

## Removal of Methylene Blue from aqueous solutions using composite hydrogel prepared by gamma irradiation

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**Abstract:** The adsorption of Methylene Blue (MB) cationic dye from aqueous solution was carried out by using polymeric hydrogels of Poly (vinyl alcohol) (PVA)/Poly (acrylic acid) (PAA) with inorganic clay. The hydrogels were prepared by gamma irradiation technology and characterized by FTIR and SEM. The factors influencing adsorption capacity of the prepared hydrogels such as copolymer composition, clay content, pH, initial dye concentration, ionic strength, and temperature were investigated. To describe the adsorption data, Langmuir and Freundlich isotherm models were used and the results clarified that these models were well fitted. The kinetic studies showed that the adsorption process was consistent with the pseudo-second order kinetic model. The results demonstrated that the PVA/AA/clay composite hydrogel can be used as efficient adsorbent for the removal of MB dye from waste water.

[H. Kamal. **Removal of Methylene Blue from aqueous solutions using composite hydrogel prepared by gamma irradiation.** *J Am Sci* 2014;10(4):125-133]. (ISSN: 1545-1003). <http://www.jofamericanscience.org>. 16

**Key words:** Composite hydrogel, gamma radiation, Methylene Blue, adsorption isotherm

### I. Introduction:

Synthetic organic dyes present certain hazards and environmental problems. Disposal of these dyes into water can be toxic to aquatic life. They cause a health problem because they may be mutagenic and carcinogenic [1-3].

Methods and effluent treatment for dyes may be divided into three main categories; physical, chemical, and biological. Among them adsorption technology is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent [4]. In recent years polymeric adsorbent have been increasingly used to remove and recover organic pollutants from waste waters [5]. Polymeric hydrogels have been the focus of research for environment scientists due to their characteristic properties such as adsorption-regeneration, economic feasibility and environmental friendly behavior. Also, hydrogels possess numerous ionic and non-ionic functional groups, which can absorb and trap ionic dyes from waste water [6]. Based on the type of functional group attached, the properties of hydrogels may get varied with respect to pH and temperature. The poor mechanical properties of hydrogels restrict their applications widely. To improve these properties of hydrogels, many layered clays were used by many researchers [7-11]. Clays have sandwich-like structures with one octahedral Al-sheet and two tetrahedral Si-sheets. Because of their hydrophilic nature, clays are suitable for use in water absorbent as additives. The polymer/clay composite hydrogel has received great attention because of their

relatively low production cost and high adsorption capacity for some dyes [12].

Acrylic acid (AA) is the mostly used functional monomer to prepare the hydrogels [13]. Poly (vinyl alcohol) (PVA) has been widely explored as water-soluble polymers for numerous biomedical and pharmaceutical applications due to its advantages of non-toxic, non-carcinogenic and bio adhesive properties [14].

Methylene Blue (MB) which is having a wide range of use in different fields such as biology and chemistry [15]. The aim of this study is to investigate adsorption of MB dye as a model of cationic dyes by polymeric hydrogels of PVA/AA that prepared in presence of organic crosslinker; methylene bis acrylamide (MBAM) or inorganic crosslinker; Bentonite (clay) and synthesized by gamma irradiation from  $^{60}\text{Co}$  as initiator.

### 2. Experimental

#### 2.1. Materials:

Acrylic acid ( $\text{C}_3\text{H}_4\text{O}_2$ ) stabilized with 200 ppm MEHQ 99.55%, purchased from ACROS ORGANICS New Jersey, USA

Poly (vinyl alcohol) ( $\text{C}_2\text{H}_4\text{O}$ )<sub>n</sub>, purchased from BLULUX laboratories (p) Ltd., INDIA, M.W app. 14,000 LR[Laboratory Rasayan s.d.finf-chem ltd .Boisar 401501].

Organic crosslinker; N,N Methylene-bisacrylamide (MBAM)  $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$  (M=154.17 g/mol) purchased from MERCK-Schuchardt ,85662 Honbrunn ,Germany.

Inorganic crosslinker; Bentonite clay from china  
Distilled water was used as a solvent

Cationic dye: Methylene blue purchased from LOBA CHEMIE PVT. Mumbai 400005.INDIA

## 2.2. Gamma radiation source

Irradiation of samples was carried out using  $^{60}\text{Co}$  gamma source installed at the National Centre for Radiation Research and Technology (NCRRT), Egypt, with a dose rate of 2.7kGy/h.

## 2.3. Preparation of PVA/AA hydrogels

Series of samples of the same concentration (15 wt%) and different PVA/AA compositions with 1 (wt%) MBAM as crosslinking agent were synthesized using gamma irradiation with a total dose of 20 kGy. The ratios of PVA and AA in the mixtures were 50/50, 30/70, 20/80, 15/85, 10/90 (wt%). The resulted hydrogels obtained in cylindrical shape were cut to disks of 2 mm thickness, then washed and soaked overnight in distilled water to remove the unreacted monomers (if any) and dried in oven at 50 °C until constant weight and stored for later evaluations.

