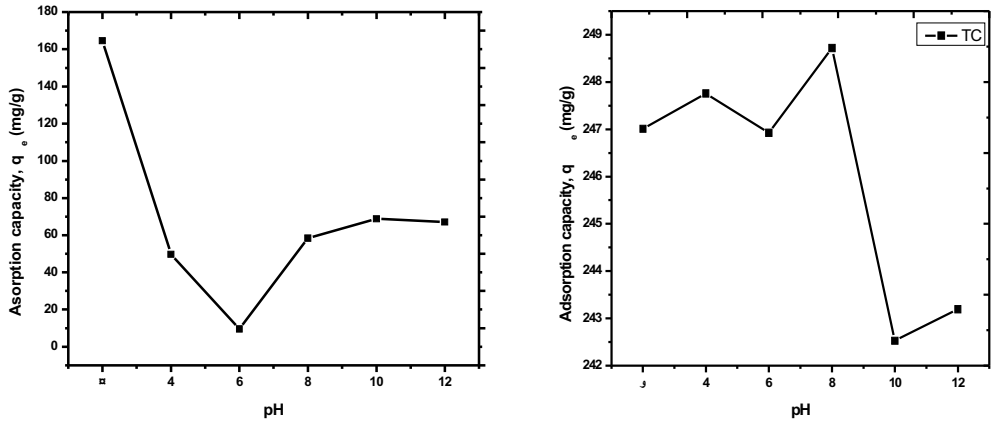
(d)

Figs. 1: FESEM images of the MPSBAC at (a) 10µm (b) 20µm(c) 100µm: WD = 8.3 mm and (d) 100µm: WD = 8.4 mm.

The Effect of PH

The solution pH can affect the surface charge of an adsorbent and the structure of the adsorbates (Ai,Li & Li, 2011). Fig. 2.0(a) and (b) shows the effect of pH on the adsorption of CR dye and TC respectively. CR is an anionic dye, which exists in aqueous solution in the form of negatively charged ions. As a charged species, the degree of its adsorption onto the MPSBAC surface is primarily influenced by the surface charge, which in turn is influenced by the solution pH (Ai *et al.*, 2011). The equilibrium adsorption capacity of the MPSBAC was minimum at pH 6 (8.5 mg/g) and maximum at pH 2 (164 mg/g). That is, CR dye adsorption increases towards strong acidic region. This could be as a result of the interactions between

the excess H^+ and the negatively charged nature of the dye. This increased up to 2 and remained nearly constant over the initial pH ranges of 8-12. The rise of q_e from pH 6-8 towards the alkaline region may be due to the presence of few available active sites on the MPSBAC. From pH 8-12 towards the strong alkaline region, q_e is almost constant, and this could be explained by the competitive electrostatic repulsion between the free OH^- groups on the MPSBAC and the anionic CR molecules. Namasivayam and Yamuna (1992) and Namasivayam, Muniasamy, Gayathri, Rani & Ranganathan, (1996) reported the same trend. The adsorption of TC on MPSBAC is greatly influenced by the pH of the solution as well as the pKa of TC. The maximum adsorption capacity of 248.6 mg/g was achieved at pH 8. The adsorption of TC unto the surface of MPSBAC sharply decreased at pH 10 (241 mg/g), where minimum q_e was recorded and there was slight increase towards pH 12. This trend could be the repulsion effect of like-ions between the MPSBAC and the TC molecules. In the acidic region, TC adsorption increased slightly from pH 2 to 4 and then decreased slightly towards pH 6. This trend generally may be explained by the existence of TC as cations in strong acidic solutions at pH lessthan 3.3, as zwitter ions at pH 3.3 to 7.7 and negative ions at pH greater than 7.7 (Zhang, Niu, Zhang, Meng and Cai, 2011; Qiang & Adams 2004).



(a) (b)

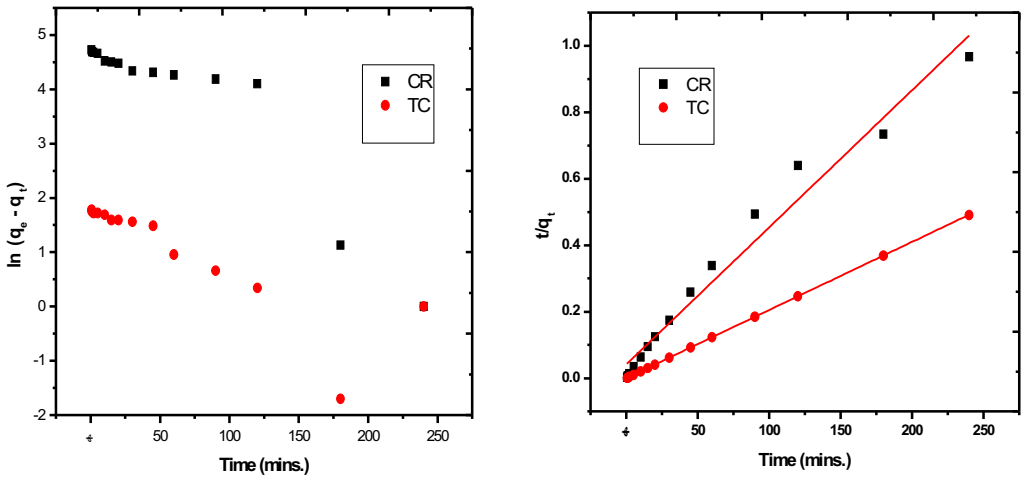
Fig. 2: The plots of q_e against pH for the adsorption of (a) CR onto MPSBAC and (b) TC onto MPSBAC. (Biosorbent dose = 100 mg; initial dye concentration = 100 mg/L; temperature = 298 K; agitation time = 180 minutes; agitation speed = 200 rpm)

