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# Sorption Behavior of Methylene Blue From Aqueous Solution By Using PVA/SA/Kaolin Composite

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# Article Info

<u>Received: 05-04-2020</u> Revised: 07-07-2020 Accepted: 10-07-2020 Published: 12-07-2020 **Abstract:** This research shows a method of elimination of methylene blue from aqueous solutions using PVA/SA/Kaolin Composite. The prepared was characterized by Fourier transform infra red spectroscopy (FT-IR), X-Ray diffractogram (XRD), Thermo gravimetric analysis (TGA) and Scanning electron microscopic (SEM). Furthermore, the analyses of batch mode experiments were performed to study the experimental important parameters such as pH, metal ion concentrations, adsorbent dosages and contact time are discussed. From the experimental data, the adsorption isotherms are well described by Langmuir and Freundlich model, the adsorption of methyleneblue was fitted with Freundlich isotherm confirms the physical adsorption phenomena involved in this process. The kinetic parameter was correlated with the pseudo-second-order kinetic model. From the results, it was concluded that the material of PVA/SA/Kaolin Composite is an excellent adsorbent for the removal of methylene blue dye from aqueous solution.

Keywords: Methylene blue dye, Adsorption, Composite, Polyvinyl alcohol.

# I. Introduction

Wastewaters from dyeing and finishing operations in the textile industry are generally high in both color and organic content. Color removal from textile effluents has been the target of great attention in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems [1]. The discharge of dyes directly into aqueous effluent can endanger living organism and its aquatic ecology because most dyes are toxic. Once the dyes enter wastewater, they become more stable and are more difficult to biodegrade because of their complex chemical structures [2]. Hence we had chosen methylene blue dye in our studies.

Several treatment methods have been developed for decontamination purposes. Adsorption has been shown to be an efficient and economical alternative for the removal of dyes from aqueous solutions [3] and it has been tested with many adsorbents. It is one of the promising methods to remove the dye pollutants from aqueous system completely and the most efficient in terms of operation and can remove the contaminant even at very low concentration [4].

However, the choice of the adsorbent is based on economical and practical reasons and clay minerals are natural materials with low cost. Many adsorbing materials have been tested to lower the dye concentration from aqueous solutions, such as activated carbon, rice husk, silica, chitin, fly ash, saw dust, bagasse pith, and orange peel [5]. Therefore, poly vinyl alcohol, sodium alginate and kaolin was chosen because of their abundant nature, low toxicity, low cost and adsorption potential.

Based on the literature review an attempt has been made to utilize an inexpensive adsorbent system (PVA/SA/Kaolin Composite) for the removal of methylene blue dye from aqueous solution using batch studies approach as a function of various parameters such as pH, adsorbent dose, contact time and initial metal ion concentration. The adsorption isotherms such as Langmuir and Freundlich models were used to fit with the adsorption equilibrium data and the adsorption kinetic models such as pseudo-first order, pseudo-second order were investigated.

# **II. Material And Methods**

### Materials

Poly vinyl alcohol (MW =72000g/mol) and sodium alginate (high viscosity) was obtained from sigma chemical co. and Aldrich, Kaolin (Aluminium Silicate hydrated) and Methylene Blue were obtained from Nice Chemicals Pvt. Ltd., Kochi.

### Preparation of PVA/SA/Kaolin Composite

The method of preparation is 5gram of Polyvinyl alcohol dissolved in 50ml of de-mineralized hot water and stirred well to get a clear solution. Then 1gram of Sodium alginate dissolved in 50 ml of de-mineralized water and stirred well to get a clear solution and 9gram of Kaolin was dissolved in 100 ml of de-mineralized water. The bio-polymer solutions of Polyvinyl alcohol, Sodium alginate and Kaolin solutions were mixed to form a homogeneous solution by stirring at room temperature and then poured into clean Petri dishes and dried well to get composite film.

# Fourier Transform Infrared Spectroscopy (FT-IR)

The prepared composite was characterized by FTIR spectroscopy. Fourier Transform Infrared (FT-IR) spectra of the composite were recorded in the frequency range of 4000-500cm<sup>-1</sup> using Thermo Nicollet AVATAR330 Spectrophotometer. The samples were pressed into pellets with KBr.

