Application of Nano Bio-clay Composite in a Scaling-up Study for Wastewater Treatment

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Abstract: A scaling-up study integrating experimental and field experiments was managed to explore the most appropriate catalysis method to assist industries in getting rid of the Congo Red (CR) dye from industrial wastewater. The adsorption potential of kaolinite (K) modified by Ulva Lactuca (UL) was evaluated to eliminate CR dye from aqueous solutions. The novel kaolinite/alga nanocomposite (KUL) was synthesized following steps of the wet impregnation method and then subjected to characterization using different techniques. The newly reported KUL nanocomposite shows a significant increase in adsorption ability higher than that of K and UL. To research different experimental factors' effects, batch experiments were evaluated, and each of the kinetics/isotherms of CR adsorption were explored either. The CR removal% is clearly affected by catalyst dose, working temperature, and pH value with high percentage. The best temperature for CR adsorption onto KUL is 40°C at pH>7. CR adsorption on KUL following the first-order diffusion model, while K and UL appeared to follow two different kinetic adsorption models depending on the CR concentration. Moreover, the field tests (scaling-up experiments) revealed optimistic results with 91% efficiency for KUL nano-adsorbents in eliminating mixed dyes from industrial wastewater, which means the foundation of novel environmentally benign nano-adsorbents to help in industrial wastewater recycling.

Keywords: kaolinite (K); Ulva Lactuca (UL) alga; nanocomposite; industrial wastewater; adsorption; dyes removal.

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1. Introduction

Nobody can deny the importance of water as an essential source for the subsistence of life on the earth. While industrialization and invention improved humanity's lifestyle, they were also the main reason for the pollution of clean water supplies [1-3]. Not only are heavy metal ions, dye molecules, pharmaceutical molecules, surfactant molecules, pesticides, personal hygiene products, and some other substances considered everyday sources of pollution of pure
and minimal water supplies, but they also harm all living species [4-8]. Synthetic dyes developed by various industrial sectors such as paper, rubber, textiles, pigments, cosmetics, plastics, and printing leave many water contaminants [7, 9, 10].

Dyes are used in a wide range of industries to color products and enhance the status of the products [11-14]. This great expansion of using dyes leads to Water Pollution in the environment [15, 16]. These dyes are known for their toxicity, stability, and non-biodegradability to a large degree [17-19], and it causes genetic mutations, cancers, fractures in different chromosomes, and toxicity in the respiratory system [20, 21]. For example, when exposed to CR dye, he will suffer from serious eye and skin irritation in a few minutes. In addition to the ingestion of Congo red can result in stomach irritation, nausea, vomiting, and diarrhea [22]. Removing dyes from solutions using either physical, chemical, or biological techniques is all reported. Filtration, reverse osmosis, flotation, electrochemical, dilution, coagulation, membrane separation process, reverse osmosis, and softening technologies have been used for this proposal [23-27].

Compared to the above techniques, adsorption is the most convenient because it is inexpensive, quick, easy to manage, and sediment levels are smaller than the other methods [26, 28-33]. In the last decades, dye elimination from wastewaters using cheap and efficient adsorbents such as biomass wastes, fly ashes, algae, mineral clays, and agricultural wastes was studied [5, 34-37]. This is ascribed to the presence of active functional groups that inspire contaminants attached to the wall of the biomaterial; these functional groups may be carboxylic, hydroxyl, amino, carbonyl, phosphate, or sulfonic [38, 39]. The importance of kaolinite as a clay mineral used in many industrial products has been reported, including its uses in eco-friendly treatments, constructions, papers, paints, refractories, ceramics, and plastics [40, 41]. This is due to its strong adsorption properties [42]. Kaolinite, with the chemical formula [Al₂Si₂O₅(OH)₄] and layer structure stacked in the order (1:1) where each separate layer reveals a sheet from Si₂O₅²⁻ tetrahedrons in addition to the alumina [Al₂(OH)₄]²⁺ octahedrons, these sheets bind together through mutual oxygen atoms keeping their lamellar structures through the hydrogen bonds [43-45]. The location of hydroxyl groups (OH) in kaolinite structure is considered the most important feature as they are involved in various chemical reactions [46, 47].

In our work, a scaling-up study including laboratory and semi-pilot scale experiments was conducted to find the most appropriate catalysis system that effectively removes waste dyes, especially Congo Red dye, from industrial wastewater. The adsorption performance of K, UL, and KUL nanocomposite was studied for Congo red dye removal from wastewater under different experimental conditions to investigate the effects of UL on K's adsorption capability. UL and K were chosen for several factors, including their natural abundance, low-cost processing, cheap reusability, and recyclability. These factors play a major economic character in applying and generalizing this low-cost technique. Batch experiments were performed, including studying the effect of starting CR concentrations, reaction times, nano adsorbent doses, reaction temperatures, and pH values on CR dye removal%. Adsorption isotherms and kinetics are also studied.
2. Materials and Methods

2.1. Raw materials, dyes, and reagents.

Kaolinite ore was supplied from El-Nassr company for mining and used as it without any further modification. UL macroalga was collected from the inter-tidal area of Egyptian Red Sea shores at a distance between Quoseir and Marsa-Alam cities. Congo Red dye was purchased from Sigma Aldritch and subjected to dissolving in distilled water. Granules of sodium hydroxide with purity 99.99% and 36% hydrochloric acid were supported by Sigma Aldrich and used for pH adjustment.

