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RESEARCH PAPER

The Study of Adsorption Efficiency on the Red Blood Cells Membrane Coated Polyethylenimine Nanocomposite

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ABSTRACT

This thesis is concerned with preparing a nanocomposite surface consisting of (red blood cell membranes and polyethyleneimine and characterizing the prepared compound using different techniques. The surface was prepared in several steps. Red blood cell membranes were extracted from human blood through the main blood bank and collected in a Petri dish. The prepared polymers were also added in a ratio of 1:3 to each of the red blood cell membranes and polymers. Polymers are considered solid materials at a temperature of 50 C. Then the compositional, chemical and surface properties of the nanoparticles of the prepared surface were characterized and studied using techniques (FT-IR, XRD and SEM) from its aqueous solutions in several ways. The results indicated that the adsorption process was S-type according to Giles classification and the equilibrium time was 70 min for CV, on CP. Similarly, the analyses showed that the measurements of adsorption for the one dye decreased with increasing temperature at equilibrium, which means that the adsorption was exothermic. Langmuir and Freundlich isotherms were used, and the results showed that the (model Freundlich isotherm) is fit with the experimental data, as it gives correlation coefficients (R2) greater than Langmuir's correlation coefficients.

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INTRODUCTION

Adsorption is a process that takes place on the surface of a substance and is made up of two components: [1] the material that accumulates on the interface is referred to as the adsorbate and [2] the solid on which adsorption occurs is referred to as the adsorbent [1]. As a consequence of this, adsorption entails bringing an adsorbent into touch with a fluid that already contains contaminants [2].

According to [3], C.W. Scheele conducted the first quantitative investigation in 1773, which was published, and he used coal and clay to absorb gases. Desorption is the process that occurs in the opposite direction of adsorption. It entails removing the adsorbent material from the adsorption surface, which in turn needs the system to absorb the energy that was produced during the process. Adsorption is what happens, and it is accompanied by a decrease in entropy (ΔS) because the molecules that undergo adsorption become restricted due to their attachment to the adsorption surface and, as a result, lose some of their temperatures in comparison to the state in which they were before adsorption, Adsorption is typically accompanied by a change in the

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surface's free energy, which is denoted by the symbol ΔG. Adsorption is also accompanied by a change According to the following connection, a simultaneous reduction in free energy and entropy energy results in a reduction in enthalpy.

According to [4], it has been shown to outperform alternative mechanization of wastewater treatment in terms of its simplicity of design, starting cost, ease of operation, and insensitivity to dangerous compounds. The forces that govern adsorption might be either chemical or physical. Adsorption, as a consequence, may be divided into two primary categories, namely, physical adsorption and chemical adsorption.

Polyethylene mines are aliphatic polymers with a 1:2:1 ratio of primary, secondary, and tertiary amino groups. They are fundamental and positively charged. Thus, amino nitrogen that is capable of protonation makes up every third atom in the polymeric backbone. PEIs are also very soluble in water because the polymer comprises repeating units of ethylamine. PEIs have molecular weights ranging from 700 Da to 1000 kDa and can be found in both linear and branched forms [5].

PEI has long been utilized in non-pharmaceutical activities such as the production of paper, shampoo, and water purification. Additionally, it has been observed that PEI is reasonably safe for both human and animal internal use. PEI is frequently used to help in the purification of soluble proteins by flocculating cellular impurities, lipids, nucleic acids, and debris from cellular homogenates. PEI was also employed in the field of enzymatic reactions in bioprocesses, where it was used as a soluble carrier of enzymes, an immobilizing agent for biocatalysts, or to produce macrocyclic metal complexes that mimicked metalloenzymes [6].

RBC is one of the most often utilised bioactive drug carriers since it is naturally biocompatible, biodegradable, and non-immunogenic. Red blood cells (RBCs) are one of the most popular bioactive medication transporters, thus this makes sense. Coating red blood cells (RBCs) with a unique biomarker of CD47 confers a stealth effect on the carriers, which is helpful for their immune evasion and blood circulation. The RBC membrane coating provides the carriers with stealth effect via a particular biomarker of CD47, and the natural surface of the RBC carriers may shield cargos from inactivation [7].

