

# Evaluation of aqueous phase adsorption of Acid Brown on mesoporous activated carbon prepared from Azolla Pinnate seaweed

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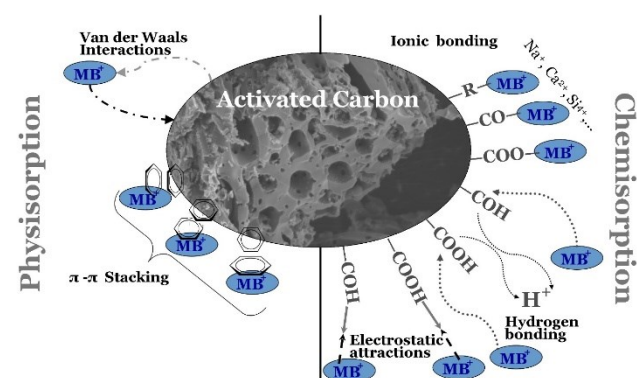
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## Graphical abstract



## Abstract

A mesoporous activated carbon was produced from the Azolla Pinnate (AP) seaweed by two-step chemical activation technique using sulphuric acid as activating agent. The adsorption of Acid Brown (AB) from aqueous solutions is examined using the produced carbon (AP). The produced activated carbon renders a homogeneous porous structure, predominantly mesoporous with 686.5 m<sup>2</sup>/g of BET surface area. The infra-red spectrum revealed AB affinity by multiple functional groups. The point of zero charge and the pH studies evidenced that the surface charge responsible for electronic affinity favours adsorption at higher pH. The SEM and FTIR analysis of AP before and after adsorption of acid brown shows multiple interactions, which is further substantiated by equilibrium, kinetic and thermodynamic models. Equilibrium adsorption data matched best with Langmuir isotherm model, thus primarily follows chemical interaction. However, physical affinity and heterogeneity of surface and species interaction also do exist nearly equally. Pseudo-second order kinetics provided the best explanation

of the adsorption kinetics. The temperature variation studies revealed that acid brown adsorption is endothermic with high surface affinity.

**Keywords:** Acid Brown, azolla pinnate, activated carbon, adsorption isotherms, kinetics

## 1. Introduction

Synthesis of activated carbons from biomass waste is gathering pace for the last 50 years, which led to the production of activated carbons with high surface area (2000-3500 m<sup>2</sup>/gm), unique functionalities and complex affinities from low-cost precursors. Biomass carbons have successfully replaced coal-based carbons and ease of solid waste handling. The excessive discharge of colored effluent to water bodies poses a major threat to ecosystem and public health (Robinson et al., 2001; Kheira et al., 2016). The cationic methylene blue was used frequently for dyeing wood, paper, cotton, wool and silk (Robati et al., 2016). The dye molecules released in water absorbs sun light, thereby affects the growth and existence of phytoplankton, which inturn recalcitrate the whole aquatic ecosystem. Acid Brown (AB) inhalation cause allergic rapid breathing, ingestion is also toxic to humans it may cause irritation, vomiting, diarrhea, gastric discomfort and nausea (Jie et al., 2016; Hatice & Ismet 2016; Hariharan et al., 2016). Higher doses of AB may cause methaemoglobinaemia, micturition, chest pain, stomach pain, excessive perspiration, and mental disorientation (Ahmed et al., 2009; Dimitris et al., 2015; Mehrorang et al., 2015). The major difficulty in the removal of such dyes lies in their stability and complex aromatic structure (Garg et al., 2004).

Activated carbon adsorption is widely considered as an effective process in the removal of such complex dyes for its surface electronic properties and large interior surface area. Carbon characteristics, pore structure and surface