2.2. Preparation of kaolinite/alga (KUL) nanocomposite.

The kaolinite/alga nano-composite (KUL) was synthesized through a wet impregnation technique [48, 49]. Kaolinite/alga nanocomposite was prepared by the following steps: in the first step, 1gm of kaolinite + 1 gm of algae were mixed with 20 ml of deionized (DI) water then magnetically stirred at 500 rpm for 60 min then in ultrasonic for 60 min and repeated for 3 times after that, it the resultant kaolinite/alga nanocomposite was subjected to filtration, wash using DI water for many periods, and finally dried using a vacuum oven at 60 °C during 24 h. The K, UL, and KUL nano-composites were subjected to crystallographic characterization using X-ray diffractometer (XRD), surface characterization using Scanning electronic microscope (SEM), and finally active function groups using Fourier transformer- infrared (FT-IR) spectrometer, and optical spectroscopy.

2.3. Preparation of adsorbate.

The regular and well-known anionic dye, Congo red (CR), was chosen as the adsorbate in this study. CR dye is a sodium-based salt of 3,30-(1,10-biphenyl)-4,40-diyl bis (4-amino naphthalene-1-sulfonic acid) with a molecular formula: C_{32}H_{22}N_{6}Na_{2}O_{6}S_{2}. Figure S1 (Supplementary data) illustrates the structure of the CR dye. A 1000mg/l solution in stock was prepared by dissolving an adequate amount (1000mg) of CR in 1000 ml of DI water. Then, the stock was diluted by DI water to obtain the required concentrations of the working solutions. The pH of all prepared solutions was adjusted to 3, 5, 7, and 10 using either 0.1 M solution of HCl or NaOH.

2.4. Samples characterizations.

The XRD characterization was carried out by PANalytical diffractometer (Empyrean) using CuKα of wavelength λα = 0.154056nm and operating at 40 kV, 35 mA with scan step of 0.02° within the range 20 - 70°. The average crystallite size, Ds, of the prepared nanoparticles was obtained by Scherer formula, Ds = 0.94 λα/βw cosϕ; where βw and ϕ are the corrected full width at half maximum and the diffraction angle [50]. SEM micrographs were measured using Quanta FEG 250 microscope (Switzerland). FT-IR spectra were measured using a Bruker VERTEX 70 FT-IR spectrophotometer using the dry KBr pellet technique.

2.5. Adsorption studies.

Batch mode scale was selected for all CR adsorption experiments in various conditions, including initial CR concentrations (5 – 25 mg/l), contact time (up to 480 min), adsorbent
Dosage (10–50 mg), pH (3–10), and temperature (25–90°C) with shaking during the time. A series of four adsorption experiments were implemented on K, UL, and KUL adsorbents at diverse adsorption circumstances; these experiments included initial dye concentration, the temperature of adsorption, adsorbents dose, and initial pH of the solution as displayed in Table S1 (Supplementary data). The experiment time was set at 480 minutes with 25 ml solution volumes in all experiments. The variation in the CR concentration was elucidated from the absorption peak measured by UV/Vis spectrophotometer.

The reusability tests of both K, UL, and KUL adsorbents were examined 5 times using 0.02 g of all adsorbents, 25 ml of 10 mg/L initial concentration of CR for 480 minutes contact time at 25 °C and pH 7. K, UL, and KUL adsorbents were collected from the solution after each run, then cleaned from dye residues by distilled water and set for the next run.

The quantity of CR uptake by the synthesized nanocomposite at equilibrium ($q_e$(mg/g)) and time t ($q_t$) and CR dye removal% have been obtained utilizing equations 1 and 2, respectively [7, 51]:

$$q_i = \left( C_o - C_i \right) \frac{V}{m}; \ i = e, t \quad (1)$$

$$CR \ dye \ removal \% = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

$C_o$, $C_i$, and $C_e$ are the concentrations of CR in mg/l at the start, after time t, and at equilibrium e, respectively. V is the CR volume in mL, and m is the K, UL, and KUL mass in mg.

2.6. Adsorption isotherms, kinetics, and mechanisms.

Langmuir, Freundlich, and Tempkin isotherms have been applied to explain the reaction isotherm of the fabricated K, UL, and KUL nanocomposites for the tested CR [52-55].

