Adsorption of Congo Red on Pb doped \( \text{Fe}_x\text{O}_y \): experimental study and theoretical modeling via double-layer statistical physics models

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ABSTRACT

Size-controlled \( \text{Pb}_{0.06}\text{Fe}_{0.7}\text{O}_3 \) nanoparticles (Pb-FeONPs) were fabricated by the thermal co-precipitation method and characterized by FE-SEM, EDX, XRD, and IR techniques. The SEM and XRD images showed the average size distribution and average crystallite size of 19.21 nm and 4.9 nm, respectively. The kinetic model of Congo Red (CR) adsorption onto Pb-FeONPs was verified and found to be a pseudo-second-order reaction. The Langmuir plot was better fitted \((R^2 = 0.990)\) than other isotherm models with a \(Q_{\text{max}} \) (mg/g) of 500 for Congo Red (CR) dye in 40 min. The double-layer statistical physics model based on two energies was used to calculate the significant parameters. The \( n \) (stoichiometric coefficient) values obtained from the statistical physics double-layer model were found to be 0.599, 0.593, and 0.565, which are less than 1, indicating the multi-docking process. The regeneration of Pb-FeONPs was used for up to 5 cycles effectively, making the material highly economical. The Pb-FeONPs were fruitfully applied for the removal of CR dye from wastewater on a laboratory and industrial scale.

Key words | double-layer model, isotherm modeling, Pb-FeONPs, statistical physics model

HIGHLIGHTS

- Pb-FeONPs of 19.21 nm size material were synthesized.
- Pb-FeONPs utilized as an efficient adsorbent for removal of Congo Red dye from water samples.
- High specific surface area of Pb-FeONPs indicated favorable adsorption behavior for dyes.
- The Pb-FeONPs was successfully applied for the removal of CR dye from laboratory and industrial waste.

GRAPHICAL ABSTRACT

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INTRODUCTION

In recent years, the world has been moving toward huge industrialization. The impact of industrial growth is seen in the form of industrial effluent and solid waste, which contains numerous toxic contaminants (Dehghanian et al. 2016). Several industries including textiles, pulp, paper, and plastic produce a massive quantity of dye effluents (Zhou et al. 2015). The treatment of industrial effluents for protecting and making a clean and healthy environment is the prime target of the scientific and intellectual communities (Singh et al. 2015; Shu et al. 2015). The adsorption process is a simple and widely used technique for the treatment of wastewater and has a high potential for the reuse of adsorbent (Arshadi et al. 2015). Azo dye (CR) is being utilized in textile, leather, and foodstuffs. However, it is toxic to the aquatic ecosystem and reported as a potential carcinogen for humans and animals (El-Gamal et al. 2015). Albadarin et al. reported activated lignin-chitosan pellets for the adsorption of methylene blue (MB) dye (Albadarin et al. 2017; Khan et al. 2017). Naushad et al. successfully developed modified activated carbon 2-amino-5-guanidinopentanoic acid for the efficient adsorptive removal of MB from wastewater (Naushad et al. 2019a). Ahmed et al. reported magnesium/iron (Mg/Fe)-layered double hydroxides (LDHs) nanoparticles for the removal of CR dye (Naushad et al. 2019b; Ahmed et al. 2020). Nano-sized materials have a wide surface area, offer efficient, fast adsorption, and are readily spread in an aqueous solution. Nanoparticles with a high number of active vacant sites can be used for the adsorption of toxic materials (Sohrabi et al. 2014; Jethave et al. 2019a). In this study, Pb-FeONPs were synthesized by a thermal co-precipitation process and their application was explored towards the removal of CR dye, and its determination by UV–Visible spectrometer at 498 nm. The kinetic order, ΔG°, ΔH°, and ΔS° were determined for CR adsorption on the surface of Pb-FeONPs. The isotherm model revealed a possible adsorption mechanism. The double-layer model is ideally tailored to analyze the desorption process. The Pb-FeONPs was regenerated up to 5 cycles and successfully used for the laboratory and industrial scale removal of CR dye from wastewater. The findings from this study are very encouraging due to the effective adsorption and reusability of the adsorbent.