## 2.4. Preparation of PVA/AA/clay composite hydrogels:

Different weight ratios clay powder 1-5 (wt%) were added under good stirring to PVA/AA mixtures of the same concentration 15 (wt%) and composition 30/70(wt%). The mixtures were then poured into test tubes and subjected to gamma radiation to a total dose of 20 kGy. The resulted composite hydrogels were treated as previously mentioned in 2.5.

## 2.5. Adsorption studies:

The adsorption of MB dye onto PVA/AA hydrogels and PVA/AA/clay composite hydrogels were investigated as a function of copolymer composition, clay content, pH, initial dye concentration, contact time, ionic strength, and temperature. Accurately weighed dry samples (0.05 g) were immersed in aqueous MB dye solution of a definite volume (20 mL) and allowed to equilibrate for 48h at 25 °C, the amount of dye adsorbed (mg/g) was calculated by using the following equation [16]:

$$q_e = \frac{[(C_0 - C_e) \times V]}{W}$$

Where W is the weight of dry hydrogel (g), V is the volume of the aqueous phase (L),  $q_e$  is the amount of dye adsorbed onto unit dry mass of the hydrogels (mg/g),  $C_0$  and  $C_e$  are the concentrations (mg/L) of the dye solution before and after adsorption, respectively, that were determined by using an UV-vis spectrophotometer at 663nm.

## 2.6. Fourier transform infrared spectroscopy (FTIR)

Infrared spectra were run in KBr disc using a Mattson 5000 FTIR spectrophotometer product of Unicam Ltd., England, in the frequency range of 4000 – 500  $\text{cm}^{-1}$ . A dry constant weight from each hydrogel

was ground with 3 mg KBr and pressed to form transparent discs.

## 2.7. Scanning electron microscopy (SEM)

The surface of hydrogels before and after clay treatment and dye adsorption were examined using (JEOLJSM-5400) Scanning electron microscope (SEM). The surface of the samples was sputter-coated with gold before examination.

## 3. Results and discussion

### 3.1. FTIR:

The FTIR spectra of the prepared hydrogels and the clay are shown in fig.1. The PVA spectra (Fig.1.a) show a characteristic broad band at 3429  $\text{cm}^{-1}$  corresponding to stretching vibration of H-bonded alcohol. The sharp band at 1638  $\text{cm}^{-1}$  corresponds to stretching vibration of C=O in amide of MBAM. Asymmetric stretching of C-H in PVA gives sharp band at 2934  $\text{cm}^{-1}$ . The absorption peak at 1097  $\text{cm}^{-1}$  has been assigned to the C-O stretching mode for PVA and the bands observed at 1410  $\text{cm}^{-1}$  have been attributed combination frequencies of (CH-OH). It seems that the intensity of hydrogen bonding has been increased as a result of the co-polymerization of PVA and AA leading to the abroad absorption band in the region 3000-3500  $\text{cm}^{-1}$  (Fig.1.b).

This may explain the formation of hydrogen bonding between the carboxylic groups of AA and hydroxyl groups of PVA. The appearance of new absorption band at 1729  $\text{cm}^{-1}$  represents the C=O of COOH group. It is also observed that the band at 1097  $\text{cm}^{-1}$  which corresponding to C-O stretching mode of PVA (Fig. 1.a) become shifted and appear at 1089  $\text{cm}^{-1}$  in PVA/AA hydrogel (Fig. 1.b). FTIR spectrum of composite hydrogel by comparison with clay spectrum (Fig.1.d), the absorption peaks at 1074 $\text{cm}^{-1}$  and 625 $\text{cm}^{-1}$  in composite hydrogel is clearly attributed to the addition of clay. It is possible to note that the position of these peaks is shifted when compared to those of clay in which those appear at 1050 and 511  $\text{cm}^{-1}$  (corresponding to asymmetric and symmetric stretching of silanol groups O-Si-O of clay) and that indicating formation of PVA/AA/clay composite hydrogels.

### 3.2. Effect of copolymer composition on MB adsorption

The amount of MB dye adsorbed by PVA/AA copolymer hydrogel of different compositions is shown in figure (2). As can be seen from the figure, the adsorption of MB increases with decreasing AA content and the maximum adsorption was obtained at PVA/AA composition 30/70 (wt%).

Obviously, the equilibrated amounts of MB adsorbed on the hydrogels decreased as the AA content increased. This decrease in MB adsorption could be attributed to the decrease in the degree of swelling, which decreases the diffusion of MB

molecules into the hydrogels to reach adsorbing and interacting sites. This result is accordant with Li et al., [17]. The decrease in the amount of MB adsorbed with increasing AA content due to more macromolecules chains being entangled.