### X-ray diffraction (XRD)

X-ray diffractograms of the composite were obtained using X-ray powder diffractrometer (XRD-SHIMADZU XD – D1). With Ni-filter, Cu K<sub>a</sub> radiation source. The relative intensity was recorded in the scattering range of  $2\theta$  of  $10^{\circ}$ - $90^{\circ}$ /min.

### Thermo Gravimetric Analysis (TGA)

The dynamic weight loss experiments of composite were carried out on TA instrument 2050 thermo gravimetric analyser (TGA). The test was conducted in a N2 gas (25ml/min). The temperature range was varied from 27-800°c with the heating rate of 10°C/min. in this technique the change in mass of the substance was measured as a function of temperature.

### Differential Scanning Calorimetry (DSC)

DSC analysis of the composite were carried out with the DSC Q200 V24.4 Build 116 Perkin Elmer Thermal analysis instrument, pierced lid in the nitrogen atmosphere at a heating rate of 10°C/min.

#### Scanning Electron Microscope (SEM)

The surface morphology and cross sectional morphology of PVA/SA/Kaolin composites were observed with Scanning Electron Microscope to verify the compatibility of the mixtures of PVA/SA/Kaolin. To analyse the composites, films were cut into pieces of various size and wiped with a thin gold – palladium layer by a sputter coater unit (UG – microtech, UCK field, UK) and the cross section topography was analysed with Cambridge stereoscan 440 Scanning Electron Microscope (SEM, Leica, Cambridge, UK).

# III. Results and Discussion

#### FTIR Analysis

FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". FTIR is important for screening and identifying polymer or plastic samples. The following section describes the FT-IR spectral details of Polyvinyl alcohol, Sodium alginate, kaolin and PVA/SA/Kaolin composites.



Figure -1: FT-IR spectrum of PVA

2000

2500

1000

1500

500 1/cm

0 + 4000 PVA

3500

3000



Figure -2: FT-IR spectrum of Sodium alginate







The FT-IR spectra of Polyvinylalcohol shows a broad band at 3280.92 cm-1 corresponding to O-H stretching, the peaks at 2908.65 cm<sup>-1</sup>, 1728.22 cm<sup>-1</sup>, 1087.85 cm<sup>-1</sup> shows the presence of C-H alkyl stretching, C=O and C-C stretching, C-N stretching. The peaks at 1581.63 and 839.03 cm<sup>-1</sup> shows the presence of aromatic C=C and N-H bending vibrations. The peak at 1438.90 cm<sup>-1</sup> shows the presence of C-H Stretching [6].

The FT-IR spectra of Sodium alginate shows a broad band at 1735.93 cm<sup>-1</sup> corresponding to Carbonyl – HC=O stretching, the peaks at 1597.06, 1365.60 and 1026.13 cm<sup>-1</sup> shows the presence of -COO asymmetric and symmetric stretching, tertiary alcohols C-O stretching, C-O stretching. The peak at 1099.43 cm<sup>-1</sup> shows the presence of C-N coupled vibration. The peak at 611.43 cm<sup>-1</sup> shows the presence of O-H out of plane.

The FT-IR spectra of Kaolin shows a broad band at 3672.47 cm<sup>-1</sup> corresponding to O-H stretching of innersurface hydroxyl groups, the peaks at 1120.64 cm<sup>-1</sup>, 1037.70 cm<sup>-1</sup> shows the presence of Si-O bonds in the SiO<sub>4</sub> molecules. The peaks at 945.12 cm<sup>-1</sup> shows the presence of Si-O bonds in the SiO<sub>4</sub> molecules. The peak at 833.25 cm<sup>-1</sup> and 810.10 cm<sup>-1</sup> shows the presence of OH deformation linked to Al<sup>3-</sup>, Mg<sup>2-</sup>. The peak at 514.99 cm<sup>-1</sup> shows the presence of Si-O-Al and the peak at 449.41 cm<sup>-1</sup> shows C-C bending.

