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RESEARCH ARTICLE

# Adsorption of Indigo Carmine Dye on Chitosan Grafted Poly (Methyl Methacrylate)

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## ABSTRACT

This study investigated the adsorption of indigo carmine dye (a chemical considered to be a pollutant in water) onto chitosan nanocomposite grafted with methyl methacrylate (Ch-g-PMMA) polymer. Absorption values are found for solutions at different conditions of concentration, temperature, weight and acidity. The adsorption process was studied to choose the best weight of the compound from 0.01–0.07. It showed that the largest amount of dye adsorbed on the surface of the triple composite was at pH = 4. The results of the effect of ionic strength on the process of absorption of salts (sodium chloride, calcium carbonate) were also presented. It has been found that $CaCO_3$ has greater solubility because it affects the amount of adsorbed material compared to NaCl salt. The results also showed that the adsorption kinetics study is pseudo-second order. Freundlich and Langmuir adsorption isotherms were used, and the results showed that the dye applied to the Freundlich isotherm. The kinetic results also showed that the adsorption of dyes follows pseudo-second order kinetics. It was found that the reaction is a thermal release of the dye solution through the negative value of the enthalpy function $\Delta H$ and that the adsorption process takes place automatically to remove the dye through the negative value of the free energy $\Delta G$ and the low randomness of the dye. The indigo carmine dye solution increases the negative value of the entropy function when the solid adsorbent interacts with the liquid adsorbent (dye) on the surface of the adsorbent.

**Keywords:** Adsorption, Crab shells, Chitin, Chitosan, Indigo carmine

## Introduction

Water pollution increases in population and as a direct result of such increase, a rise in the number of activities carried out by humans is directly correlated to an increase in the proportion of water that is polluted.[1,2] Water pollution occurs intentionally or unintentionally when substances such as chemicals and garbage from homes are released into the environment.[3,4] Clean water is a necessary with sufficient condition for the growth of healthy organisms free of diseases.[5]

Adsorption technology is considered one of the most important methods used in removing pollutants and treating water. Dyes are among the pollutants that have the greatest impact on environmental systems and human health. This has been confirmed by many studies on the use of this technology in removing pollutants, where F.F. Karam et al. studied the adsorption of toxic crystal violet dye using (Chitosan - OMWCNTs) from aqueous solution. The study examined the effect of pH and study the effect of ionic density on dye removal. The best weight obtained at the adsorbed surface was 0.035 g. The results showed that the best communication time to reach equilibrium was 90 minutes. By studying the pH, it was found that the best acidic medium was pH-4, and the deletion rate was 99% in the acidic medium with a concentration of 100 mg.L. As for the study of ionic density, both sodium chloride and potassium carbonate salts were studied. The dye absorption rate decreases as salt ions compete for the

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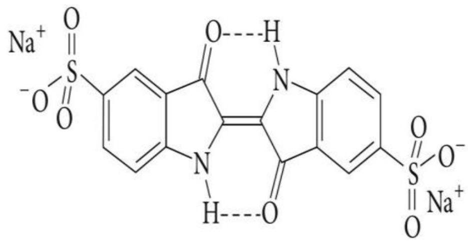

**Fig. 1.** The structure of Indigo Carmine dye.

active sites on the surface of the adsorbent.[6] In this study, the nanocomposite (Ch-g-PMMA) poly(methyl methacrylate) grafted with chitosan was used and used to adsorb the anionic dye sulfonated indigo carmine from water. It is considered one of the secondary polymeric compounds that has a wide range of applications due to its improved properties such as (mechanical and thermal properties, water permeability, and the cheapness and availability of its materials). These properties can be obtained in very small quantities of nanomaterials compared to other materials.[7] Indigo carmine It is considered an industrial anionic dye from the indigo group, which is of great importance in the pharmaceutical, food, and cosmetics industries.[8] It is also known as acid blue 74, Fig. 1. Indigo carmine is a type of indigo dye that is extremely dangerous to human health. Even the slightest contact with it can irritate the skin and eyes. In addition, it has the potential to cause irreversible damage to the cornea and conjunctiva, and the dye is another potential cause of death when consumed. It has also been shown that the tincture can lead to the development of tumors where it is applied. It has been documented to produce mild to severe hypertension as well as vascular, cardiac, and respiratory consequences in patients when it is administered intravenously for the purpose of determining the efficiency of the urine collection system. It can also irritate the digestive system, causing symptoms such as nausea, vomiting, and diarrhea. Tests to determine the toxicity of the dye showed that it was harmful in the long term for mice but had only a short-term effect on pigs. Hence, keeping in mind the toxicity of this dye, removing indigo carmine from water and wastewater has been the subject of a number of different attempts. The dye features a single C=C bond that is subsequently replaced by two NH groups (donor groups) and two CO groups (acceptor groups). In the solid state, the dye exists mainly in the trans conformation, which is characterized by hydrogen bonding between the NH and CO groups. A comprehensive look has been given at the composition, chemical properties and uses of indigo carmine and indigo dyes.[9] The dye indigo carmine (IC) has found particular use in analytical chemistry as an indicator, in the food industry as an additive, and in biological research as a microscopic dye. There has been, however, only very little in-depth research on indigo cochineal dye documented in the scientific literature. The dye has been shown to be particularly sensitive to oxidizing chemicals and has been the subject of research in kinetic studies involving such species. The molecule was first used in the 19$^{th}$ century for the purpose of determining the peroxide properties of blood. Since then, it has also been used in the kinetic determination of peroxides as well as in studies related to catalytic peroxidation. The scope of these studies was very limited. In the same vein, only a limited amount of dye was produced in aquatic and acidic conditions.

