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REMOVAL OF ERICHROME BLACK T FROM AQUEOUS SOLUTION USING YAM PEEL ACTIVATED CARBON

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ABSTRACT
The present study was carried to evaluate the adsorption potential of yam peel activated carbon as adsorbent for the removal of Erichrome Black T (EBT). The adsorbent was characterized using Fourier Transform Infrared (FTIR) spectroscopy and Field emission scanning electron microscopy (FESEM).The Adsorption was carried out as a function of adsorbent dosage, contact time, initial concentration, pH and temperature using batch method. Equilibrium data were analyzed through isotherms, kinetic and thermodynamic modelling. The experimental adsorption isotherm data fitted well with Freudlinch in comparison to the other models tested. The n values obtained were greater than one indicating a favorable physical adsorption. The mean free energy (Ea.) from D-R was found to be <8 kJ/mol indicating physiosorption of the adsorbate onto adsorbent. Kinetics data were analyzed using pseudo first order, pseudo second order Elovich and intraparticle diffusion models. The results revealed that the adsorption was best described by pseudo second order model. Study of the thermodynamic behavior revealed a negative value of ΔG and positive values of ΔH and ΔS indicating spontaneous and endothermic nature of the adsorption process. The results of this study reveal that the yam peel can be utilized as a good adsorbent for the removal of dye from aqueous solution.
Keywords: Yam peel, Activated carbon, Erichrome Black T.

INTRODUCTION

The increase in business activities and population alongside industrialization have positively impacted humanity and at the same time enhanced environmental pollution (Hannachi *et al*., 2012). Pollutants discharged from various industries are posing threat to the earth biodiversity. Water is of major concern among the various type of environmental pollutions. Dye-based industries contribute to this pollution, because the dyes and other chemicals wasted by this industries are among the main sources of water pollution (Kose, 2008). Environmental pollution control has been a concerned issue in many countries (Ekpete *et al.,* 2010). The most major environmental pollution is air and wastewater pollution .The source of wastewater pollution comes from the industrial effluents`` as well as domestic sewage. One of the major problems concerning wastewater pollution is that it gives bad effect on public water supplies which can cause health problem such as diarrhea. Additionally, it is also an esthetic concern caused by odors and discoloration which interfere bathing facilities and recreation (Ekpete *et al.,* 2010). It can also cause property damage such as discharge of sewage, affect industrial water supply by charging the character of the water. It also affect real estate by causing paint to discolor as well as damage to boat.

In the past many techniques such as ion exchange, chemical reduction, electrochemical process, advanced oxidation processes (Gupta *et al.,* 2007), bio sorption (Gupta and Rastogi, 2009) and membrane technology have been applied for the removal of dyes from industrial effluents. However, these methods are in-effective because they require high skilled man power and production of large sludge.

Therefore, there is a need to develop a cost effective and facile method for the removal of these dyes. Recently, adsorption has proven to be economical and efficient for removing heavy metals, organic pollutants and dyes from polluted waters (Insuk *et al.,* 2009) because of its low-cost, high efficiency, minimization of chemical sludge, and regeneration of bio sorbent and possibility of metal recovery.

Various types of adsorbents used by many researchers for the removal of dyes from industrial waste waters include coffee bean (Baek *et al.*,2010), ginger waste (Ahmad and kumar,2010), sea shell powder (Chowdory and Saha,2016),fly ash (Kao *et al.*,2000). In this research yam peel activated carbon will be used as adsorbent for the removal of Erichrome Black T from aqueous solution.

MATERIALS AND METHODS

Sample collection and preparation

Yam peel was collected from Dawanau market, Kano state, cut into small pieces, washed with distilled water two to three times to remove dust and soil and then air dried for some days. The dried yam peel were crushed using mortar and pestle to get the powder. The powder obtained was further sieved using 450 µm sieve. The sieved adsorbent was well-preserved in a plastic container for further used.

