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Kinetic and Thermodynamic Study of Malachite Green and Phenol Red Dyes removal from Wastewater using Nanocomposites

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ABSTRACT

This study investigate the ability of a PVC–CuO nanocomposite to adsorb Malachite Green (MG) and Phenol Red (PR) dyes from aqueous solutions. We initiated our batch investigation with 10 mg of the nanocomposite and 25 ppm of dye. We employed Pseud first order and Pseudo second equations to construct a model of the kinetics. The inadequate correlation values (R^2) indicate that the Pseud first order model inadequately represented the adsorption of body dye The Pseudo second equations model exhibited better fit, particularly for PR, which outperformed MG. Evaluating the thermodynamic properties at several temperatures, ranging from 20 to 40 degrees Celsius. The negative Gibbs free energy values (ΔG) indicated that adsorption occurs spontaneously, and MG exhibited greater capacity at higher temperatures. The positive elevation in entropy (ΔS = 93.21 J/K·mol for PR and 69.66 J/K·mol for MG) indicate that the interface between the solid and liquid is becoming less organized. PR has the most impact. The positive enthalpy values (ΔH) further indicated that the adsorption processes for both dyes were endothermic. The result demonstrated that the PVC–CuO nanocomposite act as an effective adsorbent for the removal of MG and PR dyes, utilizing spontaneous and endothermic thermodynamic process. Adsorption follows the Pseudo second equations kinetic model.

Keywords: Phenol Red; Malachite Green; Nanocomposites; Thermodynamics; Kinetics.

1. Introduction

The textile industry uses a variety of colors, which leads to serious problems with water pollution. Paper and textiles are two of the many sectors that frequently use more than 10,000 colors. MG, or malachite green, is a common dye. The molecule is organic and has a specific molecular structure. Among the many industries that use malachite green dye are textiles, food, medicine, and agriculture. It is highly carcinogenic for aquatic animals, including fish and mammals. With longer exposure times, higher temperatures, and higher concentrations of the toxin, the danger increases. Among other effects, it causes chromosomal fragmentation, cancer, mutagenesis, and respiratory toxicity. Thus, it is crucial to assess the various methods for its mitigation and separation before releasing it into aquatic habitats [2]. Industrial effluent is mostly colored phenol red (PR). Phenol red is a triphenylmethane dye that is soluble in water. It appears as a crimson crystal [4]. Toxicity studies demonstrate that phenol red inhibits the proliferation of renal epithelial cells [5]. Contact with the dye, whether

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direct or indirect, causes irritation to the eyes, skin, and respiratory system [6]. Phenol red dye is detrimental to muscle fibers and has been demonstrated to induce mutations [7]. Ion exchange [8], extraction [9], photocatalytic degradation [10], improved oxidation/reduction [11], membrane filtration [12], and adsorption are all modern methods for removing dyes from wastewater. However, some treatment methods may not work well for completely getting rid of dyes. Adsorption stood out among these methods since it was very effective, easy to use, cheap, not affected by poisonous substances, and released very few dangerous substances [13]. The nano adsorbent could be made of individual nanoparticles, nanocomposites (mixtures of nanoparticles or other materials with nanoparticles), or even just one nanoparticle. Particles measuring between one and one hundred nanometers in size are known as nanoparticles. Surface contacts, a high surface area to volume ratio, magnetic separation, and selectivity for pollutants are some of the unique features and efficient mechanisms possessed by nanoparticles [15]. Nano adsorbents have recently been developed and used to remove various pollutants from water [16]. Polyvinyl chloride (PVC) undergoes rigorous testing in desalination and other water treatment processes due to its exceptional chemical stability and robust physical strength. Because of their positive charge, copper oxide nanoparticles (CuO NPs) have a considerable capacity for dye adsorption and aid in dye breakdown. This structure strengthens chemical adsorption by establishing coordinating bonds with the dyes' nitrogen atoms' lone pairs of electrons [17]. In the course of this investigation, we have developed a novel, simple, affordable, and effective adsorbent that consists of a polyvinyl chloride composite of copper oxide nanosheets. The kinetics and thermodynamics of the composite, which is used to extract Phenol Red and Malachite Green from aqueous solutions, were examined.

2. Experimental

2.1. Thermodynamic study:

Batch tests were done to see how well PVC-CuO nanocomposite could adsorb PR and MG dyes. In most cases, 0.01 g of PVC-CuO adsorbent was put into 25 mL of dye solutions at a rate of 100 rpm for 24 hours. After the equilibration period, the samples were separated by magnets and then examined with UV spectroscopy. We figured out how much dye was deposited at equilibrium by:

$$qe(mg\backslash g) = C_0\text{-}C_e \frac{V}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Twenty to forty degrees Celsius was used for the thermodynamic experiments. In an Erlenmeyer flask, 10 mg of PVC-CuO nanocomposite was combined with 25 mL of 25 mg/L PR and 25 mL of 25 mg/L MG solutions. The combination was then heated for 60 minutes at 293, 298, 303, 308, and 313 K in order to investigate desorption. It took 60 minutes to get the dye solutions out of the PVC-CuO nanocomposite. Using UV spectroscopy, the concentrations of the solution phase dyes were measured during the equilibration period. Separation of the solutions followed.