MATERIALS AND METHODS

Reagents, instrumentation, and experimental setup

Both chemicals and reagents used in the synthesis and experiments were purchased from Merck, Darmstadt, Germany, and are of analytical reagent grade. Metrohm 713 pH-meter, Bruker S-4800, PM, EDX, X-ray diffractometer Bruker D8-advance, FT-IR Bruker, and Shimadzu UV-1800 spectrophotometer instruments were used for the characterization and execution of experiments. The pH studies were performed in the range pH 3–12.0 and with a mechanical shaker time of 0 to 90 min. The effect of adsorbent dosages was investigated by varying the dose from 50 to 200 mg. The detailed experimental for adsorption of CR dye on Pb-FeONPs is presented in supplementary data.

Preparation of Pb-FeONPs

The Pb-FeONPs were prepared using a co-precipitation method. Firstly, 7.2 g of ferric chloride and 0.61 g of (CH3-COO)2Pb were added into 200 ml of deionized distilled water containing 1 g of sodium lauryl sulfate (SLS) and heated up to 60 °C. A 5M NaOH solution was used to maintain the pH of 11 ± 0.2. The solution was continuously heated at 60 °C for 2 h. The synthesis of Pb-FeONPs is schematically depicted in Figure 1. The brown stable precipitate was filtered and washed vigorously with distilled water until the filtrate pH was reduced to 7.5. The precipitates were dried in an air oven at 90 °C for 12 h. The material was converted to a fine powder and then calcined at 400 °C for 3 h.

Statistical physics model for dye adsorption mechanism

To evaluate the experimental effects, three mathematical physics models were used. They believed that the 2-NP adsorbate has generated a fixed and non-fixed number of layers on the surfaces tested (in fact, one, two or more layers) (Nayak & Pal 2020). According to mathematical mechanics theory and basic theories, these models were formulated.

The adsorption model was derived by considering the assumption of this statistical physics system.

\[ nD + R \leftrightarrow D_nR \]  

(1)
where, \( n = \) stoichiometric coefficient (may be an integer or not, lower or greater than 1).

The fraction of molecule adsorbed per site of adsorbent when \( n < 1 \); that is, multi-docking adsorption is involved and if \( n > 1 \), multi-molecular adsorption is assumed, which means a single site is occupied by the number of molecules. The isotherm can be interpreted within this principle by a single layer method or by simulating the formation of two or more layers. To estimate experimental dye adsorption, the use of a two-energy double-layer model was necessary.

### Monolayer adsorption model

The monolayer adsorption model believes that CR dye molecules form a single layer with adsorption energy \( \varepsilon_1 \). So, the adsorbed quantity \( Q \) of dye is given by:

\[
Q = \frac{nN_M}{1 + \left( \frac{C_{1/2}}{C} \right)^n}
\]  
(Model 1)

In this model, there are three variables:

- \( C_{1/2} \) is the concentration at half-saturation;
- \( N_M \) = receptor sites density on the nanoadsorbent;
- \( n \) = number of dye molecules per site of nanoadsorbent.

The obtained theoretical model values can be fitted with the experimental data. From this, \( Q_{sat} \); that is, the adsorbed quantity of molecules at saturation, was calculated using the relation:

\[
Q_{sat} = n^*N_M^* \left( 1 + N_2 \right)
\]

Here \( 1 + N_2 \) is the formed layer number. For monolayer \( N_2 = 0 \).

### Double-layer model

This means that for an additional layer of dye molecules, the first layer must provide acceptor sites, thus requiring two adsorption energies, \( \varepsilon_1 \) and \( \varepsilon_2 \), as mentioned above. This model was equated as given below:

\[
Q = nN_M \left( \frac{C}{C_1} \right)^n + 2 \left( \frac{C}{C_2} \right)^{2n} \left\{ \left( \frac{C}{C_1} \right)^n + \left( \frac{C}{C_2} \right)^{2n} \right\}^{-1}
\]

(Model 2)

Four important variables can be described from Model 2 including \( n \), \( N_M \), (significance of \( n \) and \( N_M \) is the same as the previous model). The \( C_1 \) and \( C_2 \) are the first- and second-layer concentrations at half-saturation, respectively.

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Complete adsorbed layers were described in this case as \( N_c = 1 + N_2 \) (Layer).