Preparation of Activated carbon (AC)

The sieved adsorbent was impregnated with 40% phosphoric acid and left for 24 hours, then the excess solution was decanted off and air dried. The dried materials was carbonize at 450^0C for 120 minutes in a muffle furnace, powdered and then activated at 800°C for 10 minutes. The resulting AC was allowed to cool at room temperature and washed severally with distilled water to remove the acid until the pH remained constant at around 6.0 then the AC were dried in an oven to remove residual moisture, ground and sieved. The AC was then stored in dry, clean and well closed container for further use.

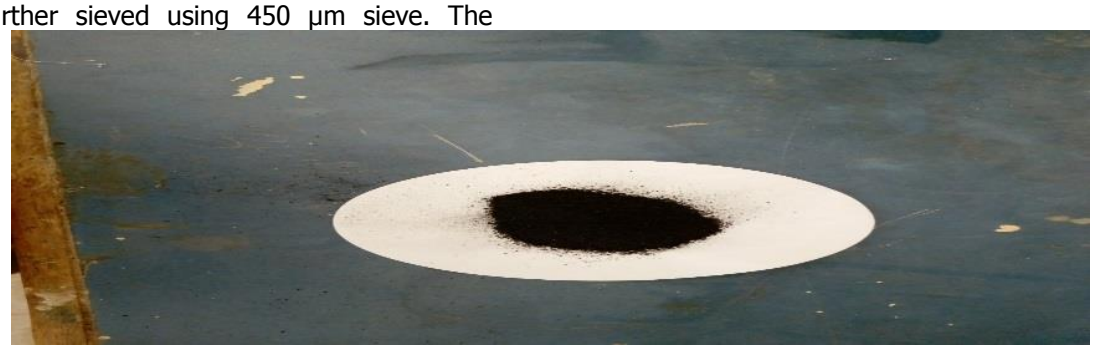

Figure 1: Activated Yam peel

Characterization of Activated Carbon Adsorption Studies

The adsorption studies was prepared by dissolving 1g of EBT dye in 1000 ml of distilled water to get a dye solution of 1000 ppm. Adsorption experiment was carried out by agitating a known weight of Activated Yam Peel on 50 ml of the EBT solution on a shaker at 30 ^{0}C. The dye solution was separated from the adsorbent by filtration. The residual concentration of the EBT dye was estimated by determining the absorbance at maximum wavelength of 555 nm using UV spectrophotometer.

The percentage adsorbed and amount of adsorbent dye molecules per gram of solid q_e were determined as follows:

$$\% \text{ adsorbed} = \frac{(C_O - C_e)}{C_O} \times 100 \quad \ldots\ldots (1)$$

$$Q_e = \left(\frac{C_O - C_e}{m}\right)v \quad \ldots\ldots (2)$$

Where C_o=initial concentration of EBT dye (mg/l)

C_e=equilibrium concentration of EBT dye (mg/l)

V=volume of solution

m=mass of AC

RESULTS AND DISCUSSION

Characterization: FTIR spectroscopy

The results of the properties of yam peel before and after adsorption were shown in figure 2.

The major peak of importance on the IR spectrum in figure 2 seen at 3379 and 3268cm^{-1} is an indicator of O-H Stretching which shows the presence of carboxylic acid, and the peaks observed at 2921 is due to the presence of aliphatic C-H Stretching, and the peaks observed at 1774 and 1622 are characteristics of carbonyl groups, the peaks at 1562 are associated with N-H bending which confirms the presence of primary amines, the peaks at 1067 are due to C-O bonds. All these bonds are associated with the presence of polyphenols, tannins, proteins and flavonoids which act as reducing agent (Ibrahim and Abdullahi, 2017).