The degree of favorability of the Langmuir isotherm for the equilibrium data could be predicted from the value of the dimensionless separation factor ($R_L$) based on equation 3 [56].

$$R_L = \frac{1}{1+K_L C_{max}} \quad (3)$$

Where $C_{max}$ represents the maximum initial CR concentration.

Different adsorption mechanisms and kinetics models such as intra-particle diffusion, pseudo-first-order, pseudo-second-order, and simple Elovich kinetic model are used for identifying the adsorption mechanisms and kinetics models that best match with the adsorption of CR onto K, UL, and KUL adsorbents [4-6, 57-60]. All linear isotherms and kinetics equations and their parameters are explained in supplementary data.

2.7. Statistical analyses.

All adsorption results were measured in triplicates, and the average values were presented. The values of regression coefficients($R^2$) for the different kinetic and isotherm models were obtained using the statistical functions of OriginPro 2016.

2.8. Field experiments.

The newly synthesized catalysis system was tested as an effective eco-friendly catalyst that could be applied on a large scale to remove industrial waste dye from industrial wastewater. For this purpose, wastewater containing waste dye was supported by clothes dying plants in
Beni-Suef city. The wastewater containing waste dye was used as it is without any further treatment or dilution. The appropriate catalysis system was selected depending on our adjusted computational and experimental results.

3. Results and Discussion

3.1. Adsorbent characterizations.

3.1.1. SEM characterization.

Figure 1 illustrated SEM images of K, UL, and KUL adsorbents. Figure 1A shows agglomerated rounded regular shape particles, rough surfaces, different particle sizes, and porous cavities on the surface for kaolinite. The SEM image of UL, Figure 1B, shows that UL exhibits a less porous surface, consequently affecting the surface area for UL, which affects its adsorption capacity. When kaolinite is treated with algae UL, the SEM image of the nanocomposite, Figure 1C, shows that the pores in the kaolinite surface are covered with the UL particles and converted into agglomerated particles. The formation of the KUL nanocomposite could be established from the noted changes in the morphology of the nanocomposite relative to that observed for K and UL.

Figure 1. SEM micrographs of (A) K, (B) UL, and (C) KUL adsorbent.
3.1.2. FT-IR analyses.

The FT-IR charts of K, UL, and KUL adsorbent are displayed in Figure 2A. The FT-IR spectrum of K, Figure 2A (red color) illustrated a wide mode of OH groups. The modes at 3691 and 3621 cm\(^{-1}\) refer to the inner OH stretching [61-63]. The peaks at 1109 and 1023 cm\(^{-1}\) are related to Si-O vibration modes [64]. The peaks at 469, 543, and 919 cm\(^{-1}\) are related to the Si-O-Si bending, Si-O-Al, and octahedral aluminum (Al-OH) [65]. The peaks that appeared in the region from 400 to 800 cm\(^{-1}\) are related to the metal oxides [66].

From the FT-IR chart of UL algae, Figure 2A (blue color), the band at 3777 cm\(^{-1}\) characterizes an amine group (-NH) stretching, and the band at 3424 cm\(^{-1}\) characterizes of the hydroxyl function (-OH) of phenolic groups. The peak at 2928 cm\(^{-1}\) was allocated to the stretching mode of alkyl groups -CH, whereas the mode at 1618 cm\(^{-1}\) corresponded to -C=O. The band at 1429 cm\(^{-1}\) was attributed to the C-H vibration [35, 67]. The bands located around 1110, 1120, and 1140 cm\(^{-1}\) are attributed to the C-O bond or refer to the sulfate group [68]. The bands at 3300–3500 cm\(^{-1}\) and 2500–3000 cm\(^{-1}\) are referred to as amine N—H stretching and carboxylic acid O—H stretching, respectively [69].

Finally, FT-IR peaks of the newly synthesized catalyst KUL are shown in Figure 2A (green color). The characteristic peaks representing the two phases (kaolin and algae) confirm the presence of a new compound. Some peaks disappeared, especially those representing the amino group in the algae, which confirms the interlocking between algae and kaolin’s pores and surface molecules. Peak disappearance was noticed, and the peak shift happened for characteristic peaks for both kaolin and algae. Both the peak shift and peak disappearance come in line with data obtained from other characterization techniques, which confirms the formation of a new compound. Table S2, supplementary data, lists the positions of the characteristic FT-IR bands for K, UL, and KUL adsorbents.

3.1.3. XRD characterization.

The XRD charts of K, UL, and KUL are presented in Figure 2B. The main XRD peaks of kaolinite minerals were observed at 2θ of about 12.44° and 24.9° due to the crystallographic growth alongside the (001) and (002) planes [70, 71]. Additional kaolinite peaks are observed at about 19.91°, 35.06°, 36.05°, 38.50°, 39.30°, and 62.48°. The obtained d-spacing of the main kaolinite peak at 12.44° is 7.11824Å. The XRD chart of UL shows sharp peaks at 12.51°,
22.94°, 23.66°, 25.00°, and 29.3°[67, 72]. The XRD chart of KUL displays a small shift in the position of the main XRD peaks of kaolinite to shift to 12.28° and 24.71°. In addition to the appearance of another peak at 38.30°. The average calculated crystallite size using the Scherer equation was 40.3 nm, which confirms the nanoscale nature of the newly synthesized composite.