**RESULTS AND DISCUSSION**

**Characterization of Pb-FeONPs**

The SEM image of the Pb-FeO nanoparticles showed an average particle size of 19.21 nm (Figure 2(a)). The nanoparticles were uniform and well-dispersed in size. The Pb-FeONPs were spherical. However, a few larger particles are also seen due to the aggregation of smaller particles. EDX outcome reveals that nanoparticles composed of Pb, Fe, and O with 11.74, 40.85, and 47.41 wt%, respectively (Figure 2(b)).

The crystalline nature from XRD revealed the peaks at 31.82°, 35.74°, 44.58°, 52.81°, 61.83°, and 64.93° with reflection at 111, 200, 100, 220, 311, and 200 miller planes of Pb-FeONP (Figure 2(c)). The average crystallite size obtained from XRD was found to be 4.9 nm. FT-IR spectra of Pb-FeONPs are presented in Figure 2(d). The absorption bands at 687 cm\(^{-1}\) of Fe-O, 1,640 cm\(^{-1}\) of O-H bending vibration, 3,211 cm\(^{-1}\) of O-H stretching, band at
1,157 cm\(^{-1}\) of C-O bond, and 1,421 cm\(^{-1}\) of C-H bending vibration were observed.

**Effect of pH, time and adsorbent dose**

The adsorption capability of CR was greater at pH 6.5, and lesser when pH increased from 6.5 to 10.0 and reduced from 6.5 to 3.0 (Figure 3(a)). The maximum percentage of adsorption of about 94.42% was obtained at pH 6.5 and therefore, further experiments were performed at pH 6.5. Above and below pH 6.5, the adsorption was significantly decreased. The Pb-FeONPs with negative charges were lying face down to adsorb positive charge protonated–NH\(_2\). Due to the above mechanism (opposite charges attracted to each other), CR was adsorbed onto the Pb-FeONPs and its adsorption process became a self-occurring spontaneous reaction. The effect of time for the adsorption of dye on Pb-FeONPs was achieved by varying the time from 0 to 90 min at 298 K. The CR was adsorbed on to the surface of the Pb-FeONPs and settled down on the bottom of the conical flask, the upper supernatant aqueous solution was centrifuged and further used to determine the concentration with UV-visible spectrophotometer at 498 nm. The rate of adsorption was increased up to 40 min after a further increase in time, the adsorption process started to slow down (91.74%) and reached equilibrium (Figure 3(b)). All experiments were conducted in triplicates to validate the adsorption phenomenon. It was clear that the removal of maximum CR dye required a large amount of Pb-FeONPs and this problem was overcome by optimization studies.
on the amount of adsorbent dosage. The adsorbent dosage significantly influences the adsorption process. As the number of adsorbent (Pb-FeONPs) active sites increases proportionally the adsorption of dye (CR) increases. The findings of Figure 3(c) showed that the adsorption percentage increases with the rise in the dose of Pb-FeONPs from 50 to 200 mg. It was recognized from the data that due to the presence of a large number of adsorption sites, the adsorption efficiency of dyes increased from 69.74 to 94.42 percent.

**Kinetic models, adsorption isotherms**

The kinetics of CR adsorption on Pb-FeONPs was studied by using Ho and McKay models. Kinetic experiments have been commonly used in the adsorption of dye to the surface of solid nanoparticles (Crini 2008). The adsorption kinetic rate has a significant contribution to the selection of adsorbents. At the same time, kinetic modeling reflects adsorption rates and allows the determination of adequate rate terms and effective clarification of the reaction process. The equation of pseudo-first and second-order are given below:

\[
\log (q_e - q_t) = \log (q_e) - \left( \frac{K_1}{2.303} \right) t \\
\frac{t}{q_t} = \frac{1}{K_2 q_e} + \left( \frac{1}{q_e} \right) t
\]  

(2)