Adsorption is the association of the material on the solid surface from its surroundings of liquid or gas, that is, in the sense of trapping the atoms or molecules that fall on the surface. The adsorbent is the material to be adsorbed and is called adsorbate. It is obtained by adsorption and is called adsorbent. The difference between absorption and adsorption is that adsorption is a surface process, while absorption is a process that occurs by the total interference with the substance and not only with the surface.[10,11] There are two types of adsorptions: chemical adsorption and physical adsorption.[12] The aim of the research is to determine whether the produced compound (Ch-g-PMMA) can effectively absorb the dye (indigo carmine) or not and to discover the best conditions for the adsorption process, which may include the following: weight of the surface that was prepared, equilibrium time, pH, temperature, and ionic strength. Through the process of conducting research on the adsorption kinetics of the dye (Indigo Carmine) on the surface of the structures that were constructed. The adsorption process involves a number of thermodynamic functions, such as ($\Delta S$, $\Delta H$, and $\Delta G$), which must be understood in order to complete the process.

## Materials and methods

### *Experimental*

#### *Materials and equipment used*

The dye indigo carmine is a purple colored, water soluble powder having molecular formula $C_{16}H_8O_8N_2S_2Na_2$ (molecular weight 466.36). The most important materials that were used were: chitosan extracted from crab shells, the polymer methyl acrylate, ion-free distilled water, ethanol, potassium persulfate, ascorbic acid, hydrochloric acid, NaCl, and $CaCo_3$. The tools that were used were: digital scale, beaker, volumetric flask, conical flask, centrifuge, magnetic stirrer, hot plate, and thermometer.

## The method of work

### Preparation of the adsorbents

Preparation of Chitosan grafted poly (methyl methacrylate) (Ch-g-PMMA): The following substances were put to a standard flask with a capacity of 100 milliliters: 0.2 grams of chitosan, 3.2 grams of the monomer (MMA), 0.49 grams of ascorbic acid, and 0.06 grams of potassium persulfate. The reaction mixture was placed in a water bath with continuous stirring. By magnetic stirrer using a (Hot STIRRER) device at a temperature of 45°C and a time of 2hrs. Using the graft copolymerization.

Then, the composite or adsorbent polymer was dried at a temperature of 50°C for a period of 1hr. using an oven to avoid the hydration (or solvation) of the adsorbent.[13–15]

### Preparing the Indigo Carmine stock solution

Prepare the standard solution with a concentration of 100 mg/L by dissolving (0.01 g) of the dye in an amount of distilled water in a 100 mL volumetric bottle, then the distilled volume was completed to the mark.

### Adsorption experiments

Tests were carried out in a 250 mL baker equipped with mechanical shakers operating at 150 rpm until equilibrium was achieved at a temperature of 20 °C. The gravimetric effect of Ch-g-PMMA was determined, and weights ranging from 0.01–0.07 g were taken from the adsorbed surface. In order to calculate the effect of time, several time period was used, ranging from 10 to 140 minutes with a specific weight of the adsorbed surface. The effect of the acid function was studied by taking the pH (4, 6, 8, and 10). The effect of ionic strength was also studied using two different salts, NaCl and $CaCO_3$, where the weights of each one ranged between 0.01–0.06 grams for the pothos salts. The absorption was measured using the DV device and a wavelength (610 nm). Eq. (1) is used to calculate the amount of adsorbent.

$$Q_e = \frac{(C_0 - C_e)\,V}{W} \quad (1)$$

Where, $C_0$ and $C_e$, represent the initial concentration and dye equilibrium IC (mg/L).

V is the volume of solution (L) and W is the amount of Ch-g-PMMA used (g).