Adsorptive Kinetic Effect on the Removal of CR and TC onto MPSBAC

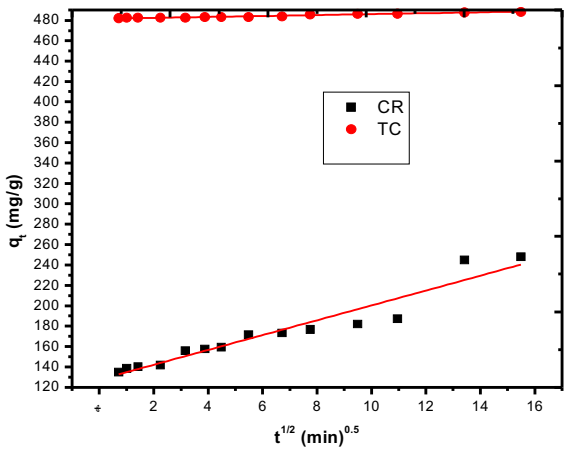
Pseudo-first order, pseudo-second order and intraparticle diffusion parameters obtained are as presented in Table 1.0. The correlation coefficient, R^2 for the pseudo-second order kinetic model for CR dye and TC was higher than the correlation factors for both the pseudo-first order kinetic model and intraparticle diffusion model for CRdye and TC at all temperatures. This indicates that the adsorption perfectly complies with pseudo-second order reaction and the adsorption process for CRdye and TC appeared to be controlled by the chemisorptions process (Kilic, Apaydin-Varol, & Putin,2011; Asgher & Bhatti, 2010).

Figure 3. (a), (b) and (c) shows plots of pseudo first order, pseudo-second order and the intraparticle diffusion models respectively for the adsorption of CR dye and TC onto MPSBAC.

Table 1: Summary of pseudo first order. Pseudo second order and intraparticle diffusion constants for the sorption of the dye and the antibiotic.



(a) **(b)**



(c)

Fig. 3: **(a)** Pseudo- first order kinetic plot for the biosorption of CR and TC onto MPSBAC, **(b)** pseudo- second order kinetic plot for the biosorption of CR and TC onto MPSBAC and **(c)** intraparticle diffusion plot for the biosorption of CR and TC onto MPSBAC.

Table 1: Pseudo first order, pseudo second order and intraparticle diffusion constants for the adsorption process.

	Temperature	Pseudo first order			Pseudo second order			Intraparticle diffusion		
	°C	k_1	q_e	R^2	k_2	q_e	R^2	k_{id}	R^2	C
CR	25	0.0180	142.0473	0.8524	4.093×10^{-4}	242.7184	0.9714	7.2779	0.9212	127.5843
TC	25	0.0116	5.8204	0.7406	1.222×10^{-2}	487.8049	1.0000	0.4446	0.9550	481.6016

Thermodynamics Effect on the Removal of CR and TC onto MPSBAC

The thermodynamic parameters obtained are shown in table 2.0. The free energy changes (ΔG^o) were negative for CRat all temperatures (298 K, 313 K and 328 K)and positive for TC at only 298 K. The negative ΔG^osuggests that adsorption process was spontaneous for CR and TC at all the temperatures. The calculated values of enthalpy change (ΔH^o) and entropy change (ΔS^o) for both the CRand TC were positive. This implies that the adsorption process was endothermic and the degree of randomness between the molecules of CR dye and TC during adsorption onto the MPSBACincreased (Bello, Adelaide, Hammed, & Popoola, 2010).

Table 2: Thermodynamics parameters for the adsorption of CR dye and TC onto PBAC at different temperatures

	ΔG^o (KJ/mol)			ΔH^o (KJ/mol)	ΔS^o (KJ/mol/K)
	298 K	313 K	328 K		
CR	-8.1708	-10.0617	-9.1092	1.6237	0.0343
TC	-2.9691	-2.0851	-13.8245	168.6748	0.0538

Conclusion

MPSBAC has been established through the FESEM, pH, kinetic and thermodynamic studies result of this research to be a good remover of CR dye and tetracycline pollutants in the simulated wastewaters from textile and pharmaceutical industries respectively and can actually be applied to a large scale removal of these pollutants from the environment.

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