The pseudo-second-order kinetic analysis between CR and Pb-FeONPs was verified in the present adsorption study, as shown in Figure 4(a) and Table 1. The five distinct isotherm equations of Langmuir (Langmuir 1918), Freundlich (Freundlich & Heller 1939), Temkin (Temkin & Pyzhev 1940), Dubinin-Radushkevich (Dubinin & Radushkevich 1947), and Hurkins-Jura (Tahermansouri et al. 2015) were used to assess the adsorption process. The graphs obtained by the adsorption isotherm are displayed in Figures 4(b)–4(d), 5(a) and 5(b). The measured parameters are tabulated in Table 2. The Langmuir isotherm assumes that the active area of the surface is equal and identical, and the adsorbent surface is homogeneous. On the surface of the adsorbents, the adsorption process of dye takes place via monolayer covering. Each of the active pockets of the adsorbent with maximum adsorption can occupy a single dye molecule. Besides, it was also assumed that around the plane surface of the adsorbent, the binding energies of the dye molecules were uniform. It was used to describe the interaction with adsorbed molecules of monolayer adsorption. The Langmuir isotherm equation is:

\[
q_e a_L / K_L = K_L C_e / (1 + K_L C_e)
\]  

(4)

The linear form of the equation:

\[
C_e / q_e = \frac{C_e a_L}{K_L} + 1 / K_L
\]  

(5)

The plot of Ce/qe vs. Ce is shown in Figure 4(b), which was linear (R² = 0.990). Table 2 reveals that the maximal adsorption potential of Pb-FeONPs for CR (qmax = 500 mgg⁻¹) was much greater. The multilayer adsorption with the interaction between adsorbed molecules is described by the Freundlich isotherm. The Freundlich isotherm model is described by:

\[
q_e = K_f C_e^{1/n}
\]  

(6)

The linear form of the equation is:

\[
\ln q_e = \ln K_f + \ln C_e / n f
\]  

(7)

The Kf and 1/n values derived from the ln qe vs. ln Ce intercept and plot slope are given in Table 2 and plotted in Figure 4(c). The heat of the adsorption and the interaction between adsorbent and adsorbate were clarified and evaluated using the Temkin isotherm model. The isotherm and linear form of Temkin is as follows. The Temkin model is plotted between qe and ln Ce (Figure 4(d)).

\[
q_e = B_1 \ln KT + B_2 \ln C_e
\]  

(8)

The isothermal model of Dubinin-Radushkevich (D-R) is used to understand the adsorption process.

D-R model is represented:

\[
\ln q_e = \ln q_D - B e^2
\]  

(9)

\[
\epsilon = RT \ln (1 + 1/C_e)
\]  

(10)

Average free adsorption energy ε, is estimated from B, using the following equation:

\[
E = 1/(2B)^{1/2}
\]  

(11)

The D-R isothermal model is used to predict whether the adsorption was physisorption or chemisorption. In
Figure 5(a), the plot-estimated constant was observed. The qD, B and R² values are given in Table 2. The high qD value, and low R², imply that the activation energy measured based on the D-R plot could not be the real one. The equation between Hurkins-Jura (H-J) is expressed as:

\[
\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e
\]  

The measured values of constants A and B from the \(1/q_e^2\) versus \(\log C_e\) plot (Figure 5(b)) are tabulated in Table 2. The correlation coefficient of all isotherm models was analyzed. The Langmuir model has the highest R² value, with well-defined adsorption of CR onto the Pb-FeONPs. The isotherm models of D-R and H-J demonstrated an unacceptable fit with the experimental results compared to the other isotherms.

Figure 4 | (a) Kinetic plots of dye adsorption, (b) Langmuir isotherm, (c) Freundlich plot, and (d) Temkin model on Pb-FeONPs.

Table 1 | Kinetic model of CR adsorption on Pb-FeONPs

| Concentration (ppm) | 50  | 100 | 150 | 200 |
|---------------------|-----|-----|-----|-----|
| \(K_{ad}\)          | 0.397 | 0.890 | 0.946 | 0.963 |
| \(q_e\)             | 7.194 | 8.850 | 9.434 | 9.615 |
| R²                  | 0.999 | 0.999 | 0.999 | 0.998 |
An essential characteristic of the Langmuir isotherm is the separation factor (RL).

\[
RL = \frac{1}{1 + \alpha L Co}
\]

(13)