chemistry determine its performance in adsorbing dyes. The type of precursor, the activation technique, and the degree of activation in turn affect the porous structure (Yupeng *et al.*, 2002; Tengyan *et al.*, 2004; Montanher *et al.*, 2005; Chan *et al.*, 2005). Activated carbons produced by chemical activation are mostly mesoporous (Harry & Francisco 2006), however all the three ranges of pores do exist (Rodriguez *et al.*, 1995; Hariharan *et al.*, 2023; Hariharan *et al.*, 2023). The interior surface is accessible and the adsorption rate is enhanced due to a well-developed pore structure and a suitable pore size distribution (Laine *et al.*, 1989). The surface functional group of activated carbon is the next most important factor that influences the adsorption of complex aromatic dye molecules. The surface groups containing oxygen and hydrogen strongly affects the adsorption, these surface groups may be inherited from raw material or obtained by activation (Bhabendra & Sandile 1999; Paul *et al.*, 2003). Different groups of oxygen, including carboxyls, phenols, lactones, aldehydes, ketones, quinines, hydroquinones, anhydrides, and ether functionalities, may be present on a surface (Roop & Meenakshi 2005). Essentially in recent decades, it was established that chemical activation by two-step process resulted in adsorbent with superior qualities (Gyu & Chong 2002).

Sulphuric acid was used as activating agent for its powerful dehydrating and strong oxidizing property. It reacts with the lignocellulosic precursor by removing water and decomposing it to elemental carbon (Albert & Geoffrey 1972). Such dehydration reactions promote the partial degradation of the cellulose and hemicellulose fractions, and also contribute to structural modification of the lignin present (Caballero *et al.*, 1997; Estefania *et al.*, 2001; Alvarez *et al.*, 2008; Olivares *et al.*, 2011).  $H_2SO_4$  improves the pore development in the carbon structure (Olivares *et al.*, 2011); it also produces a combination of micro and meso porous carbon which is suitable for the movement of the larger AB ions. The use of  $H_2SO_4$  for carbonization might be advantageous in terms of process cost and chemical composition of carbon produced; also, it may result in activated carbons with unique porous structures (Albert & Geoffrey 1972; Olivares *et al.*, 2011). A two-step chemical activation using sulphuric acid was carried out on the *Areca triandra* palm husk in this study, its surface properties and AB adsorption capabilities were examined. The main focus of this study is the adsorption of AB ions from aqueous solution on activated carbon made from the *Azolla Pinnate* (AP) seaweed. Investigations were done on the activated carbon's ability to adsorb AB, as well as its isotherms, kinetics, mechanism, and favorability.

## 2. Materials and methods

### 2.1. Materials:

*Azolla Pinnata* (AP) collected from various locations in and around Nagapattinam seashore undergoes a sun-drying process for 24 hours. Subsequently, the dried material is cut into small pieces and continuously ground. In a sealed vessel, 10g each AP, along with 10mg of citric acid as a carbonization catalyst, undergo hydrothermal

carbonization for five hours at a maximum temperature of 225 degrees Celsius. The resulting AP biochar is thoroughly washed with double-distilled water and dehydrated in an oven set at 176°F for half a day. To enhance the surface area of the hydro charcoal adsorbent, a hydrogen peroxide ( $H_2O_2$ ) solution is utilized. The prepared hydro charcoal powder is immersed in the  $H_2O_2$  solution for 24 hours, followed by additional heating in an oven. The sample is then collected, washed multiple times with distilled water, and prepared for further experimental procedures.

### 2.2. Adsorbent Preparation:

The cleaned precursor is carbonized at 350°C for three hours in a muffle furnace before being cooled to room temperature. To this pre-carbonized material conc.  $H_2SO_4$  is added in the ratio (1:3) and allowed to react for 24 h at NTP conditions. The mixture is then brought to room temperature in a desiccator after being heated at 750°C for four hours in a muffle furnace. The products of activations were washed repeatedly with hot double distilled water followed by normal double distilled water in order to remove activation residues, until a clear supernatant with constant pH is obtained. The product, activated carbon (AP), was dried in a hot air oven, ground to the proper size, the size was separated in sieves, and the material was stored in airtight containers for additional analysis and adsorption tests. On the prepared samples, Boehm titrations and point of zero charge investigations were performed (Estefania *et al.*, 2001).