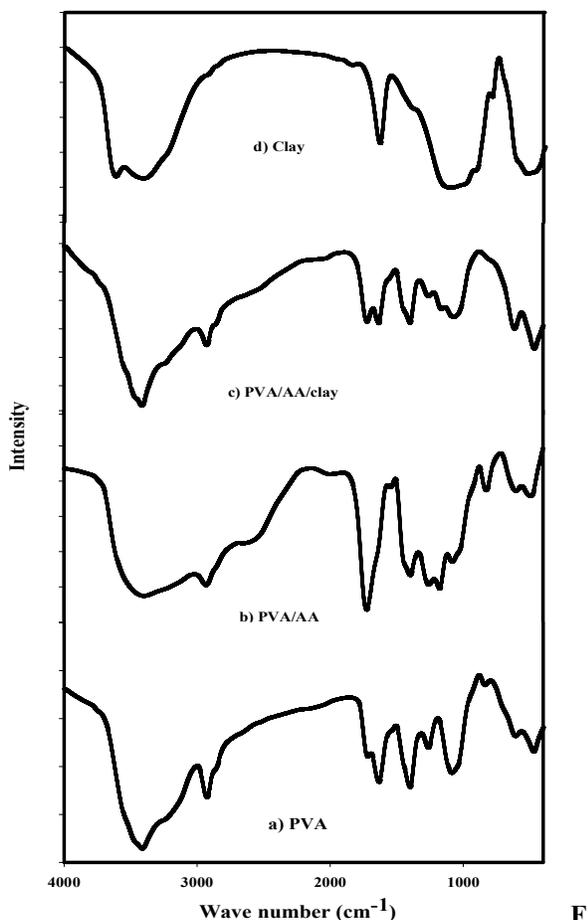


Figure (1): FTIR spectrum of clay, PVA, PVA/AA and PVA/AA/clay composite hydrogels.

### 3.3. Effect of clay content on MB adsorption

Figure 3 shows the influence of clay content in the composite hydrogel (PVA/AA/clay) on MB adsorption. It is clear that the amount of clay in the composite hydrogel is an important factor affecting MB adsorption. The adsorption concentration of MB increases when the clay content increases from 0% to 2% in the hydrogels, then it decreases. This decrease continued as the amount of clay in the composite hydrogel was increased. This situation can be explained by the interactions occurred between the clay and hydrogel components. Clay is a multifunctional crosslinker, when the clay content in the composite was increased, more hydrogen bonds formed between the clay and the PVA or PAA for this reason, dye molecules don't interact as strongly as with composite hydrogel that contain 2% clay. The

decrease of MB adsorption on the composite hydrogels with clay content more than 2% may be also due to formation of more compact copolymer network. The dye molecules are not able to diffuse sufficiently and react with the adsorbing and interacting sites.

The aforementioned results confirming that both feed composition of PVA/AA and clay concentration play a critical role in MB adsorption.

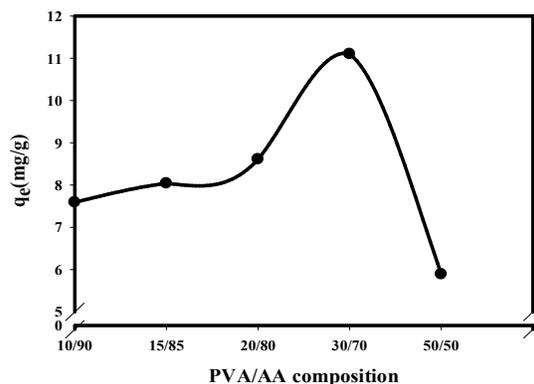


Figure (2): Effect of various PVA/AA compositions on adsorption of MB dye. Initial concentration; 50mg/L, pH; 6, adsorbent dosage; 50mg, contact time 48h at 25 °C.

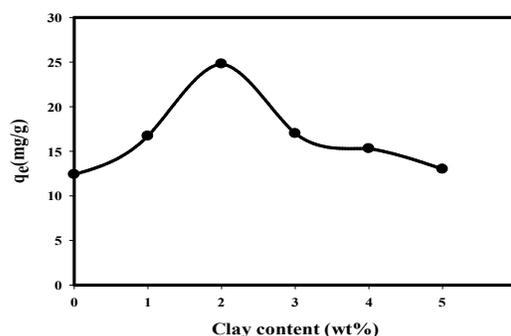
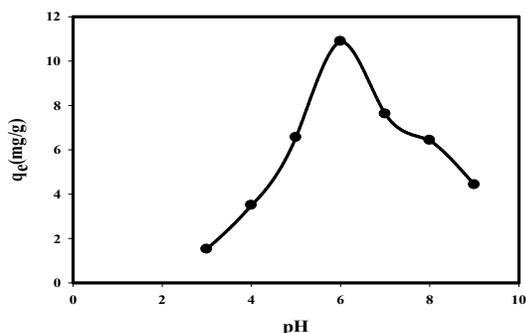