The FT-IR spectra of PVA/SA/Kaolin composite shows a broad band at 3269.34 cm<sup>-1</sup> corresponding to alcoholic and acidic O-H group, the peaks at 2937.59 cm<sup>-1</sup>, 2906.73 cm<sup>-1</sup>, 1413.82, 1327.03, 1238.30 and 1083.99 cm<sup>-1</sup> shows the presence C-H and alkyl C-H stretching, tertiary alcohol C-O stretching and C-O stretching in C-O-C.The peak at 1656.85 cm<sup>-1</sup> shows the presence of carboxylic group. The peak at 835.18 cm<sup>-1</sup> and 474.49 cm<sup>-1</sup> shows the presence of N-H and C-C bending. The peak at 596 cm<sup>-1</sup> shows the presence of O-H out of plane. The shift in wave number of composite from the pure Polyvinyl alcohol, Sodium alginate and Kaolin confirms the miscibility of the composite.

#### Thermo gravimetric analysis

Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere.



Figure - 6 : TGA Thermogram of PVA/SA/Kaolin Composite

From the **figure** -6 the decomposition starts from 20 and ended at 340°C which was explained by the removal of external water molecules together with degradation of alginate chain and it is interpreted with second degradation temperature due to elimination of side groups of PVA [7]. The third step is obviously due to the complete loss of the organic compounds and it started at 470 °C and ended at 800 °C [8] from the mass changes found in the TGA pattern it is confirmed that around 70% residue is left in the composite conforming the composite as highly thermally stable.

#### **Differential Scanning Calorimetry Analysis**

Differential Scanning Calorimetry (DSC) is widely used to characterise the thermophysical properties of polymers. DSC can measure important *thermoplastic* properties including, melting temperature, heat of melting, percentage crystallinity, Tg or softening, crystallization, presence of recyclates/regrinds, plasticizers, polymer blends (presence, composition and compatibility).

From the **figure** - 6 the DSC pattern of the organic kaolin composite, it is observed that three endothermic peaks confirms the three stages of decomposition and the last endothermic peak around 800°C. The three crystallization temperature(Tc) are 100°C, 325°C, 640°C. Presence of kaolin increases the crystallization temperature of the composite mixture. And the glass transition temperatures Tg are 200°C and 350°C. Confirming the miscibility of the three components in the composite because the DSC results of the composite showed shifting from the Tg of pure PVA (85°C) and SA (165°C) in the presence of Kaolin confirmed the high thermal stability. X - rav diffraction studies

X-Ray Diffraction Analysis (XRD) investigates crystalline structure, including atomic arrangement, crystallite size, and imperfections.



Figure - 8: XRD pattern for the PVA/SA/Kaolin Composite

The **Figures 8** illustrates XRD pattern of PVA/SA/Kaolin composite were the sharp peaks appears  $2\theta = 19^{\circ}$ , 29° and smaller dispersed peaks upto 70° in agreement with previous studies. The percentage crystallinity is calculated as 25.53%. From the literature XRD spectrum of pure PVA shows an intense reflection peak at  $2\theta = 19.7^{\circ}$  diffused in the hallow amorphous region [9]. The appearance of sharp reflections and diffuse scattering is characteristic of crystalline and amorphous phases of conventional semi-crystalline polymers. The typical diffraction of PVA appears at  $2\theta = 19.1^{\circ}$  exhibiting crystalline reflection [10].

The XRD spectrum of sodium alginate appears to be amorphous in nature, and shows that there are two distinct peaks at 9° and 15° of 2 $\theta$ . The peak at 15° of 2 $\theta$  indicates the presence of crystallinity as reported by Yang et al. [11]. From the present work as the peaks for the composite are from 19°-67° confirms the miscibility nature of this composite, and the peak shift from original of the pure component demonstrates the interaction between PVA/SA/Kaolin. SA helps in finer dispersion [12].

It is clear from the crystallinity value 25.53% for PVA/SA/Kaolin composite indicates the semi crystalline nature of the composite. Which can be used for adsorption studies. This reduction of crystallinity in turn may be due to the intermolecular hydrogen bonding between PVA/SA/Kaolin which was also evident from the FTIR studies.

#### Scanning Electron Microscope (SEM)

From the **Fig.-9** of the composite prepared from Polyvinyl alcohol, Sodium alginate and Kaolin mixture has almost uniform porosity. The morphology of the prepared composite was investigated using 5- 3400 analytical Scanning Electron Microscope SEM. The samples were stocked over a holder and sprayed with gold. The SEM micrograph confirms that the material is forming micron size agglomerates of the composite materials. SEM at the magnification shows a closer and denser nature of the blend formulation with good miscibility.