3.2. Factors influencing the adsorption process.

3.2.1. Influence of initial CR concentration.

The variations in the removal% and the amount of CR adsorbed with time using K, UL, and KUL nano adsorbents at different initial CR concentrations are shown in Figures 3 (A-C) and 3(D-F), respectively. It can be observed from these Figures that; the dye removal % and the adsorption capacity were very high throughout the primary stage of the entire adsorption process, and after that, their increasing rates are reduced to reach the equilibrium state at the end. It was also observed that; contact time has no marked effect on the adsorption process using new sorbents after reaching the equilibrium. The prompt removal rates at the early stage of the reaction are allocated to the existence of a huge surface density of uncovered active spots on the nano adsorbent's surfaces by increasing the contact period between adsorbent and adsorbate, and the hot spots are converted to fully occupied sites by CR molecules. As a result, repulsion forces are established between the adsorbed CR molecules on the surface of adsorbents and CR molecules in the bulk liquid phase [7].

The KUL nanocomposite revealed higher efficiency for Congo red adsorption at lower concentrations compared with K and UL. At 5 and 10 ppm initial dye concentration, the CR removal% was 99% and 92% for KUL, 81% and 73% for UL; and 37.7% and 28.7% for K, respectively. This trend is in line with previously reported composites with lower performance than the present [41, 73-75]. With increasing concentration to 15 ppm, the dye removal % reaches 70% for both KUL and UL, and 23.3% for K adsorbent. At relatively high concentrations, 20 and 25 ppm, the dye removal % was in the order UL >KUL >K.

The quantities of adsorbed CR are increased by raising the starting CR concentration, as shown in Figure 3(D-F). This could be attributed to the increase in the concentration gradient as the initial CR concentration increases. Therefore, an appropriate increase in the draft forces occurs to overawed the mass transfer resistance between CR adsorbates and K, UL, and KUL nano adsorbents [76]. 1.88, 2.8, 3.5, 4.4, and 5.0 (mg/g) were found to be the K’s maximum adsorption capacities, while 4.5, 7.3, 10.5, 13.18, and 15.5 (mg/g) were found to be the adsorption capacities of UL for CR dye with initial concentrations of 5, 10, 15, 20 and 25 mg/l, respectively, at pH 7 and 25°C. Whereas, the KUL maximum adsorption capacities were found to be 4.9, 9.2, 10.5, 10.58, and 8.4 (mg/g) at these starting concentrations. The results showed that the modification of K with UL is a feasible approach to enhance the CR removal performance by K at lower concentrations.

3.2.2. Influence of nanoadsorbent dosage.

To determine the adsorption cost, the influence of the nano adsorbent dose on the CR removal% was assessed for determining the optimized nano adsorbent dosage that offers the maximum performance. This is graphically depicted in Figure 4a. The adsorbent doses were varied from 0.01 to 0.05 g. It was found that 0.02 g nano adsorbent per 20 ml CR solution of 10
mg/l starting concentration was the best nano adsorbent dosage. From Figure 4a, The CR removal% for all adsorbents rises as the nano adsorbent dosage increases from 0.01 to 0.02 g. The removal% increases from 26% to 28.7% in the case of K adsorbent, while it increases from 55% to 73% in the case of UL adsorbent and increases from 80% to 92% in the case of KUL adsorbent.

For K adsorbent, the CR removal% decreases to ~ 25%, 22%, and 15%, increasing the adsorbent dose to 0.03, 0.04, and 0.05 g, respectively. For UL adsorbent, the CR removal% decreases to ~ 25%, 22%, and 15%, increasing the adsorbent dose to 0.03, 0.04, and 0.05 g, respectively.
decreases to 68, 54, and 46%, increasing the adsorbent dose to 0.03, 0.04, and 0.05 g, respectively. Also, the CR removal% decreases to 25, 22, and 15%, in the case of KUL adsorbent, by increasing the adsorbent dose to 0.03, 0.04, and 0.05 g, respectively. This finding may be ascribed to the screening effect that occurs at elevated nano adsorbent dosage due to the accumulation of the nano adsorbent particles and decreasing the distance between the nano adsorbent particles. The condensed layer at the surface of the adsorbent hid the binding sites from CR molecules. Also, K, UL, and KUL overlapping resulted in a competition between CR molecules for limited numbers of available binding sites. Aggregation or agglomeration at greater K, UL, and KUL doses also increase the CR diffusion path length, causing a decrease in adsorption % [5, 77-79].