The removal percentage (%) of DYC was calculated using the following:

$$\text{removal}\,(100) = \frac{C_0 - C_e}{C_o} \times 100 \quad (2)$$

## Theory

### Adsorption isotherm

Isotherms are considered extremely important because through them the relationship between the adsorption surface and the adsorbed substance is deduced, as well as to give an idea about the adsorption capacity by knowing the number of layers that are formed on the adsorption surface, and this number of layers can be equal to one layer or be multi-layered.

$$\text{Langmuir}: \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_l Q_m} \quad (3)$$

If $C_e$ (mg/L) represents the concentration of adsorbent residues at equilibrium, $Q_e$ (mg/g) and $Q_m$ (mg/g) represent the adsorption capacity at equilibrium and the maximum adsorption capacity, respectively, while $K_L$ (L/g) is the Langmuir constant. The value of the Langmuir constant is related to adsorption surface properties such as specific surface area and porosity.

$$\text{Freundlich}: LogQ_e = LogK_f + \left(\frac{1}{n}\right)\text{Log}C_e \quad (4)$$

whereas:

$Q_e$: amount of adsorbent (mg/g).

$C_e$: concentration at equilibrium (mg/L).

$K_f$ and n are Freundels constants.

$$\text{Temkin}: \; Q_e = \frac{RT}{b} Lnk_T + \frac{\text{RT}}{b} LnC_e \quad (5)$$

If R is the gas constant equal to 8.314 J/ mol.k.

T is the temperature (K).

KT (L/g) is an enablement constant, associated with a maximum binding energy.

b (J /mol) is an enablement constant related to the heat of adsorption.

### Kinetic modeling

Kinetics not only provides information about the adsorption mechanism and adsorption pathways, but it also controls the rate of adsorption, which in turn determines the amount of time required to reach equilibrium states for the adsorption process.

$$\text{Pseudo} - \text{first order} = Log\,(Q_e - Q_t) = Logq_e - \frac{K_1}{2.303} t \quad (6)$$

If $Q_e$ (mg/g): indicates the adsorption capacity at equilibrium.

$Q_T$: indicates the adsorption capacity at a certain time.

$K_1$ (min): is the velocity constant.

$$\text{Pseud0} - \text{second order}: \frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \quad (7)$$

where $K_2$ (g/mg.min) is a pseudosecond-order rate constant.

### Thermodynamic parameters

The thermodynamic behavior of the IC dye adsorption onto the composite (Ch-g-PMMA) was analyzed through the parameters-Gibbs free energy change ($\Delta G^0$), entropy ($\Delta S^0$), and enthalpy ($\Delta H^0$). These parameters were calculated using the following equations:

$$\Delta G^0 = -RTLnK_e \quad (8)$$

$$K_c = \frac{C_0}{C_e} \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

Where:
($\Delta G^0$): the change in free energy.
T: the absolute temperature.
R: General gas constant 8.314 J/K.mol.
($K_e$): equilibrium constant.
($\Delta H^0$): Enthalpy change.
($\Delta S^0$): Entropy change.

## Results and discussion

### Adsorption applications of the prepared compound (Ch-g-PMMA)

### Effect of surface weight

Amount of adsorbent used in adsorption is significant so it determines the sorbent-sorbate equilibrium in the system and the adsorbent treatment cost per unit of dye solution was investigated by making use of weights of 0.01–0.07 g.[16] As illustration is shown in Fig. 2 at constant concentration dye (25 mg.$L^{-1}$) and volume (50 mL), when there is more adsorbent, the sorption capacity goes down. It is possible that saturation of the adsorption sites resulting from particle interaction, such as aggregation, is the reason for the decrease in adsorption capacity that occurs when an increasing dose of adsorbent is used in the presence of a constant concentration and size of the dye. 0.01 g of adsorbent dosage is selected as the best dosage of adsorbent for further examinations.[17]