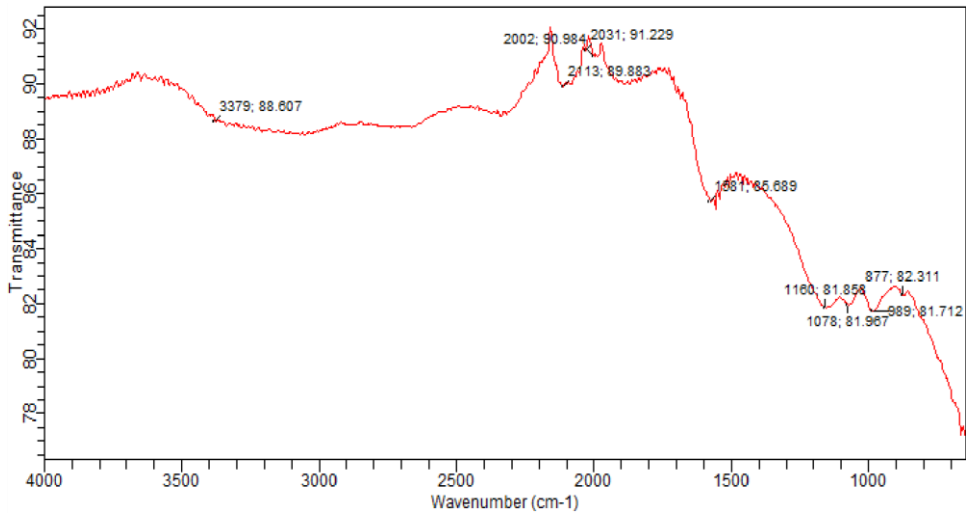

Figure 2: FTIR Spectrum of AYP before EBT adsorption

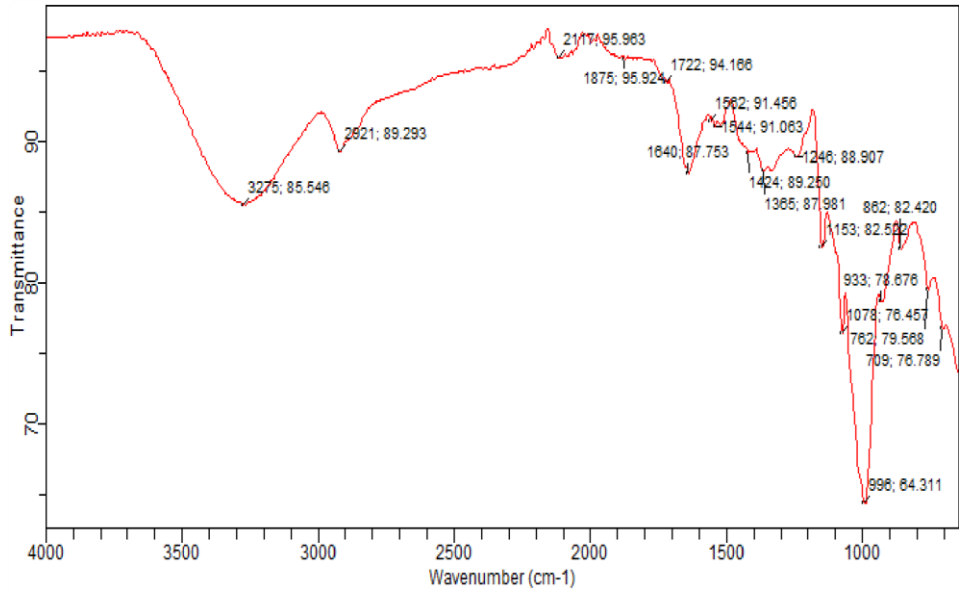

Figure 3: FTIR Spectrum of AYP after EBT adsorption

In Figure 3 it can be observed that shifting occurs both at higher and lower wave numbers after the Adsorption process. This shifting indicated that there was a binding processes taking place on the surfaces of the substrates. The functional groups could act as binding sites where hydroxyl group dissociate negatively charged active surface. The changes in wave numbers in relation to energy showed little difference which indicated the adsorption process to be physical.

Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray (FESEM-EDX)

Figure 4 represents SEM micrographs of the adsorbent before and after adsorption of EBT. The bright spots and the numerous pores clearly observed in the SEM micrographs of the adsorbent before adsorption in figure (4a) are responsible for the increase of adsorption capacity of adsorbents (Sivakumar *et al.*, 2010). In figure (4b) the pores appeared to have been covered by the dye even though not very smooth. This signifies the transfer zone due to layers of adsorbed molecules of dyes has filled up the pores and the surface of the substrate. Simmilar results have been reported by Nethaji *et al.*, (2013) for the removal of dye using char generated from lotus seed biomass. It is also evident that upon adsorbing the dye, the adsorbent structure changed.

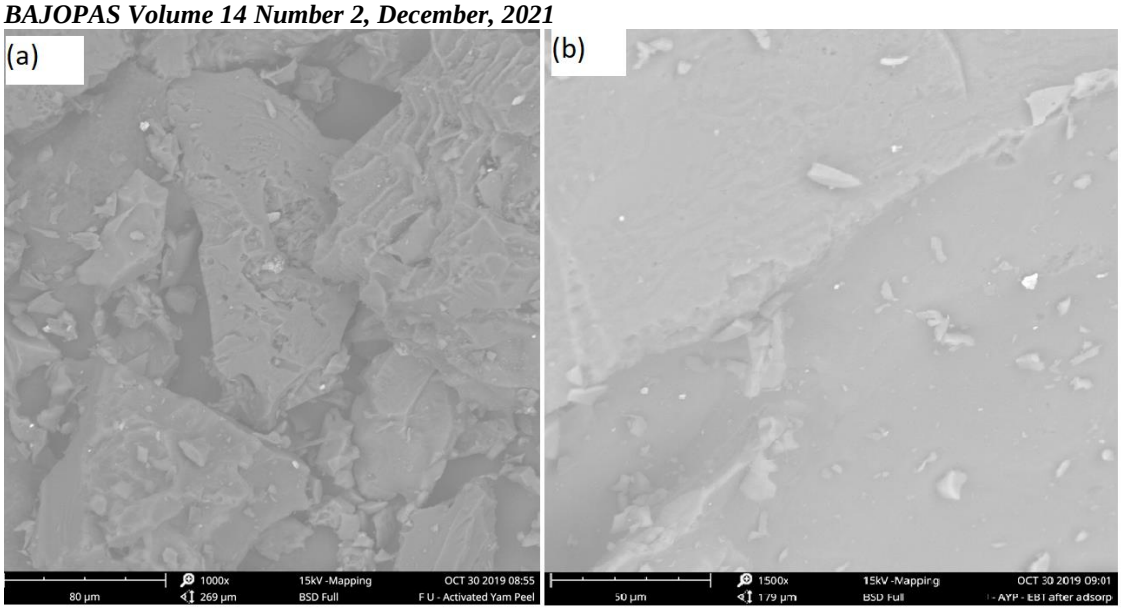

Figure 4: SEM Micrograph of (a) AYP before adsorption and (b) after adsorption of EBT

Optimization of Batch Adsorption Parameters

Effect of Adsorbent Dosage.

The effect of adsorbent dosage was studied and optimized by varying the adsorbent dosage (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6g). The effect was expressed by plotting adsorption capacity against adsorbent dosage, as shown in figure 5. 0.1g was optimum because it showed better adsorption capacity. This reveals that the adsorption sites remain unsaturated during adsorption reaction whereas the number of sites available for adsorption increases by increasing the adsorbent dose. Similar result was reported by Etim *et al.*, (2013) who study coconut as low cost adsorbent for the removal of cationic dye from aqueous solution.