2.2. Kinetic study:

To evaluate the kinetics of PR and MG dye adsorption over time, a series of conical flasks containing 10 mg of adsorbent were combined with 25 mL of dye solution (25 mg/L concentration) and allowed to stir at room temperature for durations ranging from 5 to 60 minutes. We employed a UV-Vis spectrophotometer to quantify the dye concentration at 627 nm (MG) and 558 nm (PR) at different intervals following the removal of the flasks from the shaker.

3. Outcomes and discourse

3.1. Thermodynamics of Adsorption:

Three thermodynamic parameters, standard entropy (ΔS◦), standard free energy (ΔG◦), and standard enthalpy (ΔH◦) can be used to characterize the adsorption process.You can use the following equation to determine the values of ΔH◦ and ΔS◦:

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$$\ln K_{eq} = \frac{\Delta S^\circ}{S} - \frac{\Delta H^\circ}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Here, R (8.314 J/mol K) signifies the universal gas constant, whereas T (K) indicates the absolute temperature of the solution. The values of ΔH◦ and ΔS◦ can be determined from the slope and intercept of the Van 't Hoff plot of ln Keq vs 1/T [fig. 1 (a) & (b)]. By employing the following equation, ΔG◦ can be determined:

$$\Delta G^\circ = -RT \ln K_{eq} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The ΔG° values for MG were –1.46, –1.80, –2.15, and –2.85 kJ mol−1 at 293, 298, 303, 308, and 313 K, respectively (Table 1), whereas for PR, the values were –2.25, –1.71, –1.18, –0.64, and –0.11 kJ mol−1 at the same temperatures (Table 2).

Table 1: characteristics related to thermodynamics for MG dye adsorption.

T(K)	K	ΔS˙ (J\K.mole)	ΔH˙ (KJ\Mole)	ΔG˙ (KJ\Mole)
293	0.524	69.66	18.949	-1.46
298	0.832			-1.80
303	0.907			-2.15
308	1.128			-2.50
313	1.252			-2.85

The values of ΔH° and ΔS° for MG were 18.949 kJ mol^{-1} and 69.66 J mol^{-1} K^{-1}, respectively. As the temperature rises from 293 to 313 K, ΔG° goes down, which means that MG adsorption on PVC-CuO is better at higher temperatures [18]. ΔG° values that are negative indicate that the adsorption process is possible at ambient temperature. The adsorption process is endothermic, as evidenced by the positive value of H°. The elevated randomization at the solid–solution interface during the adsorption process is the reason for the positive S° value for MG adsorption on PVC-CuO [19]. According to [17], the adsorbent material's affinity for MG is indicated by its positive S° value.

Table 2: The adsorption of PR dye depends on thermodynamic factors.

T(K)	K	ΔS˙ (J\K.mole)	ΔH˙ (KJ\Mole)	ΔG˙ (KJ\Mole)
293	0.896	93.21	25.06	-2.25
298	1.220			-1.71
303	1.316			-1.18
308	1.46			-0.64
313	1.98			-0.11

The possibilities of the process and the inherent spontaneity of adsorption are shown by the negative values of ΔG° at different temperatures. Phenol red adsorption onto PVC-CuO was endothermic, as shown by the positive ΔH° values. Also, the fact that the phenol red adsorption process had a larger positive ΔS° suggests that entropy, rather than enthalpy, played a larger role in facilitating the adsorption process, as the level of randomness at the modified adsorbent-solution interface rose during adsorption [20].

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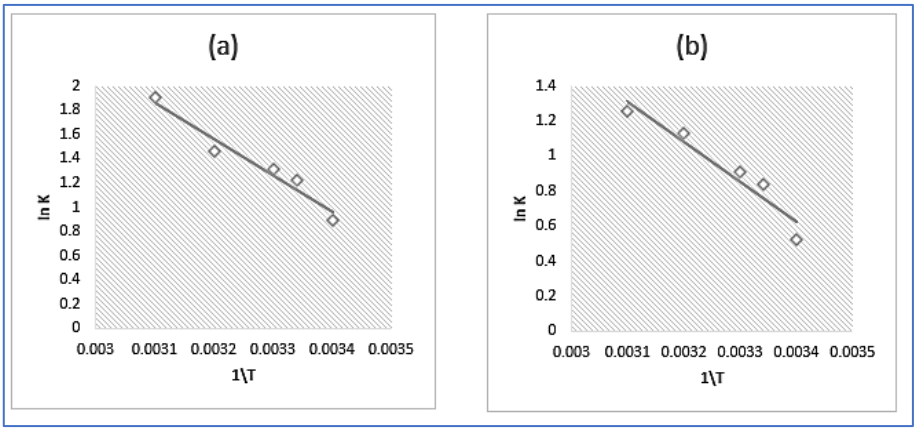