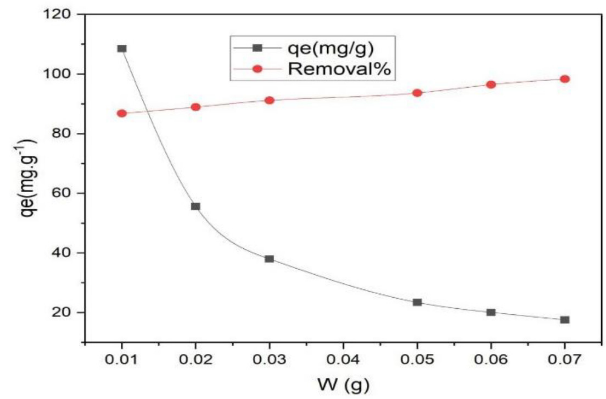


**Fig. 2.** Effect of weight (Ch-g-PMMA) on Indigo Carmine dye (Dye conc: 25 mg$L^{-1}$, tempe: 25 °C, 50 mL, pH = 7).

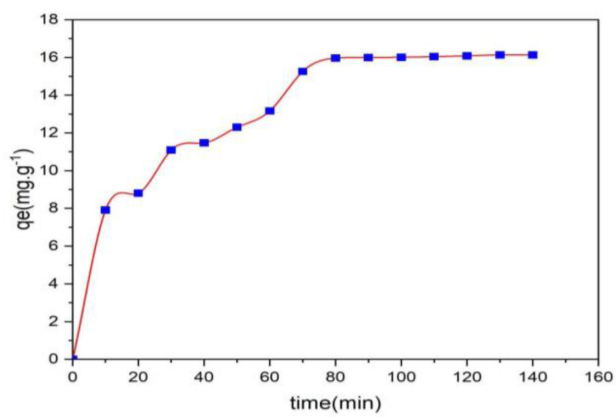


**Fig. 3.** Effect of equilibrium time (Ch-g-PMMA) on Indigo Carmine dye (w = 0.01 g, Dye cone: 25 mg$L^{-1}$, temp: 25 °C, 50 mL, pH = 7).

### Effect of contact time

Studies that include contact time relate the amount of dye absorbed to a constant mass of adsorbent and show how this relationship changes over the time. During the treatment process, it is helpful to have an idea of how long it takes to reach equilibrium. At the best weight, where an adsorbent surface of 0.01 g was reached, the effect of weighing time (10–140) minutes on the adsorption efficiency and adsorption capacity of Ch-g-PMMA was obtained. This is shown in Fig. 3, adsorption capacity and efficiency are both factors considered here. The initial five to fifteen minutes showed a significant increase (fast adsorption), which was then followed by a moderate increase over the next ten to ninety minutes (slow adsorption). Then, there was no further improvement. The maximum absorption efficiency (47.24%) and adsorption capacity (59.06 mg.$g^{-1}$) were observed at equilibrium (90 minutes)[18,19] also found that most absorption of

Indigo Carmine tincture occurred within less than 5 minutes. The rapid adsorption phase lasted less than 20 minutes resulting in dye adsorption of more than 33%. In the first step of rapid adsorption, the IC dye is adsorbed on the outer surface of Ch-g-PMMA via boundary layer adsorption due to the higher available surface area. Fast initial adsorption and longer contact time, the surface of the adsorbent becomes saturated (with large pores and meso) and this makes it resistant to further absorption of IC dye. This is because there are some repulsive forces between the IC dye molecules on the solid particles and the IC molecules in the bulk phase provide greater resistance which makes the process slower. In addition, aggregation of IC dye molecules may occur over a longer contact period.[20]

### *Adsorption isotherms*

The adsorption isotherm represents the relationship between the amount of adsorbent and the remaining concentration of adsorbent in the solution at a constant temperature.[21] The Langmuir isotherm model assumes that adsorption occurs in a monolayer on a homogeneous active surface. In this model, adsorption occurs only at certain local sites and saturated coverage is equivalent to completely occupying these sites.[22] The Freundlich equation is one of the most important isotherms used in the case of solution adsorption. This model assumes that the surface of the adsorbent is heterogeneous due to the different energy levels of the adsorption site,[23] while the Temkin isotherm effect shows some indirect interference between adsorbates and adsorbates on the adsorption isotherm.[24] The IC equilibrium isotherm of Ch-g-PMMA is an $S_3$-type isotherm according to Giles' classification.[25] According to the adsorption isotherm, the adsorption is in the shape of the letter $S_3$, and the direction of the adsorbed material on the surface is vertical, and the solvent may encounter intense or difficult adsorption on the surface of the adsorbent material. This type also indicates the occurrence of multi-layer adsorption as a result of surface heterogeneity, as shown in Figs. 4 to 6, the relationship between the amount of dye adsorbed on the surface of the composite and its concentration in the liquid phase at equilibrium. The adsorption isotherm also gives information about the nature of the interaction between the dye and the adsorbed surface. Using Langmuir, Freundlich, and Temkin expressions, the equilibrium data were analyzed. According to the calculations shown in Table 1, correlation coefficients and equilibrium constants were determined, and the results showed that the Freundlich adsorption isotherm is more applicable to the surface of the compound compared to the Langmuir and Temkin isotherms. Based on these results, it can be concluded that adsorption occurs on many layers on the surface of the composite.