Produced a kind of RBC-platelet hybrid membrane-coated nanoparticles ([RBC-P] NPs) by producing a biological covering by fusing the cell membranes of RBCs and platelets. Red blood cell (RBC) and platelet (PLT) membrane fusion were used to accomplish this. These [RBC-P] NPs, as reported by [8], combined the roles of the two cell membranes and showed impressively long blood retention. Especially for synthetic gene delivery methods that can pass undetected through RBC membranes. Significant progress has been achieved in therapeutic medication delivery using natural RBC membranes coated with synthetic NPs.

In addition, it has been shown that the ZNF580 plasmid is capable of promoting the proliferation and migratory capabilities of EC. Recently, a group has devised and constructed a variety of carriers of the polymeric genes that depend on polyethylenimine (PEI), to effectively deliver the ZNF580 gene into ECs [9].

A dye is a natural or artificial coloring substance that can be soluble or insoluble. It is used from a fine spreading solution and can occasionally be used in conjunction with a mordant to give material its color by staining or absorbing it. The scale and growth of the dye business are closely linked to the textile industries. The estimated amount of textiles produced worldwide in 1990 was 35 x 106 tons [10].

The two most important textile fibers are polyester and cotton, which is the most widely, used type. Consequently, dye firms concentrate their efforts on developing dyes for these two types of textiles. The production of dyes worldwide was estimated to be 1 x 106 tons in 1990. This means that the proportion is slightly smaller than for textile fibers because a little dye goes a long way. For instance, one ton of dye is enough to color forty-two thousand outfits [11].

Crystal violet (CV) is a widely recognized dye that finds application in many fields, including biology staining, dermatology, veterinary medicine, and poultry feed additives that prevent the growth of intestinal parasites, mildew, and fungus. It is also widely used in paper printing and textile dying. It is a mitotic toxin and mutagenic. And also, a range of treatment techniques, including biological processes, chemical oxidation, photodegradation, coagulation, flocculation, and adsorption [12].

MATERIALS AND METHODS

Prepared a stock solution for the dye (CV) by

dissolving a certain weight of the solid dyes in a quantity of distilled water, stirring to ensure full dissolution, to achieve a particular concentration. After the standard solution was diluted as needed for the experiment, diluted solutions of one color were also created. To determine the maximum wavelength (λmax) of the dye. The UV-visible absorption spectrum of the dye solution was recorded within the wavelength range of (800-400 nm). The maximum wavelength of the dye solution was determined from its highest absorbance in the UV-visible spectrum.

FT-IR spectra were measured using an FT-IR spectrometer (Shimadzu-8400S) using KBr cm-1disc and scanned at the wave number range of 4000–400 cm-1.PH Meter Is used to measure the concentration of the hydrogen ions in the aqueous phase (Hanna 211 pH Meter C-A1). Scanning electron microscopies (SEM) were done to know the nature and porosity of the prepared surface, SEM images were taken using (Fesem Tescan Mira3 France) instrument.

Preparation of Cell Membranes

10 ml of blood was taken from the blood bank directly from the donor, The blood was placed in a tube containing sodium citrate or ethylenediaminetetraacetic acid after that Plasma was separated from other blood components using a centrifugal device at a speed of 6000 rpm for 15 min, The blood was washed with phosphate buffer for ten minutes and the separation process was repeated three times, 50 microliters of RBCs solution was taken and 1 ml of sodium phosphate pH = 8 were added in a 1.5 tube. After that, these tubes were placed in ice for 30 min; we centrifuged the tubes for half an hour in a refrigerated centrifuge of 18,000 g at zero ºC. This process was repeated four times to ensure complete washing of the blood cells from other components; the tubes were collected in one 1 ml tube, Sonication this sample 10 times for 5 seconds each time. and also, centrifuged this sample for 30 minutes at room temperature at a rotation speed of 2000 g, After completing the separation process, the separated sample was placed in a petri dish and dried at 50 ºC for five days. After that, we observed the formation of a white substance.