Figure (3): Effect of clay content (wt%) in PVA/AA of composition 30/70 (wt%) on MB dye adsorption, initial dye concentration; 50mg/L, pH; 6, adsorbent dosage; 50mg, contact time; 48h at 25 °C

### 3.4. The effect of pH on the adsorption process

To evaluate the effect of pH on the adsorption capacity of these hydrogels, the adsorption experiments were carried out in solutions having different pH values. Figure 4 shows the effect of pH variations on MB adsorption from its aqueous solution, for initial MB concentration of 50 mg/L and constant weight of dry hydrogel. It can be seen that the amount of MB adsorbed on the hydrogel increases with increasing pH value until pH value of 6 after that the amount adsorbed decreases i.e. maximum adsorption of MB on such hydrogels can be obtained at pH 6.

It is also observed that there is a sharply transition when the value of pH was increased from 4.3 to 6. This phenomenon can be explained by considering that at  $\text{pH} > 4.3$  (the  $\text{pK}_a$  of poly (acrylic acid)) [18], the most of the carboxylic groups are ionized and interacted with the MB molecules, which leads the MB adsorption to stabilization. At lower  $\text{pH} < 4.3$ , the hydrogel was in a collapsed status because of the existence of hydrogen bonding between the carboxylic and hydroxyl groups of the polymer chains and hydrophobic interaction [17]. As a result, it is difficult for MB molecules to diffuse into the inner of hydrogel at lower pH and the adsorption capacity of the hydrogels decreased. However, at higher  $\text{pH} > 4.3$ , the COOH groups along the hydrogel network dissociate to form  $\text{COO}^-$  i.e. increasing the number of fixed ionized groups. This generates electrostatic repulsion forces among the adjacent ionized groups of the polymer network inducing an expansion of the polymer chains within the hydrogel structure. Therefore, at pH values 4-6, the formation of an ionic complex between the MB molecules and the hydrogel networks is provided leading to increasing MB adsorption.

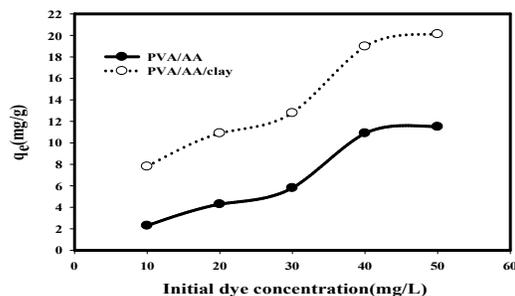


**Figure (4):** Effect of pH on MB dye adsorption by PVA/AA hydrogels of composition; 30/70 (wt%), initial dye concentration; 50 mg/L, adsorbent dosage; 50mg, contact time; 48h at 25 °C

### 3. 5. Effect of initial dye concentration

Figure 5 shows the relationship between the initial dye concentration and the amount of dye adsorbed. It is observed that the amount of dye adsorbed increased with increasing initial dye concentrations. In solution with higher MB concentration, the dye molecules move easier into the hydrogel. This may attributed to the following: with increasing content of MB in the initial solution, concentration gradients at the hydrogel–solvent interfaces could take place causing an enhancement of the MB adsorption. The higher the dye concentration, the higher the number of dye molecules at the adsorbing and interacting sites. The results obtained also gave an indication that the PVA/AA/clay composite hydrogels is more efficient adsorbent than

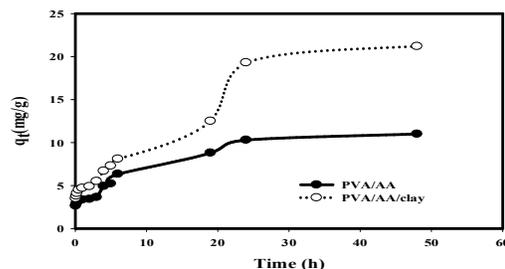
PVA/AA hydrogel, since; the maximum adsorption capacity for PVA/AA/clay composite is Ca. two times of that PVA/AA.



**Figure (5):** Effect of different initial dye concentrations on MB dye adsorption by PVA/AA and PVA/AA/clay composite hydrogels. PVA/AA composition; 30/70 (wt %), pH; 6, adsorbent dosage; 50mg, contact time; 48h at 25 °C.

### 3.6. Effect of contact time on MB adsorption

To determine the time of maximum adsorption, the adsorption of MB dye on PVA/AA and PVA/AA/clay composite hydrogels was studied as a function of contact time (Fig.6).