Figure 4. Effect of (a) adsorbent weight, (b) Initial pH of the solution, (c) adsorption temperature, and (d) reusability test on the removal% of 20 ml CR solution of 10 mg/l by K, UL, and KUL.

3.2.3. Influence of pH.

Due to its influence on the dissociation/ionization of the K, UL, and KUL nano adsorbents and their impact on the absorbent surfaces, the starting pH value of the CR solution can be a crucial player in controlling the nano adsorbent performance [69]. So, the electrostatic charges on the K, UL, and KUL sorbents and the CR sorbate are greatly affected by the pH of the solution. The effect of pH on the CR removal efficiency of the adsorbent was studied between pH 3 and pH 10 as shown in Figure 4b at 10 mg/l of CR dye initial concentration and 0.02g of adsorbent dosage. The K adsorbent shows removal percentages of 16.6%, 17.0%, 28.7%, and 33% for CR solutions of pH 2, 5, 7, and 10, in that order. The UL adsorbent shows
removal percentages of 71.0%, 96.6%, 73.0%, and 96.0%, while KUL adsorbent shows removal% of 46.0%, 47.0%, 92.0%, and 94.5% at pH 2, 5, 7, and 10, respectively, at the same formerly mentioned conditions.

The CR dye removal% generally increases with increasing the pH of CR solution from pH 2 to pH 10. The lower removal% was obtained at pH 2, which may attribute to the high mobility of H⁺ ions and the nano adsorbent surface protonation. Thus, the CR removal% decreases due to the competition between H⁺ ions and CR molecules during the adsorption process [80]. But at a higher pH value, the observed elevation in the CR removal% by all adsorbents is ascribed to the decrease of H⁺ ions concentration [81]. For UL adsorbent, the high elimination% of CR at pH 5 may attribute to the creation of accumulated +ve charges on the UL surfaces due to the protonation of the polar functional groups presented on the surface of the adsorbent in acid medium. The positively charged adsorbent surface strongly attracts the CR anions [82].

3.2.4. Influence of temperature.

The effect of temperature on the CR dye uptake% onto K, UL, and KUL was followed up at various adsorption temperatures. The adsorption tests were done at 25, 40, 50, 60, 70, 80, and 90°C. The data are presented in Figure 4c. For both UL and KUL adsorbents, the CR removal% is increased from 73% to 100% and from 92% to 100%, respectively, with rising temperatures from 25°C to 40°C. This performance could be owed to the growth of the CR diffusion rates with rising temperature due to the decrease in viscosity of the solution [83]. With more temperature rise, the CR removal% remains constant at 100 % till 70°C for UL adsorbent and till 60°C for KUL adsorbent. This could be attributed to the fact that the maximum limit of CR adsorption is reached by the nano adsorbent. With more and more increases in temperature, the dye removal% drops down again, and this is owed to the collapse of adsorption force responsible for CR dye molecule adsorption on the UL and KUL surfaces [84]. This may ascribe to active site damage and adsorptive force reduction between nano adsorbents active site and CR molecule [19, 85, 86]. So, the optimum temperature for adsorption of CR is from 40 to 70°C for UL and from 40 to 60°C for KUL adsorbent.

For K adsorbent, CR elimination% increased with the elevation of the adsorption temperature, where it increased from 28.7 to 53.3% with changing temperature from 25 to 40°C. With further increase in temperature, from 40 to 70°C, the CR elimination% reduced from 53.8 to 15.0%. By increasing the temperatures from 25°C to 40°C, the CR removal% increases due to the increase in the CR diffusion rate. The decrease in the CR elimination% at elevated temperatures could be attributed to the desorption of CR molecules caused by the destruction of the adsorptive forces responsible for CR dye adsorption on the K nano adsorbent surfaces [84]. With a further increase in temperature from 70 to 90°C, the removal % increased from 15 to 36%. The best temperature for CR adsorption onto K is 40°C.

3.2.5. Reusability of adsorbents.

The K, UL, and KUL reusability for eliminating CR was performed four 4 times with the same adsorbent and the same adsorbent dosage, Figure 4d. The results revealed that; the removal strength of K, UL, and KUL adsorbents significantly changed throughout the four adsorption cycles. For K adsorbent, the recorded dye removal% was 28.7% @ 1st cycle, 12.5% @ 2nd cycle, 10% @ 3rd cycle, and ~10% @ 4th cycle. For UL adsorbent, the dye removal%
was decreased from 73% @ 1st cycle to 15% @ 4th cycle. For KUL adsorbent, a decrease in the calculated CR removal% occurs where it changes from 92% @ 1st cycle to 20% @ 4th cycle. The drop in the CR removal% could be attributed to the agglomeration of the CR dye molecules onto the K, UL, and KUL adsorbents surface. Which consequently hind adsorbent surface and pores from the dissolved CR dye molecules, and so, a drop in adsorption capacity of K, UL, and KUL adsorbents take place [87].