### 2.3. Batch Adsorption Studies:

A set of 250 mL stoppered Erlenmeyer flasks were used for batch adsorption experiments. 10 mg of AP and 100 ml of AB solutions with varying concentrations (50-250 mg/L) were added to each flask, stirred, and stopped. Then, it is secured in an orbital shaker and shaken at 150 rpm. In a UV-Vis spectrophotometer, samples were gathered at regular intervals until they reached equilibrium and were then tested for absorbance at a wavelength of 665 nm. AP with an average particle size of 0.137 mm was used for all batch adsorption experiments (100-120 mesh). Based on the known effluent volume (L), adsorbent mass (g), initial concentration  $C_0$  (mg/L), and equilibrium concentration  $C_e$  (mg/L) of each run, the percentage of AB removal (removal %) and the adsorption capacity ( $q_e$  - mg/g) for each concentration of AB at equilibrium were computed. Isotherm and kinetics models were used to analyse the findings of the adsorption studies.

### 2.4. Thermodynamic Studies:

The adsorption process' spontaneity, kind of reaction, and randomness are revealed by the thermodynamic parameters. The influence of temperature on the change in Gibb's free energy ( $G^\circ$ ) suggests that adsorption is feasible and spontaneous (Alvarez *et al.*, 2008; Caballero *et al.*, 1997; Alok 2006). The process's energy and entropy also draw attention to the adhesion mechanism. From  $b$  (L/mol), the Langmuir isotherm constant,  $R$  (J/mol K), the universal gas constant, and  $T$  (K), the absolute temperature, the free energy change  $G^\circ$  Eqn. (1) can be calculated.

$$\Delta G^\circ = -RT \ln b \quad (1)$$

The adsorption enthalpy change ( $H^\circ$ , J/mol) and entropy ( $S^\circ$ , J/mol K) were calculated. using Eqn. (2):

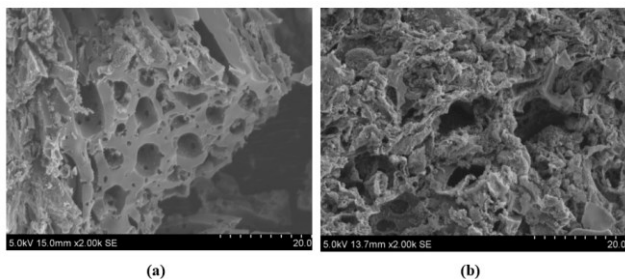
$$\ln b = \Delta S^\circ/R - \Delta H^\circ/RT \quad (2)$$

By conducting batch adsorption investigations in an isothermal shaker at various temperatures (303, 313 & 323), the thermodynamic characteristics of adsorption were assessed.

### 3. Results and discussion

#### 3.1. Surface Morphology of AP:

The surface morphology and textural properties of AP before and after adsorption of AB were determined using scanning electron microscopy (Hitachi SU-6600 Japan). The SEM image of AP (Figure 1a) shows that the activated carbon is highly porous in nature with combination of mesopores, micropores and macropores. A honey comb structure had developed during the activation of the precursor with sulphuric acid. The pores created might have undergone pore widening and transformed into wide slit shaped macropores. The geometry and distribution of the pores are determined by the characteristics of the precursor, the activating agent and the method of activation. Figure 1b shows the SEM image of AP after adsorption of AB where the surface is more irregular with non-uniform deposition. The adsorption of AB includes the interaction at the surface-active site and diffusion into the pores.