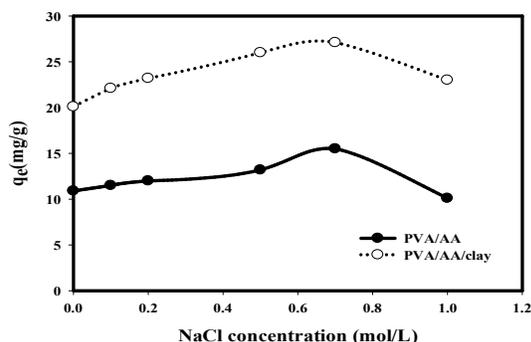
**Figure (6):** Time profile of MB dye adsorption by PVA/AA and PVA/AA/clay composite hydrogels of composition; 30/70 (wt%) , initial dye concentration; 50 mg/L, pH; 6, at 25 °C.

The MB dye showed a fast rate of adsorption during the first 6h and then the rate of adsorption decreases to become almost insignificant after 24h due to exhaustion of the adsorbing and reacting sites. The rate of adsorption capacity is high in the beginning due to large surface area of the adsorbents available for the adsorption of MB. At the beginning of the adsorption process all the reacting sites are vacant and hence the extent of removal is high. After a rapid initial uptake, there was a transitional phase in which the rate of uptake was slow with uptake reaching almost a constant value.

Consequently, the adsorption of MB was carried out in two distinct stages, a relating rapid one followed by a slower one gradually lead to a plateau one.

### 3. 7. Effect of ionic strength on MB adsorption

It is well known that some additives such as salts and surfactants were utilized to accelerate or retard dye adsorption process. Sodium chloride is often used as a stimulator in dyeing process, which may screen the electrostatic interaction of opposite charges or enhance the degree of dissociation of the dye molecules to decrease or increase the amount of dye adsorbed. The effect of ionic strength on MB adsorption is shown in figure 7.



**Figure (7): Effect of ionic strength on MB dye adsorption by PVA/AA and PVA/AA/clay composite hydrogel of composition; 30/70 (wt%), pH; 6, initial dye concentration; 50mg/L, contact time;48h at 25°C.**

It can be seen that the raising in ionic strength of MB solution causes an appreciably increase in the adsorption amounts of the dye on the hydrogel. However, at high ionic strength ( $>0.8$ mol/L), a notable decrease in adsorption capacity for MB was observed. The presence of NaCl in the solution may have two opposite effects. On one hand, the salt can screen the electrostatic interaction between the adsorbent and the dye molecules, and makes the adsorption capacity for MB decreases in the presence of high NaCl concentration. On the other hand, the salt has the positive effect for the dissociation of dye molecules by facilitating the protonation. The obtained results gave an indication that this adsorption process is mainly governed by ionic strength of the dye solution.

### 3. 8. Effect of temperature on MB adsorption

One of the important parameters which affect adsorption capacity is temperature. The effect of temperature on the adsorption of MB dye on PVA/AA and PVA/AA/clay composite hydrogels is shown in Fig. 8. The optimum temperature of the aqueous dye solution was found to be 45°C, thereafter, the adsorption capacity decreases with increasing the temperature of the dye solution.

In order to gain an insight into the adsorption mechanism involved in the adsorption process, the enthalpy change ( $\Delta H$ ) for the present system was calculated. To determine the thermodynamic parameter, adsorption experiments are repeated at a

constant dye concentration (50 mg/L) and two different temperatures 30 and 45 °C. The apparent enthalpy change value of adsorption ( $\Delta H$ ) was calculated using the following thermodynamic function [19]:

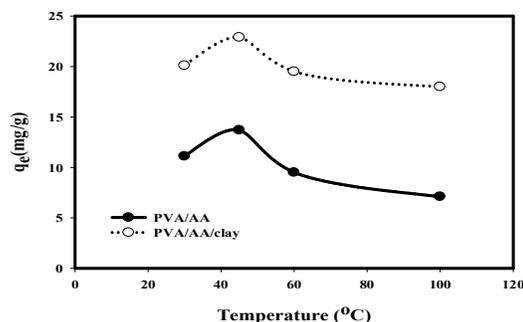
$$\ln \left( \frac{C_{e2}}{C_{e1}} \right) = \left( \frac{\Delta H}{R} \right) \left[ \left( \frac{1}{T_1} \right) - \left( \frac{1}{T_2} \right) \right]$$

Where  $C_{e1}$  and  $C_{e2}$  are the equilibrium dye concentrations at absolute temperature  $T_1$  and  $T_2$ , respectively.  $R$  is the universal gas constant=8.314 J/(mol. K).