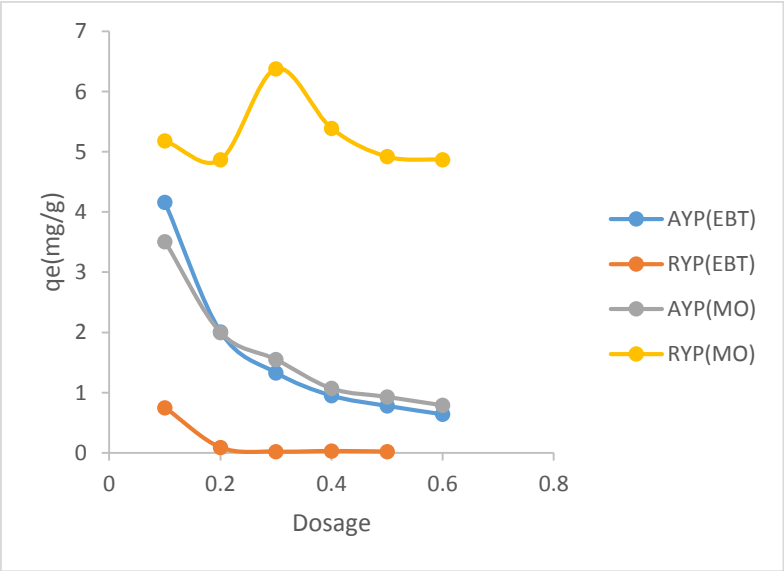

Figure 5: Effect of adsorbent dosage

Effect of Initial Dye Concentration.

The effect of initial concentration was studied and optimized by varying the dye concentration (20, 40, 60, 80 and 100ppm) at constant adsorbent dosage and ordinary pH of the solution. The effect was expressed by plotting adsorption capacity against concentration as shown in figure 6. It was observed from the concentration study that the amount of dye adsorbed increased rapidly in the beginning and then more slowly until the equilibrium.

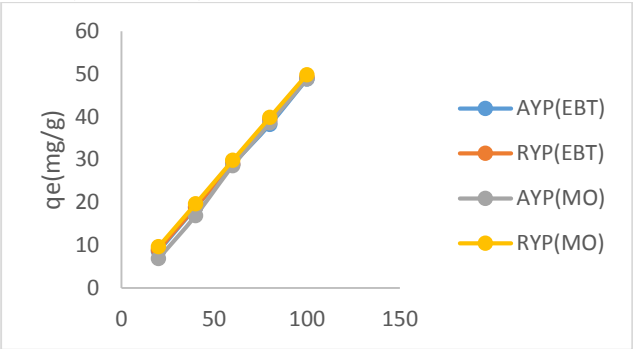

Figure 6: Influence of Dye initial Concentration.

This is due to the strong attractive forces between the dye molecules and the adsorbent. Simmilar result were reported by (Kannan and Sundaram 2001).

Effect of pH

The effect of pH was studied by varying the pH at constant adsorbent dosage (0.1g) dye concentration and time. The effect was expressed by plotting adsorption capacity against pH.as shown in figure 7

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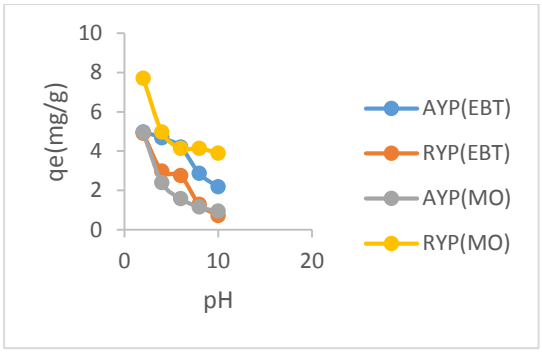

Figure 7: Effect of pH Solution

It is assumed that the rate of dye adsorption onto the adsorbent will be varied with the available pH values of solution. The pH values used in this study are 2, 4, 6, 8 and 10.The removal of MO from aqueous solution by adsorption is highly dependent on pH of solution which affects the surface properties of the adsorbent and dye structure. The sorption capacity for MO decreases from 7.71 to 3.9 mg/g when the pH of the initial dye solution was increased from 2 to 10. The pattern was similar to the adsorption of Congo red onto surfactant modified montmorillonite (Wang and Wang, (2007).

Effect of Contact Time

The effect of contact time was studied by varying the time intervals at constant adsorbent dosage (0.1g), dye concentration (20mg/l) and ordinary pH of the solution.