Figure – 9 : SEM image of PVA/SA/Kaolin Composite

#### **Batch Experimental Studies**

Study of the dye retention properties of the PVA/SA/Kaolin composites were carried out using a batch equilibrium procedure. Solutions containing MB were prepared in distilled water. Batch experimental studies were carried out with 1g of adsorbent in100 mL of MB solution of desired concentration at an optimum pH 11 in conical flasks. The flasks were agitated on a orbit mechanical shaker at 190 rpm for a known period of time at room temperature. After attaining equilibrium, adsorbent was separated by filtration using Whatman filter paper and the aqueous-phase concentration of dye was determined with UV-Visible double beam spectrophotometer.

# Effect Of Metal Ion Concentration



Figure – 10 : Effect of Initial dye concentration on removal of MB by PVA/SA/Kaolin composite

The effect of initial MB 15 to 125 mg/L on the adsorption of MB on to PVA/SA/Kaolin composite (1g) was studied for a constant sorption time 60 min at constant stirring speed, initial pH - 11 and the experiments were carried out in Orbit shaker. The removal of dye decreased from 85.6 to 54% on increasing the initial dye concentration from 15 to 125 mg/L after 60 minutes.

The result shows the percentage adsorption decreased with increase in initial MB concentration as shown in **fig-10** it means the adsorption is highly depended on initial concentration because lower the concentration, the ratio of the initial number of MB molecules to the available surface area is low [13]. At high concentration the available sites of adsorption becomes fewer and hence the percentage removal of MB is dependent upon initial concentration.

# Effect Of Dosage



Figure - 11: Effect of Dosage on removal of MB by PVA/SA/Kaolin composite

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorption dosage using the composite from 2 to 5g was shown in fig-11. In the experiment, the composite was added to each 100 ml of methylene blue aqueous solution having an initial concentration of 25 mg/L with a constant sorption time, 60 min at constant stirring speed, Initial pH – 11 and the experiments were carried out in the orbit shaker. The maximum percentage removal of MB was about 90% at the dosage of 5 gms. This result shows the removal of dye increases as the dosage of composite increases.

The results show that the percentage adsorption increasing the dose of composite until 5g. the number of sorption sites available for sorbent biosolute interaction is increased resulting increased percentage removal of MB from the solution [14].

# Effect of pH



Figure - 12 : Effect of pH on removal of MB by PVA/SA/Kaolin composite

pH is an important factor in controlling the adsorption of the dye on to adsorbent. The **Figure – 12** shows the adsorption of MB from 1g composite studied at various pH from 3 to 11 for 100 ml of methylene blue aqueous solution having an initial concentration of 25 mg/L with a constant sorption time 60 min. From the data the percentage removal of methylene blue solutions after an adsorption period of 60 min was decreased from 60 to 53% between pH values 3 to 7 then increased from 53 to 72% between pH values 8 to 11.

In the process of adsorption at lower pH up to 7 the adsorbent surface is positively charge favoring adsorption of anionic contaminants because MB is cationic dye the positive charge occupied the feasible adsorption position completes with dye molecules resulting in low adsorption of dyes, while at higher pH, the negatively charge surface facilitates adsorption of cationic contaminants [15].

#### Effect of contact time



Figure - 13: Effect of Contact time on removal of MB by PVA/SA/Kaolin composite

The effect of contact time on the percentage removal of dye by organic Kaolin composite shown in **fig-13** was found to increase with increase in time. Contact time is an important factor on removal of dye and carried out at various time of contact from 1hr to 5hrs on 1g composite to each 100 ml of methylene blue aqueous solution having an initial concentration of 25 mg/L with a constant stirring speed, Initial pH – 11. This result shows the maximum of 85% dye removed in 5hrs. During the adsorption of dyes initially MB molecules reach the boundary layer, then they have to defuse into the adsorbent surface and the porous structure so this phenomenon takes long time [16].