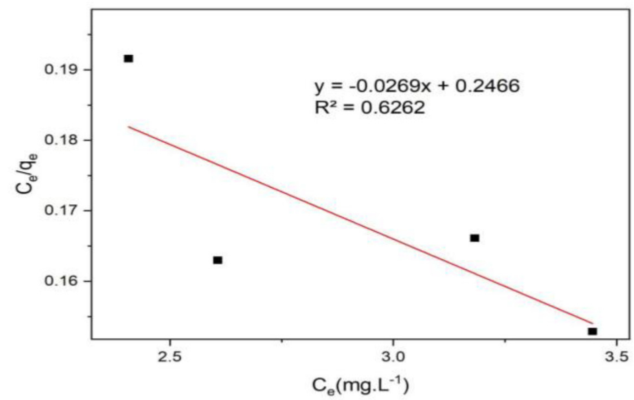


Fig. 4. Langmuir isotherm for Indigo Carmine dye adsorption on the surface of a composite (Ch-g-PMMA) at optimum condition.

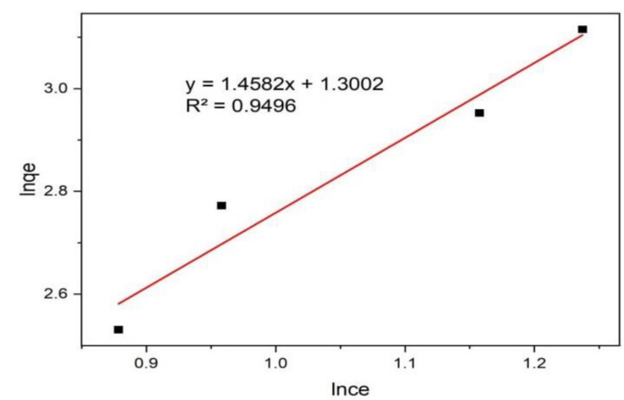


Fig. 5. Freundlich isotherm for Indigo Carmine dye adsorption on the surface of a composite (Ch-g-PMMA) at optimum condition.

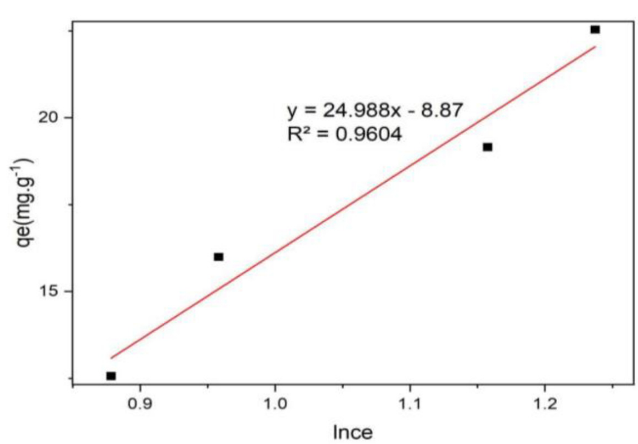


Fig. 6. Temkin isotherm for Indigo Carmine dye adsorption on the surface of a composite (Ch-g-PMMA) at optimum condition.

**Table 1.** Indigo Carmine dye uptake of ternary composites using parameters of the Langmuir, Freundlich, and Timken equations.

| Langmuir equation | | | Freundlich equation | | | Timken equation | | |
|---|---|---|---|---|---|---|---|---|
| $K_L$ | $q_m$ | $R^2$ | $K_F$ | N | $R^2$ | $K_T$ | $B_T$ | $R^2$ |
| $4.10 \times 10^{-2}$ | $4.32 \times 10^{1}$ | 0.6262 | 0.05297 | 2.074 | 0.9496 | 0.99981 | 672116.4 | 0.9604 |

**Table 2.** The amount of Indigo Carmine dye adsorbing on the surface of the composite (Ch-g-PMMA) at various temperatures.

| 5°C | | | 15°C | | 25°C | | 35°C | |
|---|---|---|---|---|---|---|---|---|
| $C_o$(ppm) | Ce(ppm) | qe(mg/g) | Ce(ppm) | qe(mg/g) | Ce(ppm) | qe(mg/g) | Ce(ppm) | qe(mg/g) |
| 20 | 9.12 | 54.39 | 11.36 | 43.17 | 12.22 | 38.88 | 13.25 | 33.71 |
| 25 | 10.15 | 74.22 | 12.22 | 63.88 | 13.25 | 58.71 | 14.29 | 53.54 |
| 30 | 11.95 | 90.22 | 14.02 | 79.88 | 15.05 | 74.71 | 16.09 | 69.54 |
| 35 | 13.77 | 106.12 | 15.73 | 96.30 | 16.87 | 90.61 | 17.69 | 86.53 |
| 40 | 14.35 | 128.23 | 16.42 | 117.89 | 17.45 | 112.71 | 18.49 | 107.54 |
| 45 | 15.51 | 147.44 | 17.46 | 137.66 | 18.61 | 131.92 | 19.64 | 126.75 |