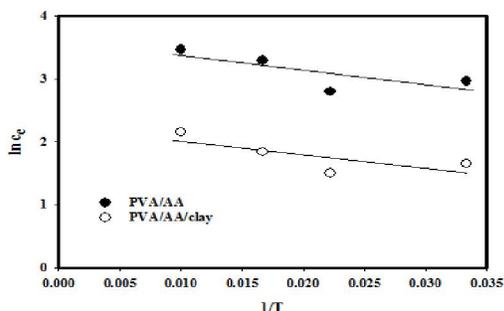
Figure (9) shows  $\ln C_e$  versus  $1/T$ , the slope of these graph give  $\Delta H/R$  values. The enthalpy change value of adsorption ( $\Delta H$ ) was found to be -193.2 KJ/mol for PVA/AA and -178.9 KJ/mol for PVA/AA/clay composite hydrogel, respectively. The negative value of  $\Delta H$  reveals that the adsorption is exothermic. The enthalpy change value ( $\Delta H$ ) for physical adsorption is generally smaller than that of chemical adsorption. Typically,  $\Delta H$  for physical adsorption ranges from 0-40 KJ/mol, compared to that of chemical adsorption ranging from 40-800 KJ/mol [19]. The value of  $\Delta H$ s was higher than those corresponding to physical adsorption. This would suggest that the adsorption process is chemical in nature.

### 3. 9. Adsorption isotherm of MB dye

An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. The Freundlich and Langmuir isotherms are the most commonly used to describe the adsorption characteristics of adsorbent used in wastewater. In the experiments of equilibrium adsorption isotherm, a fixed amount of hydrogel 50 mg in 20 ml dye solutions with concentrations ranging from 10-50 mg/L were used.



**Figure (8): Effect of temperature on MB dye adsorption by PVA/AA and PVA/AA/clay composite hydrogels of composition; 30/70(wt%), initial dye concentration; 50 mg/L, pH; 6, hydrogel mass; 50 mg, and contact time; 48h.**



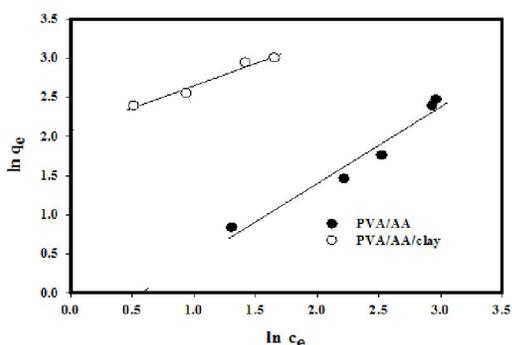
**Figure (9):** Variation of  $\ln C_e$  with  $1/T$ . PVA/AA composition; 30/70 (wt%), pH; 6, initial dye concentration; 50mg/L, adsorbent dosage; 50mg and contact time; 48h.

**Freundlich isotherm:**

The adsorption isotherms data were correlated with the Freundlich equation [20]:

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

Where  $q_e$  and  $C_e$  are the amount of dye adsorbed (mg/g) onto hydrogel at equilibrium and the equilibrium concentration (mg/L), respectively. Linear plots of  $\ln q_e$  versus  $\ln C_e$  illustrated that the adsorption follows the Freundlich isotherm (Fig. 10).



**Figure (10):** Freundlich isotherm of MB dye by PVA/AA and PVA/AA/clay composite hydrogels of composition; 30/70 (wt%), adsorbent dosage; 50mg, pH; 6, contact time; 48h at 25 °C.

The intercept of the line  $K_f$  is the Freundlich adsorption constant and represents the adsorption capacity of the adsorbent. The slope of the Freundlich equation  $1/n$  ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, which may become more heterogeneous when  $1/n$  gets close to zero [21].

The parameters of Freundlich isotherm,  $K_f$  and  $1/n$  as well as the regression coefficients  $R^2$  are given in Table 1.

It can be seen from Table (1) that the regression coefficients  $R^2$  were found to be 0.9556 and 0.9876, so the Freundlich adsorption law is applicable

for the adsorption of MB onto PVA/AA and PVA/AA/clay composite hydrogel. The Freundlich constant  $n > 1$  indicates favorability of adsorption [22].

**Table (1):** The Freundlich and Langmuir isotherm constants and regression coefficient ( $R^2$ ) for MB dye adsorption.

Models	Parameters	PVA/AA	PVA/AA/clay
Freundlich	$K_f$	6.06	7.9
	$1/n$	0.9803	0.346
	$R^2$	0.9556	0.9876
Langmuir	$q_m(\text{mg/g})$	34.2	28.8
	$b$	0.016	0.38
	$R_L$	0.53	0.05
	$R^2$	0.9664	0.9776

**Langmuir isotherm:**

The Langmuir model (Fig.11) is probably the best known and most widely applied adsorption isotherm. It is represented as the following equation [20]:

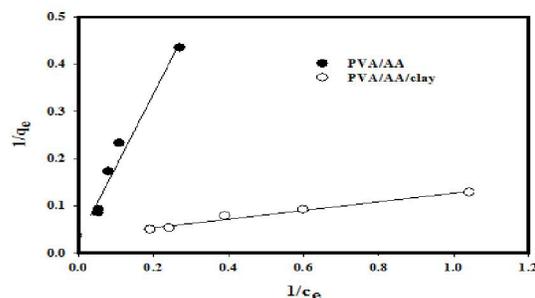
$$q_e = q_0 b C_e / (1 + b C_e)$$

$$1/q_e = 1/q_0 + 1/q_0 b C_e$$

Where  $C_e(\text{mg/L})$  is the equilibrium concentration,  $q_e(\text{mg/g})$  is the amount of dye adsorbed onto hydrogel at equilibrium,  $q_0(\text{mg/g})$  is the complete monolayer adsorption capacity, and  $b(\text{L/mg})$  is the Langmuir constant. The dimensionless separation factor,  $R_L$ , is essential characteristic of Langmuir isotherm, which is defined as equation [23]:

$$R_L = 1 / (1 + b C_0)$$

Where,  $b$  is the Langmuir constant and  $C_0$  is the highest initial dye concentration. The value of  $R_L$  indicates the type of isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ) [24]. The parameters of Langmuir isotherm,  $q_0$ ,  $b$  and  $R_L$  as well as the regression coefficients ( $R^2$ ) are given in Table 1.



**Figure (11):** Langmuir isotherm of MB dye by PVA/AA and PVA/AA/clay composite hydrogels of composition; 30/70 (wt%), adsorbent dosage; 50mg, pH; 6, contact time; 48h at 25 °C

The  $R_L$  values calculated from above expression lies in the range (0-1) indicates favorable adsorption.

### 3. 10. Adsorption kinetics of MB dye

In order to investigate the kinetic mechanism, which controls the adsorption process of MB on the prepared hydrogels, the pseudo-first-order and pseudo-second order models were used [25]. The pseudo first-order kinetic model can be as Eq. (1) and the pseudo-second-order model as Eq. (2)

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (1)$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (2)$$

where,  $q_e$  is equilibrium adsorption capacity (mg/g), and  $k_1$  is the pseudo-first-order rate constant ( $\text{min}^{-1}$ ).  $q_t$  is the amount of adsorbed dye (mg/g) at time  $t$  (min) and  $k_2$  is the pseudo-second order rate constant (g/mg/min).

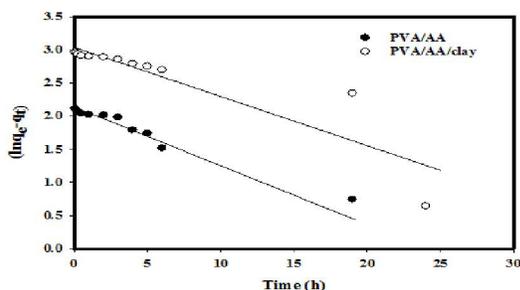


Figure (12):Pseudo-first order kinetic plots for adsorption of MB dye. Initial dye concentration;

50mg/L, PVA/AA composition; 30/70 (wt %), adsorbent dosage; 50mg, pH 6, at 25 °C.

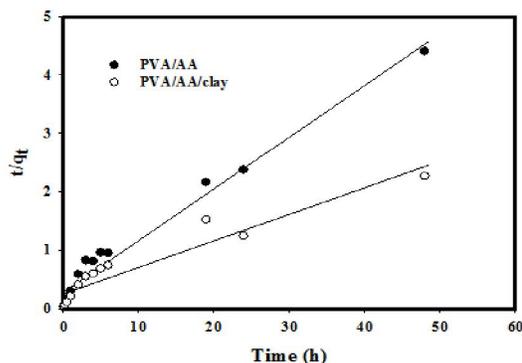


Figure (13):Pseudo-second order kinetic plots for adsorption of MB dye. Initial dye concentration; 50mg/L, PVA/AA composition; 30/70 (wt %), adsorbent dosage; 50mg, pH 6, at 25 °C.

According to the experimental data, a straight-line plot was obtained for the pseudo first-order kinetic model suggesting the applicability of this model. However, table. 2 shows that the calculated value of adsorption capacity,  $q_{e,cal}$  is lower than the value of experimental adsorption capacity,  $q_{e,exp}$ .

Table (2): Kinetic parameters of pseudo-first order and pseudo-second order model for CV adsorption.