Preparation of Polyethylenimine (PEI)

We took 0.5 g of polyethylenimine and added 20 ml of distilled water to it in a 100 ml beaker. We noticed that it dissolved well at room temperature of 25 ºC. Then we took 0.2% of the blood cell membranes and added them to a polyethyleneimine solution in which they were dissolved, these ingredients were mixed in a 100 ml beaker and placed on a hot plate at 65 C for 1h. Center at a rotational speed of 500 rpm, We took 0.03 gm. of (potassium per-sulfate) KPS and dissolved it in 5 ml of distilled water at a temperature of 25 degrees Celsius for 1 h and also, We took 0.02 g of MBA and dissolved it in 5 ml of distilled water at a temperature of 40 ºC for 15 min. after that MRA was added to the mixture after 1h of homogenization gradually. After that, KPS was added directly to the mixture, and then the mixture consisting of these mentioned materials was left for an hour on top of the hot plate with the stirrer. After that, the mixture was poured into tubes and placed in a water bath at a temperature of 65 ºC. After two hours, we observed the formation of the compound to be prepared as an adsorption surface after drying it in an incubator for a week at a temperature of 60 ºC.

The Study factors that affect the adsorption process

Effect of weight of adsorbent

To investigate how the weight of the adsorbent affects the adsorption process, one dye was used at constant volume and concentration (25, 50 ppm) and varied weights (0.02, 0.03, 0.06, 0.08, and 0.1 g) were used at 25°C. Both the pH (pH=7) and the equilibrium time (15 minutes) remain unchanged. The tubes were put in the water shaker set to 180 rpm, and the solutions were then measured using a UV-visible spectrophotometer after being filtered via microfilter paper [13].

Determination of the equilibrium time of Adsorption Systems

Find the time at which the adsorbent and adsorbate are in equilibrium. When the time factor was changed the dye concentration, weight, pH, and temperature were all constant. Using (25ml, 50ppm) for varying intervals (5, 10, 15, 20, 25 min), the weight of the adsorbent's surface was (0.1g). The dye solutions (CV) maintained their pH of 7. The tubes were put in a water-bath shaker set to 180 rpm and 25°C. The sample was taken out of the water bath after the allotted time had passed. Afterward, filter. A UV-visible spectrophotometer

was used to measure the solutions following their separation. The equilibrium time was established by tracking the change in the percentage elimination over time; 33 minutes was found to be the optimal duration [14].

Effect of Temperature

To ascertain how temperature affects the dyes' ability to bind (CV). We made a range of solutions (10-70 ppm) using the one dye. To the flasks, 0.08 g (25) was additionally added. They were agitated at three distinct temperatures (25, 35, and 45°C) for fifteen minutes at 180 revolutions per minute in a water bath shaker. The dye solutions' pH remained unchanged. The water bath shaker's regulator managed the temperature. After that, a UV-visible spectrophotometer was used to measure the solutions [15].

Effect of pH

Adsorption processes were carried out at pH values of 3, 7, and 10 to investigate how pH affects the adsorption process. Take one of the dye solutions with concentrations of (10, 20, 30, 40, and 50 ppm) and keep it at a constant volume (25 mL). The necessary amount of diluted (0.1N) sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions was added to alter the pH value. Adsorbent weight (0.08g), temperature (25°C), and contact duration (15min) are examples of constant characteristics. Subsequently, 45 conical flasks were put in the water bath shaker and rotated at 180 rpm. After that, the UV-visible spectrophotometer was used to measure the solutions [16].