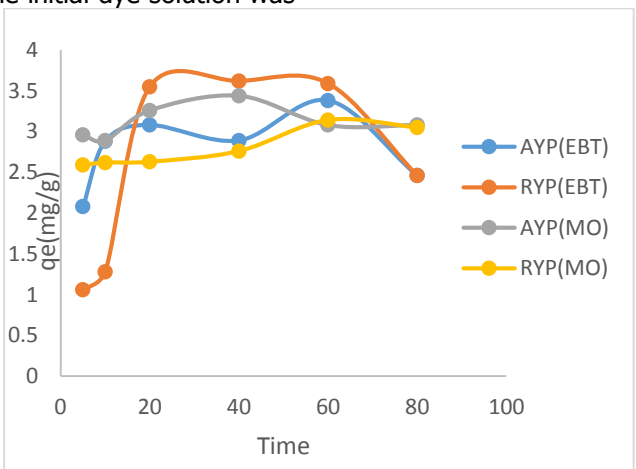

Figure 8: Effect of Contact Time

The effect was expressed by plotting the adsorption capacity against time, as shown in figure 8. The adsorption capacity increases with increase in time, this may be as a result of large number of vacant site that are available for the adsorption by increasing the time .similar result were reported by Afrah and Hadeel (2015).

Effect of Temperature

The influence of temperature on adsorption of MO and EBT onto RYP and AYP was studied by conducting different set of experiments at different temperatures that is 30, 35, 40, 50 and 55^{0}C. as shown in figure 9,the effect was expressed by plotting the adsorption capacity against temperature, the adsorption capacity increases with increase in temperature even though it shows some certain decrease at some points but still maintained the trend of decrease in the adsorption.

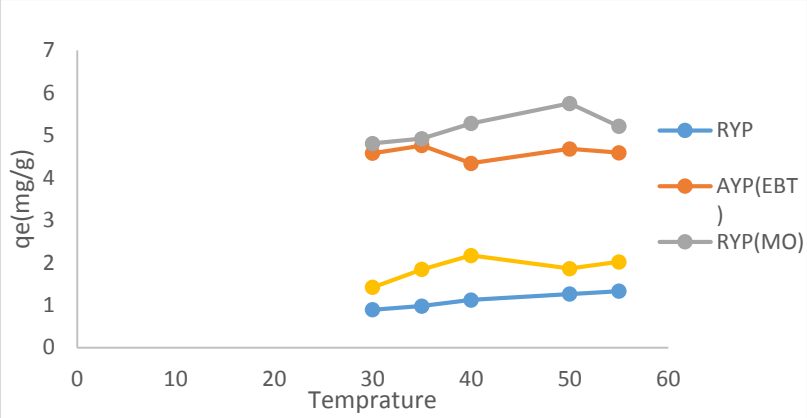

Figure 9: Effect of Temperature.

This may be as a result of increasing the mobility of dye molecules at higher temperature thereby producing swelling effect within the internal structure of the adsorbent. The increase in the quantity adsorbed with increasing temperature may suggest an increasing accessibility in the AYP and RYP and the dye molecule (Ibrahim and Abdullahi, 2017).

Adsorption Isotherms

Adsorption is usually described using isotherms, that is functions of which connect the amount of adsorbate on the adsorbents. Four isotherms models were tested and the isotherms parameters of RYP and AYP are represented in Table 1. From the results, R^2 value of Freudlinch was higher than the other models, this shows that the experimental equilibrium data was better explained by Freudlinch. From the n values, the result reveals that the adsorption of EBT (having n>1) are favorable physiosorption (multilayer) adsorption process. And it can also be understood from the table 4.2 that the adsorption of dyes cannot be explained by Langmuir isotherms since the R_L values are less than 0 and q_{cal} are far away fromq_m. Based on the D-R model, the energy is less than 8kJ/mol which shows that the adsorption is physical adsorption.