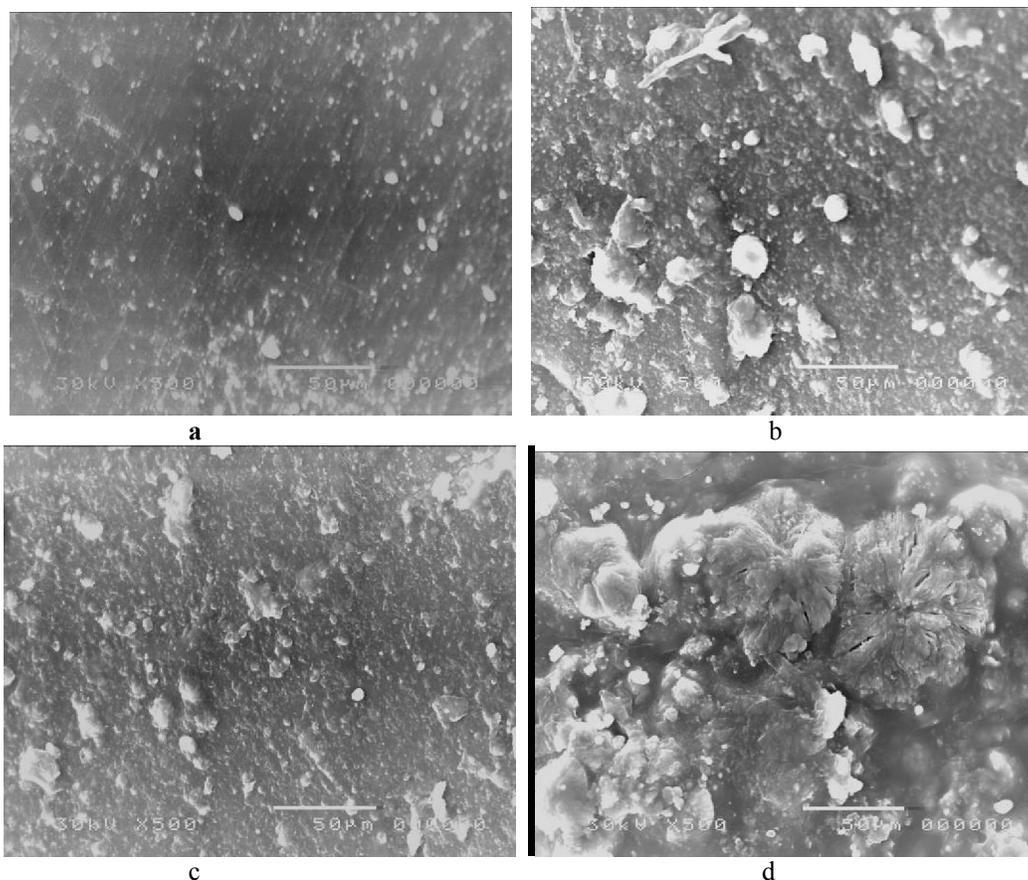
Sample	Pseudo-first order				Pseudo-second order		
	$q_e(\text{exp})$	$K_1$	$q_e(\text{cal})$	$R^2$	$K_2$	$q_e(\text{cal})$	$R^2$
PVA/AA	11.2	0.0886	8.4	0.969	0.157	11.2	0.9757
PVA/AA/clay	21.2	0.07415	20.8	0.798	0.896	21.9	0.9029

The pseudo-second-order plot is linear and the calculated value of adsorption capacity,  $q_{e,cal}$  is close to the value of experimental adsorption capacity,  $q_{e,exp}$  as shown in Table 2. Thus, it could be suggested that adsorption of MB on PVA/AA and PVA/AA/clay follows pseudo-second-order better than pseudo-first-order model. The pseudo-second-order kinetic model assumes that the rate-determining step may be chemical adsorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate [26].

### 3.11. SEM:

SEM analysis was carried out in order to confirm the adsorption of MB dye on the PVA/AA and PVA/AA/clay hydrogels. SEM images show the topography of the hydrogel matrices before and after MB adsorption where great differences between the two surfaces can be seen (Fig.14).

This differences in the morphology itself revealed the adsorption of MB onto hydrogels.



**Figure (14): SEM of PVA/AA (a, b) and, PVA/AA/clay composite hydrogel (c, d) before and after MB adsorption, respectively.**

#### Conclusion:

The aim of this work is investigation of removal of cationic dyes from aqueous solutions using composite hydrogel. For this purpose polymeric hydrogel matrices of poly (vinyl alcohol) (PVA)-co-Poly (acrylic acid) (PAA) were obtained by gamma irradiation technique in presence of methylene-bis- acrylamide (MBAM) or bentonite clay and used as adsorbents for the removal of Methylene Blue from aqueous solutions. It was found that the maximum adsorption capacity was obtained at PVA/AA composition of 30/70 (wt%). Increasing the clay content up to 2% causes an increment in dye adsorption capacity but further increase of clay causes a decrease in dye adsorption capacity. The adsorption capacity of PVA/AA /clay composite hydrogel was found to be two times greater than that of PVA/AA hydrogel. Langmuir and Freundlich isotherm models were used to describe adsorption data. The results indicated that the adsorption of MB dye onto hydrogels was well fitted with Freundlich and Langmuir.

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