RESULTS AND DISCUSSION

Characterization of the prepared Activated Soot

FTIR spectrum of activated surface (CP) The prepared surface sample was examined through infrared spectroscopy Fig. 1 shows; that the structural arrangement of the surface is explored through the components of PIE and red blood cell membranes. Therefore, the infrared spectrum gave clear bands at 3402 resulting from the vibration of a group (O-H) and (N-H) as well as the vibration of (-CH) and (-CH2) in 1917. while The band appeared from 1540 to 1660 resulting from the vibration of the (C=O) group, which goes back to the symmetry and differentiation of the COOH

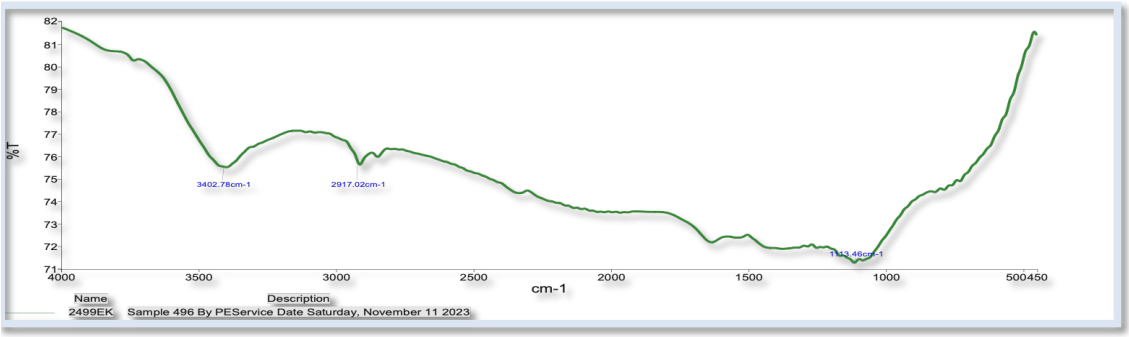

Fig. 1. The FT-IR Spectra of Polyethylenimine Nanocomposite

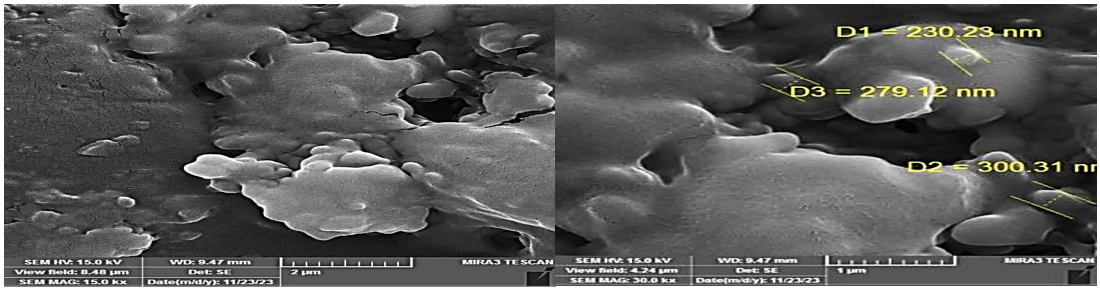

Fig. 2. SEM micrographs of Polyethylenimine Nanocomposite

group in acrylic acid, and according to the bands FT-IR [17].

After activation, the surface morphology of CP was investigated. Fig. 2 image SEM of the loaded red blood cells (PEI) showing the process of coating the red blood cells with the loaded polymers. This indicates that an interaction occurs between the molecules of the red blood cell membranes and the loaded polymers. Thus, the red blood cell membranes will have a biconcave disk shape. The following figures show microscopic images of the prepared surface at different magnification powers to determine the compatibility between the surface components (PEI) and red blood cell membranes. This is important for the adsorption process. In addition, the surface has a rough shape and the particle size ratio was from 230nm to 300nm [18].

we used to diagnose the stimulated surface, which shows the X-ray pattern (XRD) of the surface, as there is a signal at 10.32 degrees, and this indicates that the surface is sandy and non-crystalline (Fig. 3). The reason is due to the loss of Crystal due to the prepared surface containing a polymeric chain and fillings of red blood cell membranes. This is due to changes and interactions between the filling materials and the polymer [19].