Fig. 1: (**a)** Thermodynamic analysis of phenol red (PR), and (**b)** of Malachite Green MG

3.2. Adsorption Kinetics

In the present investigation, the sorption data were analyzed by employing the two primary kinetic models, which are the pseudo first-order model and the pseudo second-order model, as demonstrated by equations (4) and (5). In the equations that are presented below, the terms qt and qe represent the amounts of dye that were adsorbed, t represents the time at which the adsorption occurred, k1 represents the acceleration constant of Pseud first order kinetics, and k2 represents the rate constant of Pseudo second equations kinetics. The parameters were obtained by fitting the experimental data to the equations in order to obtain them.

$$\frac{dqt}{dt} = k_1(qe\text{-}qt) \quad \ldots\ldots\ldots\ldots\ldots (4)$$

$$\frac{t}{qt} = \frac{1}{k2qt} + \frac{t}{qe} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

By using kinetic model of pseudo first order and pseudo second order, we will be able to verify the experimental findings on the adherence of PR and MG dyes to PVC-CuO material. As can be seen in Figures 2(a) and (b), we were able to determine the kinetic coefficients by utilizing these two models simultaneously. When compared to the pseudo-first order and pseudo-second order**,** the correlation coefficient for the malachite green dye was found to be higher, indicating that the experimental findings were consistent with the Pseudo second equations model.

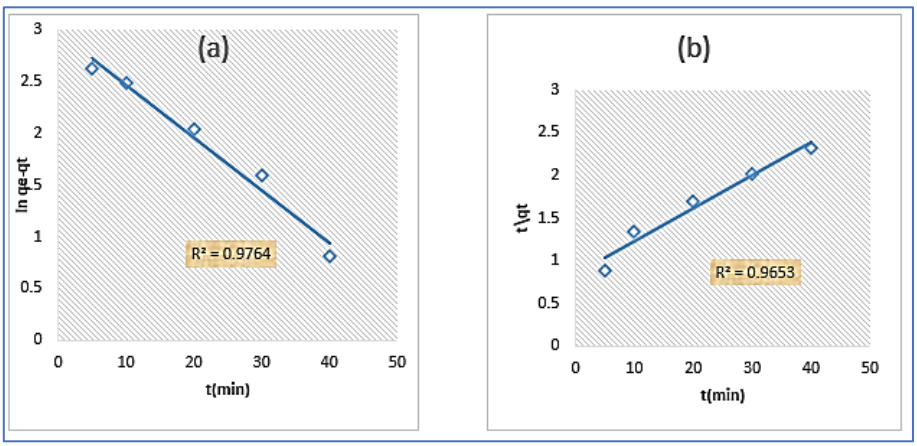


Fig. 2: (a) Pseud first order & (b) Pseudo second equations adsorption kinetic of malachite green dye.

on the subject of phenol red According to the results of fitting the experimental data to pseudo first-order kinetics, the R2 value is relatively low (figure 2). There is a substantial disparity between the experimental

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result and the estimated value of qe. Regarding the Pseudo second equations kinetics equation, the R2 value was getting closer and closer to 1.

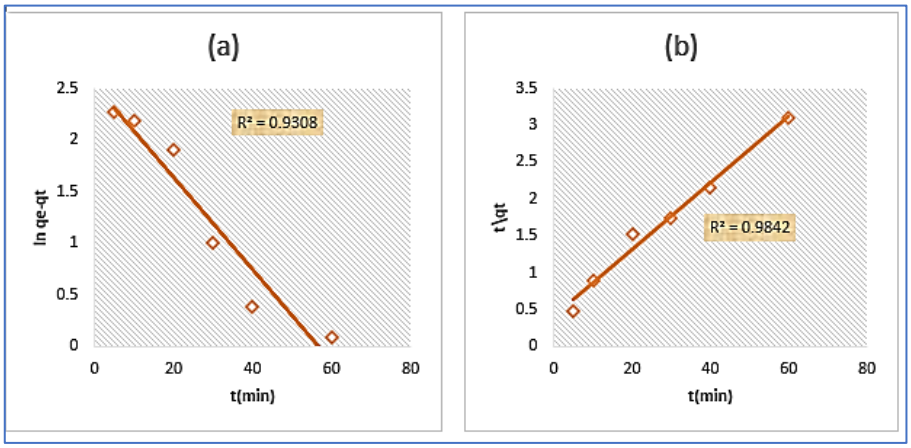


Fig. 3: (a) Pseud first order & (b) Pseudo second equations adsorption kinetic of Phenol red dye

4. Conclusions

In this study, the rapid elimination and rapid adsorption of the hazardous malachite green dye and phenol red onto the adsorbent PVC-CuO that was manufactured from aqueous solution were comprehensively evaluated and clarified. The batch adsorption tests were carried out in order to evaluate the thermodynamic analysis, which revealed that the adsorption process was both endothermic and spontaneous. It was possible to successfully model the kinetic process by employing second-order kinetics for both dyes.

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