## *Effect of temperature*

Temperature is an important parameter that can be considered as a significant factor in the adsorption process, Solubility is temperature-dependent. Different temperatures effects were studied from 5.15, 25 and 35 °C. The adsorption process is shown in Fig. 7 indicating that the adsorption process produces exothermic heat is the fact that the quantity of Indigo Carmine dye absorbed decreases as the temperature increases. The Vander Waals force between the molecules of Indigo Carmine dye and the active sites on the adsorbent's surface doubles with a rise in temperature, as indicated in Table 2. The solvent is drawn to the active sites on the surface more and more at higher temperatures, which reduces the surface's ability to adsorb material.[26] The unpredictability of the dye molecules adhering to the compound's surface also increases with temperature, which is known as entropy (ΔS). The porousness of the surface also has an impact on the adsorption procedure. The holes in the dye molecules get larger as the temperature is lower.[27]

The values of thermodynamic functions are very important because they explain chemical reactions, most notably the adsorption process. As it is possible to know the direction of the reaction and the nature of the forces controlling it. In these conditions, the interaction forces between the compound and the adsorbed dye molecules are of a physical nature, and naturally, surface adsorption does not occur. Negative entropy (ΔS) values suggest reduced disorder at the solid liquid interface for Indigo Carmine dye, while the standard enthalpy (ΔH) demonstrates exothermic adsorption.[28] When we apply Van't Hoff Arhenius equation in different temperature, we can find enthalpy. This equation can be written in concentration constant then by drawing (Inxm) versus (1.T-1) and we can extract reaction of enthalpy from slope = (−ΔH/R). as shown in Fig. 8.

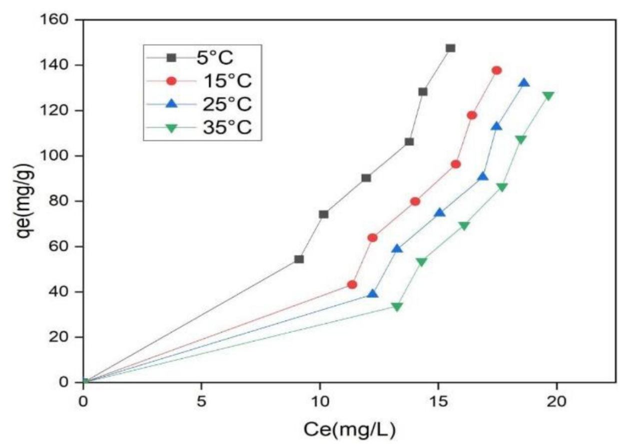


**Fig. 7.** Effect of temperature (Ch-g-PMMA) on Indigo Carmine dye removal (w = 0.01 g, Dye conc: 25 $mgL^{-1}$, 50 mL, pH = 7).

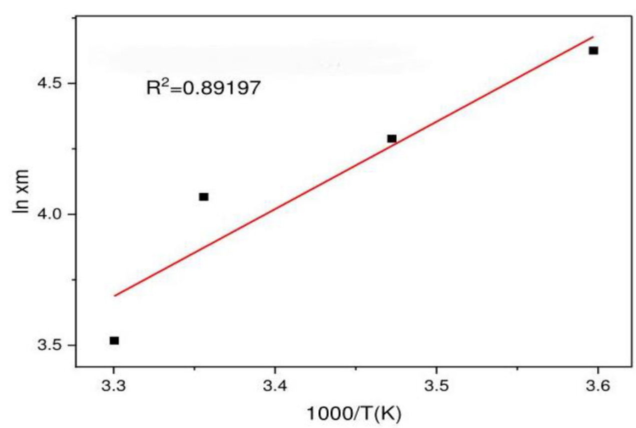


**Fig. 8.** Graph of ln Xm vs reciprocal absolute temperature for IC dye adsorption on Ch-g-PMMA nanocomposite.

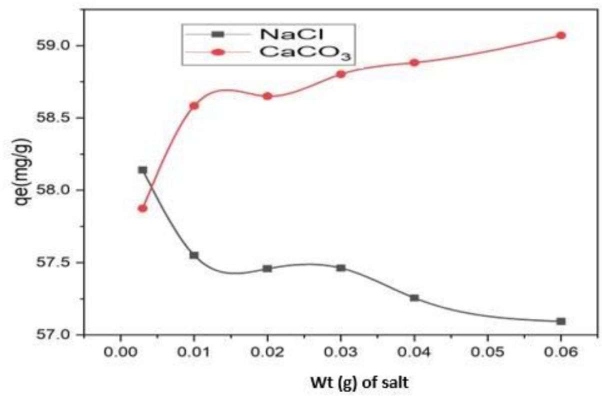


**Fig. 9.** Effect of ionic strength (Ch-g-PMMA) on Indigo Carmine dye removal (w = 0.01 g, Dye conc: 25 mgL$^{-1}$, T: 25 C°, 50 mL, pH-7).