Table 1: Isotherm Parameters for Adsorbate Adsorption onto Adsorbents

Isotherm models	Parameters	MO (RYP)	MO (AYP)	EBT (AYP)	EBT (RYP)
Langmuir	q_m (mg g^{-1})	20.24	22.43	32.44	31.34
	K_L	0.13	0.2	0.17	0.45
	R_L	0.59	0.32	0.04	0.1
	R^2	0.7136	0.621	0.0395	0.4393
Freudlinch	N	1.342	1.600	1.43	1.2336
	K_F	4.57	21.92	3.75	2.79
	R^2	0.889	0.828	0.76	0.6235
Temkin	B_T	13.40	27.62	24.76	10.90
	b_T (J/mol)	184.89	89.77	100.05	227.30
	R^2	0.6154	0.8011	0.600	0.5821
Dubinin	E(kJ/mol)	$2.5*10^{-2}$	$3.28*10^{-1}$	$3.28*10^{-2}$	$1.18*10^{-2}$
	R^2	0.5736	0.4942	0.2750	0.4955

Thermodynamic Study

The results obtained from thermodynamic study are presented in Table 2. It was evident from the results that the adsorption of both dyes are endothermic since the value of ΔH is positive irrespective of the nature of dye. Lower values OF ΔH less than 20kJ/mol signifies that the adsorption is physical adsorption.

Table 2: Thermodynamic Parameters for Adsorption of EBT onto AYP and RYP**.**

Adsorbent	Dye	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)	T (K)
AYP	EBT	6.818	1.909	-6.096	328
RYP	EBT	3.709	18.44	-1.368	328
RYP	EBT	6.818	18.44	-1.292	323
AYP	EBT	6.818	1.909	-1.967	323
AYP	EBT	6.818	1.909	-6.096	313
RYP	EBT	3.709	18.44	-2.340	313

Simmilar results was reported by Nethaji *et al*., (2013) on adsorption of anionic and cationic dye onto carbonaceous particles prepared from juglan regia a shell biomass. The adsorption of EBT was feasible and spontaneous at all temperatures since ΔG is negative. The positive value of ΔS showed an increase in the randomness of the adsorbate molecules on the solid surfaces than in the solution of dyes

Adsorption Kinetics Models

The results obtained from kinetics models are presented in Table 3

Table 3: Results Obtained for the Adsorption Kinetics

Kinetic model	parameter	AYP (EBT)	RYP (EBT)	AYP (MO)	RYP (MO)
Pseudo-first order	Q_e (mg/g)	3.88	3.62	3.67	3.14
	$q_e$cal(mg/g)	2.15	2.2	1.15	0.15
	k_1	0.001	0.0009	0.001	0.0011
	R^2	0.5557	0.8598	0.7598	0.6598
Pseudo-second order	Q_e(mg/g)	3.88	3.62	3.67	3.14
	$q_e$cal(mg/g)	3.991	3.779	3.109	3.186
	k_2(min^{-1})	0.026	0.046	0.086	0.041
	R^2	0.9857	0.9887	0.9839	0.9956
Intra particle diffusion	C	0.011	1.9092	-10.933	-18.667
	K_{id}	1.957	1.3772	5.1027	15.571
	R^2	0.1171	0.385	0.0336	0.7639
Elovich	R^2	0.1171	0.3850	0.0360	0.7638
	K_3	1.957	1.3772	5.1027	7.7638
	C	0.011	1.9092	10.938	16.682

CONCLUSION

In this study, adsorbents were prepared from yam peel using phosphoric acid and characterized using various technique. FTIR analysis revealed the presence of various functional groups on the surface of the adsorbents. SEM analysis revealed variation in surface morphology of the prepared adsorbents before and after adsorption. EDX analysis shows the differences of the carbon content before and after adsorption on activated carbon sample. Experimental parameters such as contact time, adsorbent dosage, temperature, pH and concentration were found to have effect on the adsorption process. Isotherms results revealed that the adsorption can be fitted by Freudlinch isotherm model. Thermodynamics results reveals that the adsorption process is spontaneous and endothermic in nature. The adsorbents can serve as efficient and cheap for the removal of adsorbates.

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