Table 1. Isotherm parameters for CR adsorption on K, UL, and KUL.

|                     | Langmuir isotherm |                |                |               |
|---------------------|-------------------|----------------|----------------|---------------|
| Constant            | Q_o (mg/g)        | K_L (L/mg)     | R_L            | R^2           |
| Adsorbent           |                   |                |                |               |
| K                   | 7.3313            | 0.0955         | 0.29           | 0.9549        |
| UL                  | 23.7529           | 0.1858         | 0.177          | 0.9728        |
| KUL                 | 8.5397            | 0.00183        | 0.998          | 0.9858        |

|                     | Freundlich isotherm | n       | K_F ( L/mole) | R^2           |
|---------------------|---------------------|---------|---------------|---------------|
| Constant            |                     |         |               |               |
| Adsorbent           |                     |         |               |               |
| K                   | 1.92                | 1.03    | 0.9942        |
| UL                  | 1.68                | 4.16    | 0.9978        |
| KUL                 | 9.785               | 8       | 0.5931        |

|                     | Temkin isotherm | B_J (J/mol) | K_T (L/mole) | R^2           |
|---------------------|----------------|--------------|--------------|---------------|
| Constant            |               |             |              |               |
| Adsorbent           |               |             |              |               |
| K                   | 1.635         | 1.103        | 0.9580       |
| UL                  | 4.975         | 1.132        | 0.9659       |
| KUL                 | 0.7362        | 78432        | 0.5882       |

3.3. Adsorption isotherm.

The statistical importance of the correlation coefficient ( R^2 ) for the linear fitting of q_e versus Ln(C_e), log(q_e)versus log(C_e), and C_e/q_e versus C_e was the criteria by which the data fitted to Temkin isotherm, Freundlich isotherm, and Langmuir isotherm, correspondingly.

From the linear plots, the values of Q_o, K_L, K_F, 1/n, K_T, B, and R^2 were determined from Figure 5 and recorded in Table 1. The results in Table 1 demonstrate that CR adsorption on K and UL adsorbents tracks the Freundlich isothermal model, where the R^2 value is the highest. Therefore, multilayer adsorption of CR molecules occurs at the hotspots of the nano adsorbent surfaces, where heterogeneous sites of different adsorption energies and interaction between adsorbed molecules are unequally accessible. At 25 °C, the obtained R^2 values by the Freundlich isotherms were 0.9942 and 0.9978 for K and UL adsorbents, respectively. In the adsorption process of CR on K and UL, the 1/n values for Freundlich isotherm are less than unity. This means that the adsorption process is favored, and the surface is heterogeneous with a lower interaction rate between the adsorbed CR molecules. Also, it implies that the CR adsorption mechanisms are multi-molecular and multi-anchorage adsorption [88, 89].

The modification of K with UL to form the KUL nanocomposite altered the adsorption isotherm mechanism of CR onto KUL and was found to follow the Langmuir isotherms. Therefore, the CR dye elimination occurs at the active sites of the KUL adsorbents on a single surface layer, and the adsorbed CR molecules do not interact with each other. At 25 °C, the R^2 value calculated by the Langmuir isotherms of KUL adsorbent was 0.9858. The value of R_L is < 1, which means that CR adsorption is preferred in the study case [90].
3.4. Adsorption kinetic models.

In order to study the most suitable adsorption kinetic model, the CR adsorption on K, UL, and KUL at various initial CR concentrations was addressed. The first-order, second-order, and Elovich kinetics linear graphs were represented in Figures 6 by plotting $\ln(q_e - q_t)$ versus $t$, $\frac{t}{q_t}$ versus $t$, and $q_t$ versus $\ln(t)$, respectively. The adsorption kinetics parameters $k_1$, $k_2$, $q_e$, $\beta$, and $\alpha$ of the evaluation model in addition to $R^2$ were obtained using the linear plots and depicted in Table 2.

![Figure 6](image_url)

**Figure 5.** Plots of (a) Langmuir, (b) Freundlich, and (c) Temkin adsorption isotherms for the adsorption of CR dye by 50 mg of K, UL, and KUL at 25 °C and initial pH 7.

The linear fit and regression coefficient values of all the research kinetic models in Table 2, confirm that the use of the second-order diffusion model can well handle the CR adsorption on K before the dye concentration of 10 ppm, and over this concentration, the adsorption process follows the first-order rate law, and this was also confirmed from the good
approximation between the calculated qe and experimental qe. The CR adsorption onto KUL is well handled with the first-order diffusion model, and this appears in the higher R² values and the very close values of the calculated qe and experimental qe. The CR adsorption onto UL follows two different kinetics adsorption models depending on the CR concentration where it follows the Elovich kinetics up to 10 ppm concentration, and above this concentration, it follows the first-order diffusion model.