#### Langmuir Isotherm

An alternative equation was derived by Langmuir on the basis of a definite case of the nature of the process of adsorption from solution. The Langmuir adsorption isotherm was developed assuming that a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy. The Langmuir equation (Eq. (1)), which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, is expressed as:

$C_{ads} = (K_L C_{eq})/(1 + bC_{eq})$	(1)
In this study the following linearised form of the Langmuir isotherm was used.	
$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L$	(2)
$C_{max} = K_L/b$	(3)

where

 $C_{ads}$  = amount of MB dye adsorbed (mg·g<sup>-1</sup>)

 $C_{eq}$  = equilibrium concentration of MB in solution (mg·dm<sup>-3</sup>)

 $K_L = Langmuir constant (dm^3 \cdot g^{-1})$ 

 $b = Langmuir constant (dm^3 \cdot mg)$ 

 $C_{max}$  = maximum MB to adsorb onto 1 g composite (mg·g<sup>-1</sup>)

The constant b in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant  $K_L$  can be used to determine the enthalpy of adsorption. A plot of  $C_{eq}/C_{ads}$  vs.  $C_{eq}$  yielded a straight line confirming the applicability of the Langmuir adsorption isotherm.



Figure - 14: Langmuir plot for the adsorption of MB onto PVA/SA/Kaolin composite.

The plot of the experimental  $C_e/q_e$  against  $C_e$  for the experimental data, it was observed that Methylene blue adsorption onto the PVA/SA/Kaolin composite can be fitted to the Langmuir isotherm model. From the slope and the intercept of the straight line, the values of  $C_{max}$  and  $K_L$  can be estimated. Langmuir isotherms are shown in **Figure-14**, the parameters are given in **Table 1**. Linear Langmuir plot indicates the formation of monolayer coverage of adsorbate on the surface of adsorbent.

 $C_{max}$  value for MB is 500.16mg/g. Value of  $R^2$  shows correlation or linear relationship. The relationship becomes more linear with the value closest to 1. Thus, it is found that the adsorption of MB onto PVA/SA/Kaolin composite correlates well with the Langmuir equation under the concentration studies. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter,  $R_L$  is used to predict if an adsorption system is "favourable" or "unfavourable".

where  $C_f$  is the final MB concentration (mg/dm<sup>3</sup>) and b is the Langmuir adsorption equilibrium constant (dm<sup>3</sup>/mg). If the  $R_L$  values are in the range of  $0 < R_L < 1$ , it indicated that the adsorption of MB onto PVA/SA/Kaolin composite was favourable adsorbent.

#### Freundlich Isotherm

A brief empirical equation often used to represent adsorption data is called the Freundlich equation. The Freundlich isotherm describes physical adsorption from liquids. The exponent 1/n is an index of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent.

The good fit of Freundlich isotherm to an adsorption system means there is almost no limit to the amount adsorbed and there is a multilayer adsorption. The applicability of the Freundlich equation to a particular case was

tested by plotting log  $C_{ads}$  vs. log  $C_{eq}$  from the logarithmic form of Equation 5. which was used to describe heterogeneous surface energies was expressed as:

$$C_{ads} = KC_{eq}^{-1/n}$$
(5)  
In this study the following linearised form of the Freundlich equation was used.  
$$\log C_{ads} = \log K + 1/n \log C_{eq}$$
(6)

where

 $C_{ads}$  = amount of metal ion adsorbed (mg·g<sup>-1</sup>)  $C_{eq}$  = equilibrium concentration in solution (mg·dm<sup>-3</sup>) 1/n = Freundlich constant (mg·g<sup>-1</sup>) K = Freundlich constant (g·dm<sup>-3</sup>)



Figure – 15: Freundlich plot for the adsorption of MB onto PVA/SA/Kaolin composite

From **Figure** – **15** it is evident that the values of 1/n and P, which are rough measurements of the adsorption intensity and adsorption capacity of the adsorbent, have been determined by the least-square fit and the  $R^2$  values are found to be 0.998 which showed the best fit. The 1/n value suggested that the adsorption forces of Methylene Blue onto the surface of the PVA/SA/Kaolin composite was strong.

Langmuir constant	Freundlich constants					
$K_L (dm^3/g)$	b (dm³/mg)	C <sub>max</sub> (mg/g)	<b>R</b> <sup>2</sup>	$K_f(g \cdot dm^{-3})$	N	<b>R</b> <sup>2</sup>
11.363636	0.02272	500.160035	0.931	1.07	1.15207	0.998

Table – 1:	Adsorption	isotherm	constant	and	correlation	coefficients
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The comparison of  $R^2$  values of both the isotherms reveals that the  $R^2$  (0.931) values of the Freundlich isotherm was found to be higher than the  $R^2$  (0.998) values for the Langmuir isotherm. From the observed results, it was concluded that the experimental value is better fitted with the Freundlich adsorption isotherm model when

compared to the Langmuir adsorption isotherm model and hence it was evident that the adsorption of methylene blue onto PVA/SA/Kaolin composite follows multilayer adsorption on the surface than monolayer adsorption.