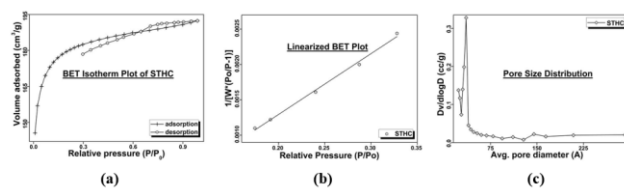


**Figure 1.** SEM images of AP (a) Before AB uptake and (b) After AB uptake

#### 3.2. BET Surface Analysis of AP:

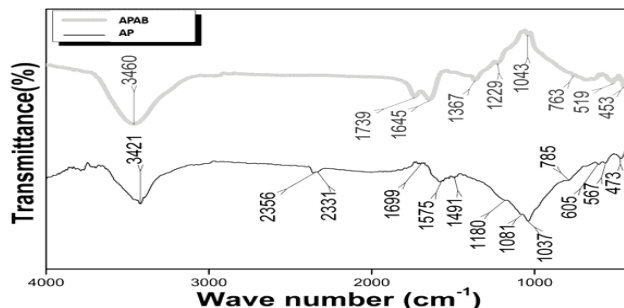
Using  $N_2$  adsorption at  $77^\circ C$ , BET (NOVA, Quantachrome) analysis is used to evaluate the pore structure and specific surface area of materials. The accessible adsorption sites and a substance's sorption potential are directly related by the specific surface area. The BET isotherm of AP (Figure 2a), initially show a long shoot up at low  $P/P_0$  followed by a long knee and a plateau, with concave shape, which represent a Type I adsorption isotherm (Sing et al., 1985). The hysteresis loop of AP shows close proximity with Type D, which characterizes the existence of slit shape pores in the microporous region (Christopher et al., 1989). Pore size distribution of the AP is shown in Figure 2c, the initial medium sized peak indicates the presence of micropores followed by the larger peak points mesopores. The linearized BET isotherm in Figure 2b indicates that AP has considerably high surface area, the plot yields the following values for the AP's BET surface area, average pore volume,

and pore diameter:  $686.5 \text{ m}^2/\text{g}$ ,  $0.2957 \text{ cc}/\text{g}$ , and  $33.91$ , respectively.



**Figure 2.** BET isotherm study of AP biosorbent

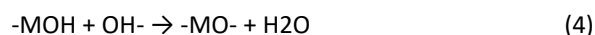
#### 3.3. Surface Chemical Characteristics:



**Figure 3.** FTIR analysis of AP biosorbent

FTIR spectra (JASCO 6300) and CHNS (Vario EL III) analysis of AP showed characteristics of lignocellulosic biomass. The FTIR spectra of sulphuric acid activated carbon before adsorption and after AB adsorption are shown in Figure 3. Specific surface functional groups involved in interactions could be stretching vibrations of  $CH_2$  ( $2356$  &  $2331 \text{ cm}^{-1}$ ), double bond stretching  $C=O$  of ketones ( $1715 \text{ cm}^{-1}$ ),  $C=O$  stretching of carboxylic acid dimers ( $1699 \text{ cm}^{-1}$ ),  $N=O$  of organic nitro and N-nitroso compounds ( $1575$  &  $1491 \text{ cm}^{-1}$ ),  $C-O$  of alcohols stretching ( $1180$  &  $1081 \text{ cm}^{-1}$ ),  $C-O$  of primary alcohols ( $1037 \text{ cm}^{-1}$ ) and aromatic  $CH$  wagging ( $785$  &  $763 \text{ cm}^{-1}$ ). The shifting of peaks shows that there was AB binding process occurring in the surface of the carbon. Remarkable difference in the absorption spectrum is noticed in the region between  $1450$  and  $700 \text{ cm}^{-1}$ .

The columbic interaction between the adsorbent surface and the adsorbate in the liquid phase is shown by the point of zero charge ( $pH_{PZC}$ ). As demonstrated in Figure 4, the pH of the final solution rises as adsorbent is present until it reaches the inversion point known as  $pH_{PZC}$ . The following Eqn. can be used to describe the electrical charge at the adsorbent surface to protonating or deprotonating (3, 4) and at the point of zero charge in Eqn. (5);



At lower pH the surface of the activated carbons is protonated and acidic with positive charges. This electrostatic repulsion between AB cations and the AP surface do not support the adsorption. At higher pH the surface acquires negative charges resulting in electrostatic attraction. The Boehm titration values and FTIR support

this observation, increased basicity of the surface by sulphuric acid activation and the increased capacity at higher pH. The fact that the point of zero charge ( $pH_{PZC}$ ) for AP is 9.3 pH reveals that the surface is basic in nature and the degree of surface oxidation (Ania *et al.*, 2002), above 9.3 pH, the surface develops a net negative charge; higher solution pH promotes AB adsorption. Table 1 displays the results of the AP Boehm titrations (Naiqin *et al.*, 2005). The precursor has more acidic groups than basic groups, whereas AP have more basic groups than acidic groups reinforcing the higher  $pH_{PZC}$ , phenolic groups are predominant among acid groups.