3.5. Sorption mechanisms.

To comprehend the adsorption kinetics process and rate-controlling steps, the practical data are fitted for Weber's Intra-particle diffusion. A straight line in the qₜ versus t¹/₂ chart, Figure S2 (Supplementary data), suggests the applicability of the intra-particle diffusion model. The values of the rate constant of the intra-particle propagation model (K₃) and boundary thickness constant (I), Table 3, are obtained using the slope and intercept of the linear fitting of Figure S2, respectively. The intercept I≠0 indicates that the intra-particle diffusion model may not be the only rate control method for estimating the kinetics of the adsorption reaction [91]. The intercept in Figure S2 refers to the boundary layer effect. The larger intercept, the greater the contribution of surface adsorption in the rate control stage [91].
Catalyst KUL was prepared and used as a new aqueous solution adsorbent.

### 4. Conclusions

The optimized parameters for the newly synthesized KUL nano adsorbent were 0.02 g adsorbent mass, near room temperature, and contact time of 420 min, while the pH of the wastewater containing the waste dye remained unchanged. The presence of different wavelengths corresponding to different dyes was detected by the optical scanning of the as-received industrial wastewater using UV/Vis Perkin Elmer spectrophotometer (lambda 950). Absorbance at various wavelengths is recorded after 420 min contact time to measure the removal efficiency of dyes from industrial wastewater. At various wavelengths, the data revealed removal efficiency ranging from 85% to 94%.

Table S3 (Supplementary data) compares the optimized conditions, removal%, and adsorption capacity, qm, of our studied K, UL, and KUL nano adsorbents for CR dye removal to those previously recorded for various adsorbents in literature [34, 41, 42, 92-95]. As shown in Table S3, our optimized KUL nano adsorbent showed high performance relative to most of the previously reported K and/or UL–based adsorbents.

### 3.6. Field experiments and Comparison of Adsorption Capability of K, UL, and KUL.

From the hydrothermal treatment of kaolinite (K) and alga(UL), a novel alga/kaolinite (KUL) nanocomposite KUL was prepared and used as a new aqueous solution adsorbent for...
CR. The morphologies and structures of K, UL, and KUL have been investigated to show the agglomeration of UL nanoparticles and kaolinite nanopores to form nanocomposite crystallites of 40.3 nm size. The adsorption studies of CR dye showed 99%, 81%, and 37.7% removal% of 5ppm CR dye using KUL, UL, and K in order. The order of the performance is turned to UL > KUL > K for CR concentration ≥ 20 ppm. Also, the CR removal % is highly affected by adsorbent mass, adsorption temperature, and pH value. By increasing the K, UL, and KUL dosage from 0.01 to 0.02 g, the removal%is increased and then decreased. The best temperature for CR adsorption onto KUL is 40°C at pH > 7. The reusability test for K, UL, and KUL showed that any adsorbents were not preferred for CR removal reuse. The CR adsorption isotherms and kinetics on K, UL, and KUL indicate that the Freundlich isothermal models are monitored by K and UL adsorbents, while KUL is better suited to Langmuir isotherms. With the first-order diffusion model, CR adsorption on KUL is well controlled, while K and UL adopt two separate models of kinetic adsorption depending on the concentration of CR. Finally, field tests showed surprising results of 91% dye removal efficiency from industrial wastewater, which confirms the foundation of a modern eco-friendly catalysis device that could assist in the reuse of industrial wastewater.

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Conflicts of Interest
The authors declare no conflict of interest.

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Supplementary materials

1. Adsorption isotherms

Langmuir, Freundlich, and Tempkin isotherms have been applied to explain the reaction isotherm of the fabricated K, UL, and KUL nanocomposites for the tested CR. The three models can be represented by equations 1, 2, and 3, respectively [52-55]:

$$\frac{C_e}{q_e} = \frac{1}{K_LQ_o} + \frac{C_e}{Q_o}$$  \hspace{1cm} (1)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (2)

$$q_e = B \ln K_T + B \ln C_e$$  \hspace{1cm} (3)

Here, $Q_o$ is the maximum amount of dye removed by K, UL, and KUL adsorbents (mg/g); $K_L$, $K_F$, and $K_T$ indicate to the Langmuir constant, Freundlich constant, and Tempkin binding constant, respectively. $B(=RT/b)$ is a constant associated with the adsorbed heat, $n$ is the adsorption density, $T$ is the absolute temperature, and $R$ is the universal gas constant.

2. Adsorption kinetics and mechanism

Different adsorption mechanisms and kinetics models such as intra-particle diffusion, pseudo-first-order, pseudo-second-order, and simple Elovich kinetic model are used for identifying the adsorption mechanisms and kinetics models that best match with the adsorption of CR onto K, UL, and KUL adsorbents.