Effect of equilibrium time on the Adsorption

Payment experiment to assess the connection between contact time and adsorption of one dye (CV) on the CP, studying the duration of contact necessary to reach equilibrium for the dye solution

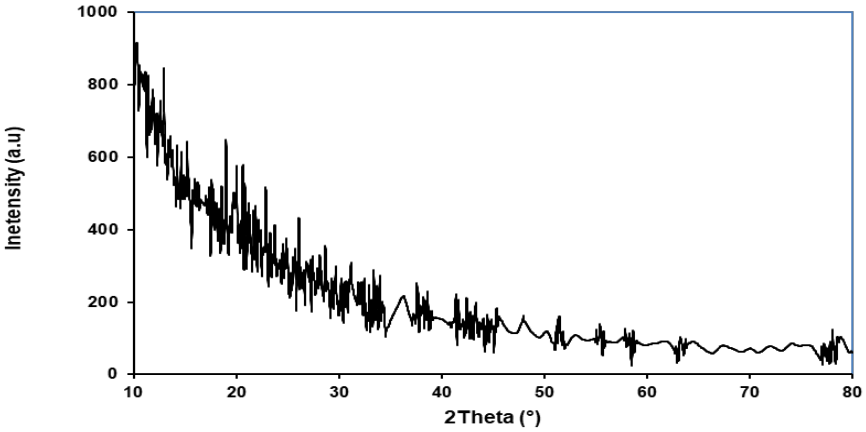

Fig. 3. The X-ray diffraction pattern for Polyethylenimine Nanocomposite

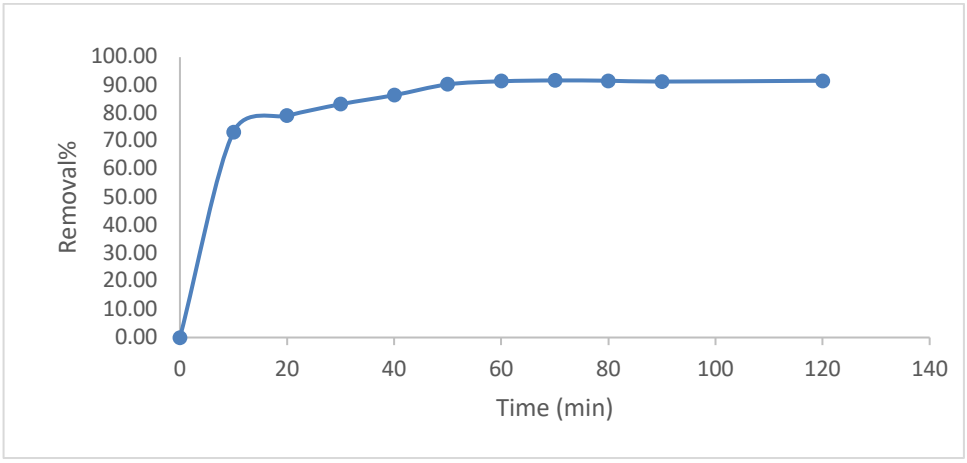

Fig. 4. The effect of contact time on the adsorption of the CV dye on to CP

on the CP surface throughout a range of times (0,10,20,30,40,50,60,70,80,90, and 120) at the same concentration (50 ppm), temperature (25 ºC), and pH of the dye solution. Fig. 4 shows the period needed to achieve balance for the three dyes are 70. All of it depends upon the surface saturation of active sites and the chemical and physical properties of the dyes. As time passes, more vacant active sites become available for the dyes to bind to, increasing the percentage of removed dyes. Eventually, all active sites are used up, resulting in a stable equilibrium state.

Effect of adsorbent mass

The suitable weight of CP is 0.2 g for the dye adsorption. Fig. 5 illustrates how the dosage of CP adsorbent affects the dye removal (CV), indicating that as the adsorbent weights of CP grow, so does the percentage of removal for dye. This could be because there were more adsorption sites available and the adsorption site had a larger surface area. The findings show the efficiency of the dye removal will rise with the increase in surface mass because the percentage of removal increases with the adsorbent weight since there are more active sites on the CP surface that are available to adsorb the dyes [20].