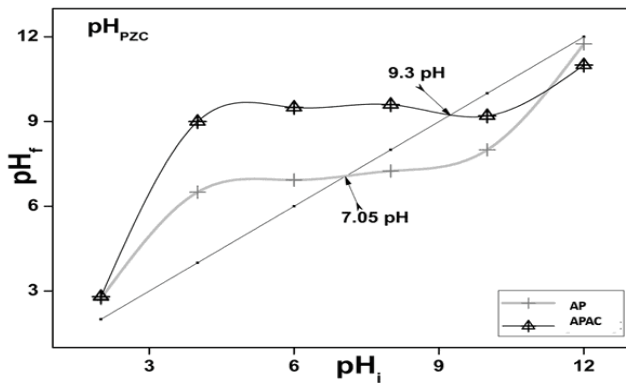


Figure 4.  $pH_{PZC}$  of the biosorption of AB using AP

Table 1. Boehm titrations results

Material	Basic (mmol/g)	Carboxylic (mmol/g)	Lactonic (mmol/g)	Phenolic (mmol/g)	$pH_{pz}$
RAW AP	0.22	0.12	0.17	0.19	7
Activated AP	0.56	0.11	0.12	0.196	9.3

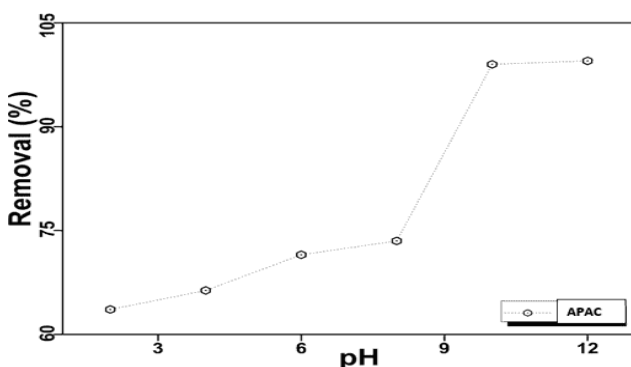


Figure 5. Impact of pH by in AB adsorption

The way that a dye molecule adheres to the adsorbent surface is significantly influenced by pH. The degree of AB ionisation and the dissociation of functional groups on the carbon surface are both influenced by the pH. As demonstrated in Figure 5, the AB adsorption rises gradually at lower pH values and sharply from pH 8 to 10. The electrostatic interaction between the AP surface and the AB molecules increased at higher pH levels.

### 3.4. Equilibrium Adsorption Data Analysis:

Adsorption system analysis and design heavily rely on adsorption isotherm models. Three models connect the solute concentrations in solutions at equilibrium at a particular temperature to the amount of solute adsorbed on the unit mass of adsorbent. For the examination of adsorption data, some of the most used models include Temkin's isotherm, Freundlich isotherm, and Langmuir isotherm. The way the adsorbate dye molecule interacts with the adsorbent surface affects the adsorption mechanism. Van der Waals forces, hydrogen bonds, hydrophobic forces, and chemical bonds may all be involved in this interaction (Yennam *et al.*, 2014).

Table 2. Isotherm model equations

Isotherm Model	Linearized form	Eqn.	Plots
Langmuir	$C_e/q_e = 1/K_L * q_m + C_e/q_m$	(7)	$C_e/q_e$ versus $C_e$
Freundlich	$q_e = K_F C_e^{1/n}$	(8)	$\ln q_e$ versus $\ln C_e$
Temkin	$q_e = RT/B \ln(AC_e)$	(9)	$q_e$ versus $\ln C_e$

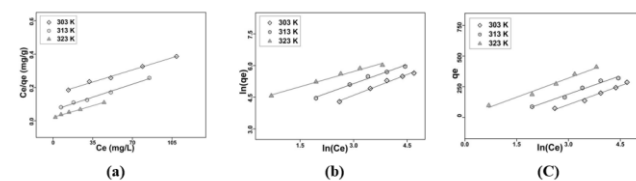


Figure 6. Isotherm studies of (a) Langmuir, (b) Freundlich and (c) Temkin models for AB adsorption using AP