Equations 4 to 7 are used to represent the pseudo-first-order, pseudo-second-order, simple Elovich kinetic, and Intra-particle diffusion models, respectively [4-6, 57-60].

$$\ln(q_e - q_t) = k_1 t$$  \hspace{1cm} (4)

$$\frac{t}{q_t} = \frac{1}{k_2q_e} + \frac{t}{q_0}$$  \hspace{1cm} (5)

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t$$  \hspace{1cm} (6)

$$q_t = k_3 t^\frac{1}{2} + I$$  \hspace{1cm} (7)

Where $k_1$, $k_2$, and $k_3$ represent rate constants of the pseudo-first-order, pseudo-second-order, and Intra-particle propagation models. $I$ refers to a constant related to the boundary thickness. $\alpha$ implies the adsorption rate at time = 0 min(mg/min) and $\beta$ represents the extent of surface coverage (g/mg).

Table S1. Conditions of experimental adsorption tests.

| Series | Dye concentration (ppm) | K, UL and KUL dose (g) | Temperature (°C) | pH value |
|--------|--------------------------|------------------------|------------------|----------|
| 1      | 5, 10, 15, 20 and 25     | 0.02                   | 25               | 7        |
| 2      | 10                       | 0.01, 0.02, 0.03, 0.04 and 0.05 | 25               | 7        |
| 3      | 10                       | 0.02                   | 40, 50, 60,70, 80 and 90 | 7        |
| 4      | 10                       | 0.02                   | 25               | 3, 4, 5, 7, 8 and 10 |
Table S2. Characteristic wavenumbers of FTIR bands for K, UL and KUL adsorbents.

| Adsorbent | Kaolin (K) cm⁻¹ | Algae (UL) cm⁻¹ | KUL cm⁻¹ |
|-----------|-----------------|-----------------|----------|
| 3276.736  | 3916.734        |                 | 3433.487 |
| 2923.320  | 3424.703        | 2928.542        | 2930.414 |
| 2378.512  | 2377.646        | 2377.646        |          |
| 2860.117  |                 |                 |          |
| 2505.973  | 2273.621        |                 | 1863.178 |
| 1480.394  |                 |                 | 1643.076 |
| 977.041   |                 |                 |          |
| 860.878   |                 |                 | 817.475  |
| 712.458   |                 |                 |          |
| 690.145   |                 |                 | 684.273  |
| 581.607   |                 |                 | 461.793  |

Table S3. Comparison of the optimized conditions, removal%, and adsorption capacity of different CR adsorbents relative to our K, UL, and KUL nanoadsorbents.

| Adsorbent                              | Conditions                                                                 | Removal % | Adsorption capacity (mg/g) | Reference |
|----------------------------------------|----------------------------------------------------------------------------|-----------|---------------------------|-----------|
| Natural kaolinite                      | Time: 120 min Catalyst dose: 0.1 g/150mL pH: 7.0 Temp: RT                | -         | -                         | [34]      |
| phosphate-modified kaolinite           | Time: 60 min Catalyst dose: 0.75 g solution pH increased from 3 to 11    | 15.0%     | 0.16 to 0.35 mg/g.        | [41]      |
| sulfate-modified kaolinite             | Catalyst dose: 5 g/L Dye Concentration: 150 mg/L pH: 7.5 Temp: 30°C      | 100% CR removal using 50 g/L | 64.24%     | 5.94       | [92]      |
| organic surfactant – modified kaolinite| pH 6.9 CR concentration= 100 mg/L Catylast dose: 0.1 g/10mL              | 98.16%    | 24.46 mg/g                |           |           |           |
| sodium acetate- modified kaolinite     | pH6.9 time : 40 min catalyst dose: 10 g/ L                               | 85% to 50%@ 10 to 90 mg/L CR concentration | 5.05      |           |           |           |
| Acid-activated red mud                 | Contact time 90 min Catalyst dose: 5 g/L Dye Concentration: 20 mg/L pH: 7.0 Temp: RT | 0.024 to 0.033 mmol g⁻¹ |           |           |           |           |
| Natural kaolinite H₂SO₄-treated kaolinite and montmorillonite | Time: 120 min pH 6.9 CR concentration= 100 mg/L Catylast dose: 0.1 g/10mL | 8%        | 5.7 mg/g                 | [95]      |           |           |           |

https://biointerfaceresearch.com/
| Adsorbent | Conditions | Removal % | Adsorption capacity (mg/g) | Reference |
|-----------|------------|-----------|---------------------------|-----------|
| CR conc.= 150 ppm adsorbent dosage 0.6 g/L Temper: RT | 99% | 10.58 | This work |
| KUL adsorbent dosage = 0.02g | 81% | 15.5 | |
| UL pH 7, Temperature: 25 °C | 37.7% | 5 | |
| K | | | |

**Figure S1.** Structure of Congo red.

**Figure S2.** Intra-particle sorption kinetics of CR dye at 25 °C and pH 7 by 20 mg of (A) K, (B)UL, and (C) KUL.