*Effect of ionic strength*

An investigation was done on how salts influenced the adsorption process. Ionic strength is the most important factor that regulates adsorption. In this case, increasing ionic strength can speed up or slow down the adsorption process. In some cases, adsorption is insensitive to the ionic strength of different ions.[29] The effect of ionic strength on the adsorbing surface was studied by Indigo Carmine dye using different weights of (NaCl) salt and ($CaCO_3$), given the optimum conditions (Temperature, adsorbent concentration, adsorbent surface weight, pH and adsorption time). Fig. 9 shows the results of the dye adsorption process in the presence of salts. We notice that by increasing the concentration of the sodium chloride salt, as a result of the effect of the positive ions of the dye and salt molecules on the active sites on the surface of the adsorbent, the amount of adsorbent will decrease. It has an effect on adsorption. The positive sodium ion is faster to compete for the active sites because it is small in size. The negative chloride ion reduces the adsorption capacity because it has the ability to form a double complex with the dye molecules. However, the amount of the adsorbed substance increases with the increase of calcium carbonate salt because of the increase in the solubility of salt in the solution compared to the dye molecules, and accordingly the adsorption increases.[30]

*Effect of pH*

The influence of pH on the adsorption process of the adsorbent surface of Indigo Carmine dye was investigated at a concentration of (25mg.L$^{-1}$) with varied pH values, all optimal conditions (temperature, adsorbent surface weight, and equilibrium time) were established. The adsorption process is shown in

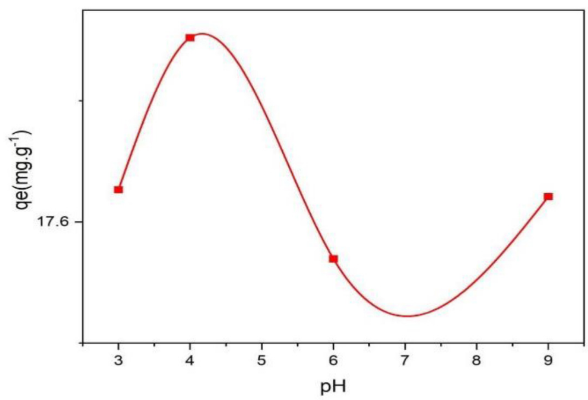


**Fig. 10.** Effect of pH (Ch-g-PMMA) on Indigo Carmine dye (w = 0.01 g, Dye conc:25 mgL$^{-1}$, tempe: 25 C°, 50 mL).

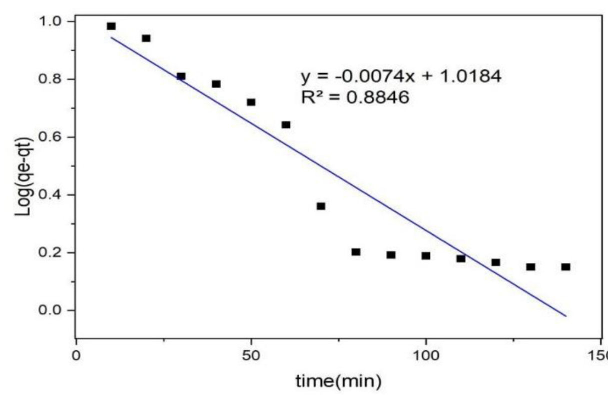


**Fig. 11.** Pseudo - first order kinetic model for adsorption of Indigo Carmine dye on the surface of the composite (Ch-g-PMMA) at (temperature of 25 °C. pH = 7. adsorbing surface weight 0.01 g and dye solution concentration 25 mg.L$^{-1}$).

Fig. 10 at different pH values. The pH is what controls the degree of ionization of the molecule and controls the absorbed surface charge, as well as controlling the groups present in the active sites by controlling the amount of functional dissociation.[31] Adsorption of Indigo Carmine dye rises at pH=4 owing to repulsion electrostatic attraction, and hydrogen affinity. The concentrations of hydrogen ions increase when the pH falls. This work on the amine group's brine in the Indigo Carmine dye.

*Adsorption kinetic study*

The effect of contact time on the adsorption of Indigo Carmine dye by (Ch –g-PMMA) nanocomposite is shown in Fig. 11. This Figure showed rapid adsorption of IC dye in the first 30 min, on adsorbents, and thereafter; the adsorption rate will stable On. (Ch-g-PMMA) are removed from an aqueous solution within 30 min where the experimental kinetic data