The Langmuir isotherm presupposes that the adsorbate molecule interacts with the adsorbent surface with uniform active sites and that a monolayer form on the surface (Hameed 2009). A dimensionless separation factor  $R_L$  is given by the Eqn. 6, the value of the separation factor  $R_L$  indicates whether the isotherm type is unfavourable adsorption ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). The Freundlich model assumes that adsorption is possible in multilayer on a highly heterogeneous surface comprising of non-identical and non-uniform energy sites (Hong *et al.*, 2009). In addition to adsorbate-adsorbent interactions, the Temkin model also takes into account binding heterogeneity and indirect adsorbate to adsorbate attractions. According to this isotherm, the heat of adsorption for every molecule in the layer will fall linearly, and the distribution of binding energies will be uniform up to a limiting binding energy (Hong *et al.*, 2009). Table 2 gives the equations for the linearized isotherm model and the related graphs.

$$R_L = \frac{1}{1 + K_L * C_0} \quad (6)$$

Where,  $q_m$  (mg/g) are the amount of dye adsorbed per unit mass of sorbent at equilibrium concentration (for complete monolayer formation),  $K_L$  (L/mg) is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption.  $K_F$  (L/mmol) is the Freundlich

isotherm constant,  $n$  is the intensity of adsorption and  $n > 1$  favours the adsorption process.  $R$  (J/mol $^{\circ}$ K) the universal gas constant,  $T$  ( $^{\circ}$ K) the absolute temperature,  $B$  (J/mol)

and  $A$  (L/g) are Temkin's constants related to heat of sorption and isotherm constant respectively.

**Table 3.** Isotherm model constants and coefficients

Isotherm Model	Temperature K	Parameters			R <sup>2</sup>
Langmuir	303	$q_m = 480.7$	$K_L = 0.013$	$R_L = 0.489$	0.991
	313	$q_m = 492.6$	$K_L = 0.033$	$R_L = 0.283$	0.991
	323	$q_m = 502.5$	$K_L = 0.095$	$R_L = 0.131$	0.990
Freundlich	303	$K_F = 13.76$	$n = 1.523$		0.985
	313	$K_F = 27.91$	$n = 1.656$		0.983
	323	$K_F = 71.81$	$n = 2.079$		0.983
Temkin	303	$A = 7.176$	$B = 102$		0.980
	313	$A = 2.991$	$B = 99.6$		0.973
	323	$A = 1.079$	$B = 104$		0.975

The linearized isotherms in Figure 6 are shown in Table 3 together with the model's parameters. With a correlation coefficient of 0.99 for all the temperatures examined, the Langmuir isotherm provided a very good fit to the data, and as temperature rises, so does adsorption capacity. The adsorption of AB on AP is advantageous, as evidenced by the computed value of the dimensionless constant  $R_L$ , which ranges from 0 to 1. It demonstrates that AB is adsorbed in a monolayer on AP. Figure 6b depicts how well the model fits the data. With the presumptions of heterogeneous surface activity and the adsorption intensity varying exponentially with adsorption heat, the linear form of the Freundlich equation is constructed. The variability of the surface activity of the AB adsorption on AP is supported by the correlation coefficient value and the Freundlich exponent  $n$ , value. The Temkin isotherm is derived under the presumption that as surface coverage increases, adsorption heat decreases. All three isotherms fit the adsorption data in the investigated concentration range, as shown in Figure 6.

### 3.5. Adsorption Kinetics Data Analysis:

In order to understand the mechanism of the adsorption process and to assess the experimental rate data, kinetic models are used. For the selection and design of the adsorption system, knowledge of adsorption kinetics is crucial. By comparing the batch kinetic data with the Pseudo-first order, Pseudo-second order, and intra-particle

diffusion models, a suitable kinetics equation is chosen. A first order rate equation based on adsorption capacity is represented by the pseudo-first order model (Ho and Mckay 1998). According to the Pseudo-second order model, the adsorption kinetic is second-order, and the rate-limiting step is a chemical process involving valent forces through electron sharing or exchange. Assuming that, the Langmuir isotherm model governs adsorption (Ho and Mckay 1998; Ho and Mckay 1999).