Effect of PH on Adsorption of AR Dye

The values of the solution pH affect both, the binding sites of the adsorbent surface and the aqueous chemistry of the dye [21]. Numerous investigations have demonstrated that an aqueous solution's pH is a crucial factor in the entire adsorption process [22]. because it has a major impact on the adsorbent's surface charge, the

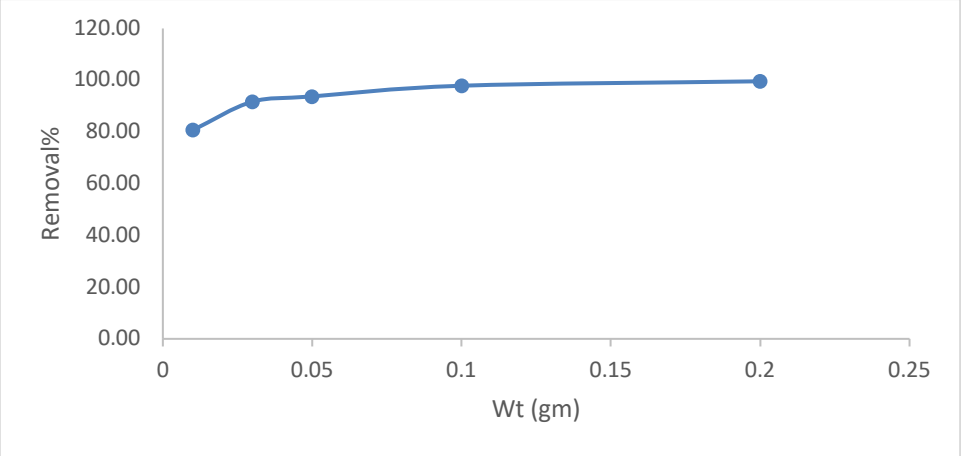

Fig. 5. The effect of weight on the adsorption of the CV dye on to CP

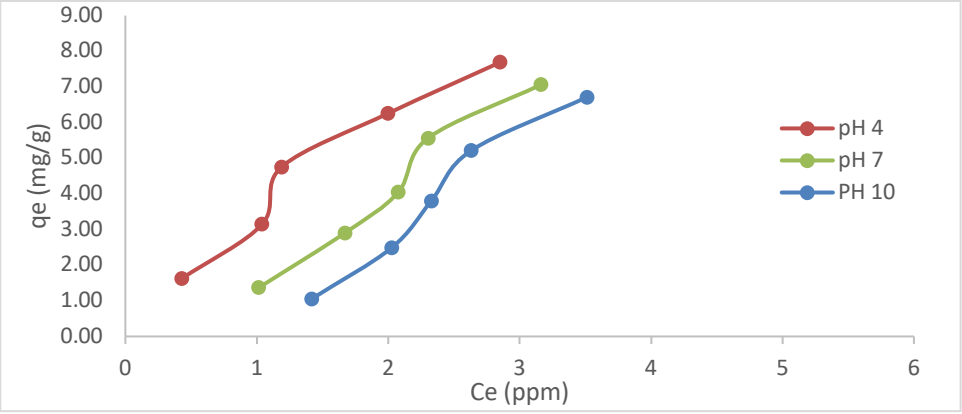

Fig. 6. The effect of Ph. on the adsorption of the CV dye on to

adsorption mechanism, the degree to which the functional groups of the adsorbate are ionized, and the adsorption capacity [23]. To examine how pH affects (CV) dye adsorption onto the surface of CP, studies were conducted at pH values of 4, 7, and 10 at 25°C while maintaining a consistent contact time of 70 minutes and a constant adsorbent weight of 0.2g. The outcomes demonstrated that the dye absorption effectiveness is influenced by pH. Where the greatest percentage of removal for