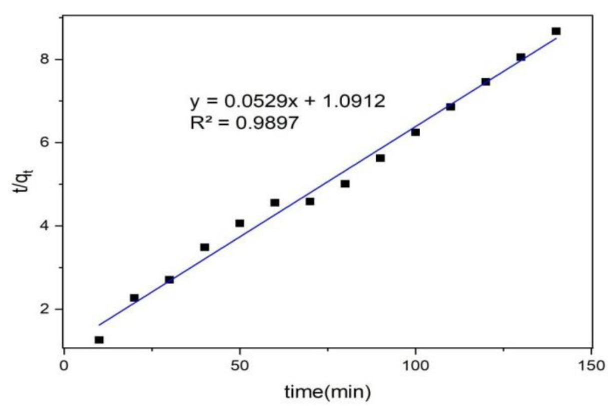


**Fig. 12.** Psendo-second order kinetic model for adsorption of Indigo Carmine dye on the surface of the composite (Ch-g-PMMA) at (temperature of 25 °C, pH = 7, adsorbing surface weight 0.01 g and dye solution concentration (25 mg.L$^{-1}$).

were adjusted according to pseudo-first-order kinetic and to pseudo-second-order kinetic. The linearity of the plots indicates the applicability of the two models' Figs. 11 and 12. IC's pseudo-first-order and pseudo-second-order correlations were 0.8846 and 0.9897 respectively. Indigo Carmine dye correlation coefficients revealed pseudo-second-order kinetic model was best suitable.[32]

## Conclusion

According to the results and inferences that can be drawn from the experimental research conducted, the results of the study indicate that the ingredient is a chemical capable of eliminating more than 98% of the indigo carmine dye present in contaminated wastewater by absorbing the dye. The results showed that an equilibrium time was needed for adsorption. The dyeing process takes 90 minutes. Through studying the isotherms, it was found that the adsorption isotherm on the surface of the prepared compound is of class $S_3$ for indigo carmine dye, which applies to the Freundlich models, which allows and indicates the heterogeneity of the surface in terms of energy. By studying the adsorption at different temperatures on the surface of the compound, the results showed that the adsorption is exothermic, meaning that the value of all is negative for the adsorption of indigo carmine dye. By studying different pH levels, the highest amount of adsorbent was at pH = 4. Increasing the ionic density increases the amount of adsorbent for indigo carmine dye using calcium carbonate salt, and decreases with increasing sodium chloride salt concentration. The kinetics of dye uptake follows an expression representing the pseudo-second-order $\Delta G$ value. The study showed that the adsorption process is a spontaneous process.

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## Authors' declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.
- Ethical clearance: The project was approved by the local ethics committee at the Al-Qadisiyah University.

## Authors' contribution statement

Both authors participated in the conception, design, acquisition of data, analysis, interpretation, drafting of the MS, revision, and proofreading.

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# امتزاز صبغة النيلي كارمين على بولي الشيتوزان المطعم (ميثاكريلات الميثيل)

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## الخلاصة

تناولت هذه الدراسة امتزاز الصبغة القرمزية النيلية (مادة كيميائية تعتبر ملوثة في المياه) على المركب النانوي الشيتوزان المطعم ببوليمر ميثاكريلات الميثيل (Ch-g-PMMA). تم العثور على قيم الامتصاص للمحاليل عند ظروف مختلفة من التركيز ودرجة الحرارة والوزن والحموضة. تمت دراسة عملية الامتزاز لاختيار الوزن الافضل للمركب من (0.01-0.07). بينت أن أكبر كمية من الصبغة الممتزة على سطح المتراكب الثلاثي كانت عند (pH=4). كما تم عرض نتائج تأثير القوة الأيونية على عملية امتصاص الأملاح (كلوريد الصوديوم، كربونات الكالسيوم). لقد وجد أن $CaCO_3$ لديه قابلية ذوبان أكبر لأنه يؤثر على كمية المادة الممتزة مقارنة بملح NaCl. كما أظهرت النتائج أن دراسة حركية الامتزاز هي من الدرجة الثانية الزائفة. تم استخدام ايزوثرم الامتزاز فروندليتش ولانجموير، وأظهرت النتائج أن الصبغة مطبقة على ايزوثرم فروندلش. كما أظهرت النتائج الحركية أن امتزاز الأصباغ يتبع حركية الدرجة الثانية الزائفة. وقد وجد أن التفاعل عبارة عن إطلاق حراري لمحلول الصبغة من خلال القيمة السالبة لدالة الإنثالبي $\Delta H$ وأن عملية الامتزاز تتم آلياً لإزالة الصبغة من خلال القيمة السالبة للطاقة الحرة $\Delta G$ والعشوائية المنخفضة للصبغة. يزيد محلول الصبغة القرمزي النيلي من القيمة السالبة لوظيفة الإنتروبيا عندما تتفاعل المادة المازة الصلبة مع المادة المازة السائلة (الصبغة) على سطح المادة المازة.

**الكلمات المفتاحية :** الامتزاز ، قذائف السلطعون، الكيتين، الشيتوزان، القرمزي النيلي.