The homogeneous solid diffusion model (HSDM), also known as the intra-particle diffusion model, postulates that mass transfer within an amorphous, homogeneous sphere is the limiting step. Many adsorption investigations have shown that adsorbate absorption changes with  $t^{1/2}$  rather than  $t$ . In order to determine if intra-particle diffusion is the only limiting step, this model is used (Yennam et al., 2014). Table 4 displays the governing equations for each of the three kinetic models along with the corresponding graphs. Where,  $q_t$  (mg/g) is the adsorption capacity at any instant of time,  $k_{p1}$  (min $^{-1}$ ) is the pseudo-first-order rate constant for the kinetic model.  $K_{p2}$  (g/(mg.min)) is the pseudo-second order rate constant and  $k_{int}$  (min $^{-1}$ ) is the intra-particle diffusion rate constant. With the help of experimental data on the AB adsorption on AP, pseudo-first order, pseudo-second order, and intra-particle diffusion models are evaluated.

**Table 4.** Kinetic model equations

Kinetic Model	Linearized form	Eqn.	Plots
Pseudo-first order	$dq/dt = k_{p1}(q_e - q_t)$	(10)	$\ln(q_e - q_t)$ versus $t$
Pseudo-Second Order	$dq/dt = k_{p2}(q_e - q_t)^2$	(11)	$t/q_t$ versus $t$
Intra-particle diffusion	$q_t = k_{int}t^{1/2}$	(12)	$q_t$ versus $t^{1/2}$

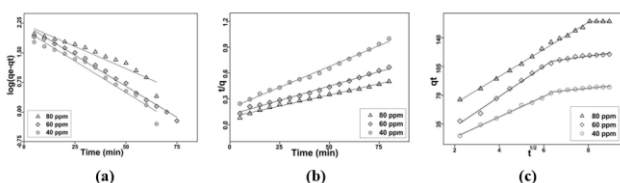
**Table 5.** Kinetic model constants and coefficients

Kinetic Model	Ci -ppm	Parameters		R <sup>2</sup>
Pseudo-First order	80	$k_{p1} = 0.0507$	$q_e = 9.253$	0.905
	60	$k_{p1} = 0.0713$	$q_e = 9.235$	0.976
	40	$k_{p1} = 0.0713$	$q_e = 8.069$	0.953
Pseudo-Second order	80	$k_{p2} = 0.029$	$q_e = 200$	0.991
	60	$k_{p2} = 0.031$	$q_e = 166.6$	0.992
	40	$k_{p2} = 0.043$	$q_e = 111.1$	0.995
Intra-Particle diffusion	80	$k_{int} = 8.869$		0.923
	60	$k_{int} = 15.25$		0.971
	40	$k_{int} = 12.61$		0.907



Table 5 displays the model parameters and correlation coefficients. Pseudo-second order model, one of the investigated models, has a 0.99 correlation coefficient with the experimental data. The pseudo-second order model is predicated on the idea that chemisorption, which involves valence forces through the sharing or exchange of electrons between sorbent and sorbate, may be the rate-limiting phase (Ho and McKay 1998). The outcome indicates that there are electrical interactions between the AB dye and the heterogeneous AP surface.

The first stage corresponds to the initial binding of the AB molecule with the solid surface's active spots. Since there are no other molecules present, the sorbate-sorbate interactions are minimal, which results in the formation of a monolayer. This interpretation can be made from the two linear regions in the pseudo-first order model in Figure 7a. Rearranging the sorbate molecules may take place as this monolayer approach's saturation, leading to an increase in sorbate molecules and the second linear step (Varshney *et al.*, 1996).



**Figure 7.** Adsorption kinetic studies of (a) Pseudo-first order, (b) Pseudo-second order and (c) Intra-particle diffusion models for AB adsorption using AP

Figure 7c shows the AB adsorbed ( $qt$ ) against  $t^{1/2}$ . Two linear steps are shown in the plot, signifying two processes. The exterior surface diffusion is indicated by the first step, while the adsorption process is indicated by the second step, where intra-particle diffusion is rate limiting. There is no straight line in the  $qt$  vs  $t^{1/2}$  figure. Travelling through the origin, show that, there are other rate-limiting processes besides intra-particle diffusion. Kinetics is also impacted by film diffusion (Gurusamy & Menjeri 1997).