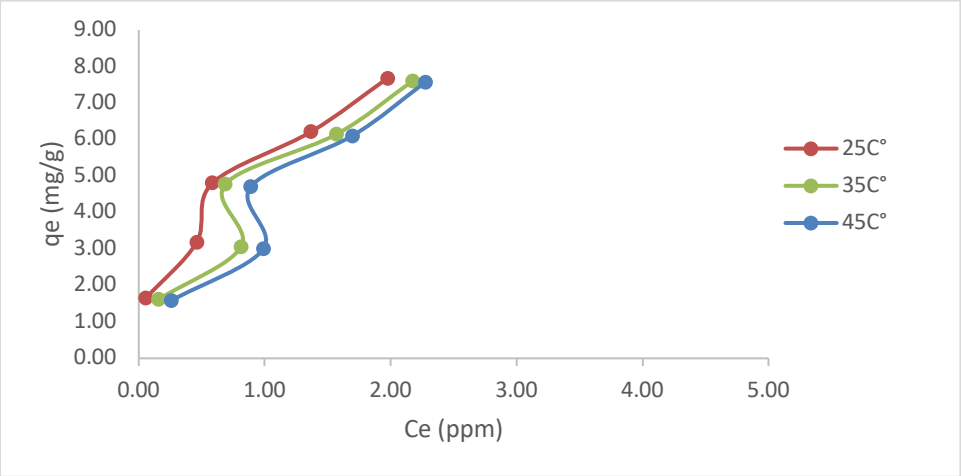

Fig. 7. The effect of temperature on the adsorption of the AR dye on to CP

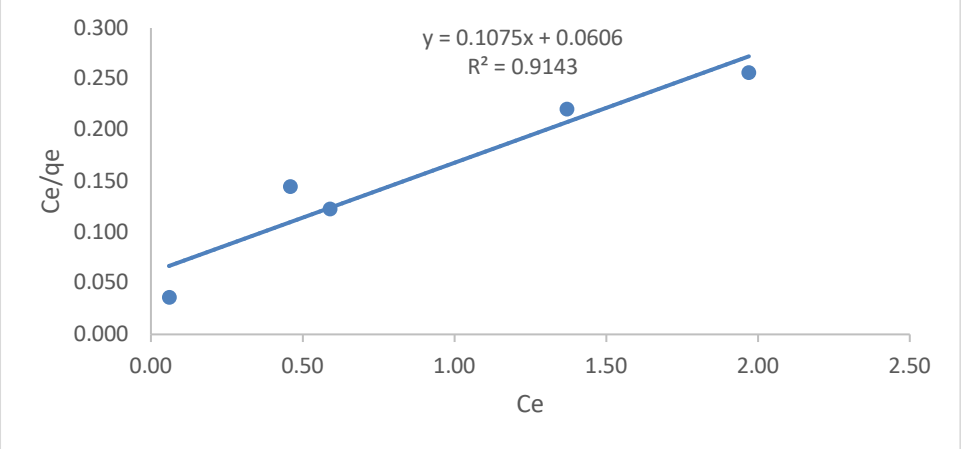

Fig. 8. The linear of Langmuir equation of CV dye for CP

Table 1. Values of the parameters of Langmuir equation for CV into CP.

Ce mg/l	qe(mg/g)	Ce/qe	q_{max}(mg/g)	K_L(L.mg^{-1})	R^2%
0.06	1.65	0.036			
0.46	3.18	0.145			
0.59	4.80	0.123			
1.37	6.21	0.221	9.302	1.774	20.9143
1.97	7.68	0.257			

CV dye was obtained at pH = 4, while the lowest percentage of removal was obtained at pH = 10, in that order: 10 > 7 > 4, as shown in Fig. 6.