#### Kinetic parameters

In order to examine the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, kinetic models were used to test the experimental data. The kinetics of MB adsorption on the PVA/SA/Kaolin composite was determined with three different kinetic models, i.e., the pseudo-first and pseudo-second order and the intra-particle diffusion model.

The pseudo-first order equation of Lagergren (Eq. (2) is one of the most widely used equation, being the first rate equation developed for sorption in liquid/solid systems.

$$\log (q_e - q_t) = \frac{\log q_e - k_1 t}{2.303}$$
(8)

where qe and qt are the amounts of ion metalic adsorbed at equilibrium (mmol/g) and at time t, respectively, and k1 is the rate constant of pseudo-first order sorption (g/mmol min). The slopes and intercepts of plots of log (qe -qt) versus t (**Figure 16 and 17**) were used to determine the pseudo-first order rate constant k1 and qe, the values obtained were presented in **Table 2**.



Figure - 16: Pseudo-first-order kinetics for MB

The theoretical qe values estimated from the pseudo-first order kinetic model gave significantly different values compared to experimental values, and the correlation coefficients were also found to be lower. These results showed that the pseudo-first order kinetic model did not describe these sorption systems.

The adsorption data were also treated according to the pseudo-second-order kinetics (**Eq. 9**) because it was shown to be more likely to predict the behavior over the whole range of adsorption being based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and sorbate.

$$\begin{array}{rcl}
t & 1 & t \\
\hline
q_t & k_2 q_e^2 & q_e
\end{array} \tag{9}$$

where

k<sub>2</sub> is the rate constant of pseudo-second order sorption (g/mmolmin).

The values of  $q_e$  and  $k_2$  were obtained from the slope and intercept of the straight line obtained by plotting  $t/q_t$  against t (Fig. 17)



Figure – 17: Pseudo-second-order kinetics for MB

Table – 2 : Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for MB sorption by PVA/SA/Kaolin composite

	Des	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
	Dye	qe (mg/g)	k1 (min <sup>-1</sup> )	R <sup>2</sup>	qe (mg/g)	k <sub>2</sub> (g mg <sup>-1</sup> min <sup>-</sup>	<b>R</b> <sup>2</sup>	
	MB	7.49894	0.0009212	0.907	22.7272	0.00019979	0.996	

The results obtained from pseudo-first-order kinetics demonstrated that the experimental qe (mg.  $g^{-1}$ ) values did not agree well with the calculated values obtained from the linear plots. The correlation coefficient,  $R^2$  of pseudo first order kinetics for MB is 0.907 respectively. This confirms that it is not appropriate to use the Lagergren first order kinetic model to predict the adsorption kinetics for MB onto PVA/SA/Kaolin composite for the entire sorption period.

The correlation coefficient,  $R^2$  for the second order kinetic model were almost equal to unity this shows that sorption of MB on to the composite followed the pseudo second order kinetic model. A good agreement for this adsorption model was confirmed by similar value of calculated qe and experimental one. The best fit to the pseudo second order kinetic indicated that the adsorption mechanism depended on the adsorbate and adsorbent [17].

#### III. Conclusion

From the results of the current work, it can be concluded that the prepared PVA/SA/Kaolin composite has some specific chemical interaction between polyvinyl alcohol, sodium alginate and kaolin was confirmed by FTIR. XRD and SEM images show a rough surface morphology for the composite with many pores and imperfections. Thermal analysis was carried out to study the thermal behavior, from the results it was observed that the composite had high thermal stability of the prepared composite. This study appends to the sorption capacity of PVA/SA/Kaolin composite of methylene blue dye from the aqueous solution. Based on Langmuir and Freundlich isotherm, the sorption capacity of PVA/SA/Kaolin composite was high and the adsorbent favored Freundlich isotherm i.e multilayer adsorption taken place effectively. The kinetics studies showed that the adsorption adhered to pseudo second order kinetics. Thus, the prepared composite is found to be a very good ,low cost biosorbent for the removal of methylene blue dye from aqueous solution.

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