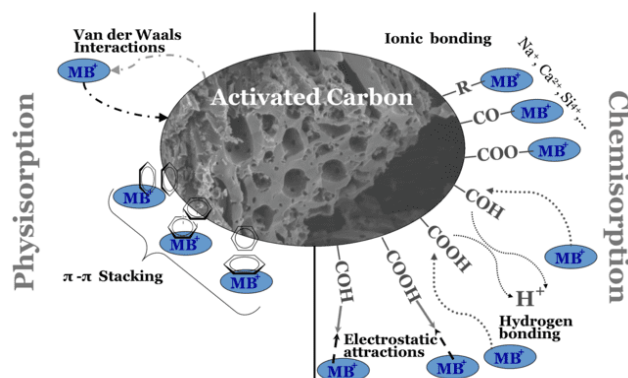
### 3.6. Thermodynamic Parameters:

Table 6 lists the thermodynamic parameters for AB adsorption on AP. The values of  $G^\circ$  were observed to decrease with rise in temperature suggests that higher temperature favors AB adsorption. The negative Gibb's free energy ( $G^\circ$ ) for three temperatures imply that adsorption is feasible and spontaneous. Adsorption is endothermic, according to the positive enthalpy change ( $H^\circ$ ) value (78.1 kJ/mol), which supports the finding that adsorption rate rises with temperature. Additionally, the increased randomness at the AP-AB interface is confirmed by the positive entropy ( $S^\circ$ ) (269.7 J/mol K), which shows that AB ions have replaced the previously adsorbed water molecules with ones that have a stronger affinity (Yasemin & Haluk 2006; Nasuha & Hameed 2011).

**Table 6.** Thermodynamic parameters

T (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)
303	- 3.617	78.1	269.7
313	- 6.287		
323	- 9.012		

### 3.7. AB Adsorption Mechanism:



**Figure 8.** Adsorption mechanism of AB using AP biosorbent

The dye ions and carbon surface experiences physical and chemical interactions by nature, namely electrostatic or non-electrostatic (van der Waals forces, hydrophobic interactions and hydrogen bonding) (Shilpi *et al.*, 2016). The adsorption of AB on the heterogeneous adsorbent AP involves physical activity i.e., the van der Waals force of attractions and electrostatic attraction and electronic/chemical bonding (Figure 8). The  $pH_{pzc}$  and pH analysis indicate the electrostatic interaction between AB and AP. The FTIR analysis shows the role of surface complexation between the AB and AP. The functional groups -OH, -COOH, -CO and -CH functional groups might be participating in AB binding. The kinetic studies affirm the binding of AB on AP (Fatma *et al.*, 2016; Shisuo *et al.*, 2016). Below pH 9, the electrostatic attraction between the functional groups and the anionic dye molecule may be the cause of the dye molecules adhering to the adsorbent, and above pH 9.3, the carboxylic groups may be deprotonated, causing the negatively charged carboxylate ligand to bind to the positively charged AB molecule. The aromatic structures of AB make the adsorption easy by n-n stacking interactions which contribute to the shifting and weakening of the peaks (Fatma *et al.*, 2016).

## 4. Conclusions

Activated carbon prepared from AP by two-step  $H_2SO_4$  activation resulted with good adsorbent properties, moderate surface area having combination of three types of pores suitable for easy toxin transport, surface morphology showing cylindrical pores with network, well oxidized surface with basic nature and a variety of surface functionality having affinity for toxins with different charges. Higher pH values favor AB molecule adsorption. The adsorption process, which is governed by chemical reaction, is defined by pseudo-second order kinetics, according to kinetic studies. The endothermic nature of the

process is confirmed by the positive enthalpy change, the strong affinity for AB is indicated by the positive entropy, and the negative values of Gibb's free energy values support the spontaneity of the adsorption. Thus, all the studies suggest that the activated carbon prepared have good qualities of adsorbent suitable for AB dye removal.

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