Effect of temperature

Three different temperatures (25, 35, and 45) °C were used to study the impact of temperature on the adsorption of (CV) dye on CP while maintaining constants for the adsorbent weight (0.2g), pH, and contact time (70 minutes). The quantity of CV adsorbed dye (qe) was estimated using the equation:

$$qe = (c_o - c_e)\, v / m$$

Fig. 7 shows how temperature affects adsorption, showing a reduction in the amount of CV dye adsorbed as temperature increases. This indicates that the nature of the interactions between the adsorbate (CV) and the adsorbent CP is exothermic. The (qe) of the dye decreases as the temperature rises. This is because as the temperature of the solution rises, the mobility of the adsorbate molecules increases, which causes the dye molecules to tend to separate from the solid phase and enter the solution [24].

Adsorption isotherm

The Adsorption isotherm plays a vital role in optimizing the usage of adsorbents by providing insight into the nature of the solute-adsorbent interactions [25]. Adsorption occurs at concentrations (10–60 ppm) and for 15 minutes at 25°C. The general form of adsorption isotherms is given by the general form of adsorption for (CV) dye on the CP surface. Based on the Giles categorization of adsorption isotherms, the Figure was classified as S-type [26]. The S-type isotherm shows that the adsorbent tends to stack regularly and vertically on the surface [27]. Two isotherm models were used in this study: the Freundlich and Langmuir isotherm models. The values of

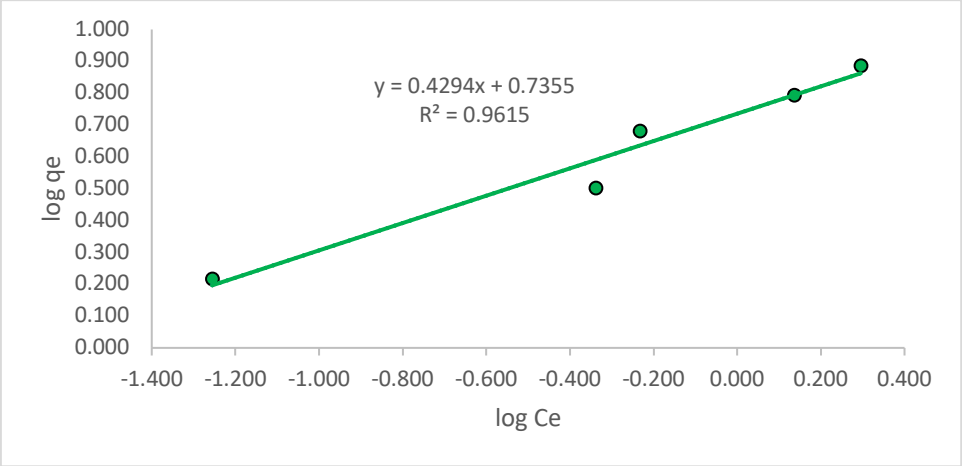

Fig. 9. The linear of Freundlich equation of three dyes for CP

Table 2. Values of the parameters of Freundlich equation for CV into CP.

Ce mg/l	qe	log Ce	log qe	n	K_f (mg/g)	R^2%
0.69	1.65	-0.164	0.217			
0.96	3.18	-0.018	0.502			
1.29	4.80	0.109	0.682	0.688	5.439	0.9615
1.58	6.21	0.198	0.793			
1.97	7.68	0.296	0.885			

Langmuir constant (b), coefficient of correlation (R2), and maximum adsorption capacity (max) have been calculated as shown in Tables 1 and 2. are analyzed according to the Freundlich equation (2), and Fig. 8 shows the linear plots of the Freundlich equation for CP surfaces at different concentrations. The values of constants (1/n and Kf) are calculated from the linear plot of log Ce against log qe. Where (Kf) is useful for knowing the amount of adsorption, (1/n) ranges between (0-1), and is a measure of the adsorption intensity or the surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. (Fig. 9)

CONCLUSION

The adsorption procedure is an effective way to remove dyes from water, The adsorbent is commercially available and inexpensive, At pH=10, the adsorption mechanism is favorable for dye removal CV; As the adsorbent dose is increased, the adsorption capacity increases; and The Freundlich isotherm is more suitable for the adsorption processes.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding this article.

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