RL values indicate the desirable adsorption process within the 0 < RL < 1 range. In this study, the RL value of Pb-FeONPs was obtained to be 0.583 (Weber & Chakravorti 1974) for the initial RHB concentration of 20 mg/L (Figure 5(c)) and indicates favorable CR adsorption. Multi-layer adsorption is considered, accompanied by the interactions between the adsorbed molecules and the heterogeneous energy distribution of the active sites. Thermodynamic parameters (Figure 5(d)) for the adsorption of CR on to the Pb-FeONPs at various...
temperatures of 298, 308, and 318 K were studied. The thermodynamic parameters for the CR-Pb-FeONPs system, including $ΔH$, $ΔS$, and $ΔG^*$ were calculated as a function of temperature (Selim et al. 2019).

$$\ln K_L = \frac{ΔS^*/R} - \frac{ΔH^*/RT}$$  \hspace{1cm} (14)

where $R$ (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ are in Kelvin. The value of $ΔG^*$ was calculated from the equation:

$$ΔG^* = RT \ln K_L$$  \hspace{1cm} (15)

$$ΔG^* = ΔH^* - TΔS^*$$  \hspace{1cm} (16)

Table 3 displays thermodynamic parameters obtained from the adsorption of CR on the surface of Pb-FeONPs at different temperatures. The temperature analysis anticipates the exothermic or endothermic existence of the mechanism of adsorption. The variance of the model of CR dye adsorbed on the Pb-FeONPs due to solution temperature is shown in Figure 5(d) (Weber & Chakravorti 2014). Adsorption is assigned to physisorption when the $G^*$ is between $-20$ and $0$ kJ mol$^{-1}$ and chemisorption when the $G^*$ is between $-40$ and $-80$ kJ mol$^{-1}$. For CR adsorption on the Pb-FeONPs, the shift in free energy at 298 K was $-2.918$ kJ mol$^{-1}$ (Table 3). The increase in the adsorption potential at higher temperatures was due to the increased mobility of the active adsorbent surface sites of dye molecules. The $ΔH^*$ and $ΔS^*$ were estimated as $-0.008$ kJ mol$^{-1}$ and $-0.033$ kJ mol$^{-1}$, respectively. The negative $ΔG^*$ showed that the adsorption of CR on Pb-FeONPs is a spontaneous process. The negative $ΔH$ and $ΔS$ reflect the exothermic nature of the solid/solution adsorption and decreased randomness, respectively. The outer parts of nanomaterial (Pb-FeONPs) are normally enclosed with negatively charged -OH groups and positively charged NH$_2$ groups. The opposite nature of both materials attracts each other, due to which adsorption takes place in solution very effectively. Hence, the adsorption ability of the Pb-FeONPs was efficient as shown in the proposed mechanism (Figure 6).

**Table 3 | Thermodynamic parameters for CR-Pb-FeONPs adsorption system**

| Temp (K) | $ΔG^*$ (kJ mol$^{-1}$) | $ΔH^*$ (kJ mol$^{-1}$) | $ΔS^*$ (J mol$^{-1}$ K$^{-1}$) |
|----------|------------------------|------------------------|-------------------------------|
| 298      | $-2.918$               | $-0.008$               | $-0.033$                      |
| 308      | $-3.580$               |                        |                               |
| 318      | $-4.173$               |                        |                               |
| 328      | $-4.709$               |                        |                               |

It is important to understand the adsorption isotherms of the CR by the statistical physics model. The results of the two-energy double layer of the statistical physics model and its relationship in the adsorption of CR onto the Pb-FeONPs are shown in Figure 7 and Figure 8. These figures depict a simple example of adsorption of CR onto the Pb-FeONPs surface. The data from Table 4 reveal the fitting parameters of the two-energy double-layer model; that is, $n$, $N_M$, $Q_0$, and adsorption energies $ε_1$ and $ε_2$.

**Parameters $n$, $N_M$ and $Q_{sat}$**

To provide the basic information of the absorption process between Pb-FeONPs and CR, the determination of the $n$ parameter is very important and useful. The multi-docking ($n < 1$) and (case 2) multi-molecular ($n > 1$) values are two main instances of the adsorption mechanism (case 1), as opposed to unity. The first case applies to several active sites of Pb-FeONPs that adsorb one ion, while the latter represents the potential to absorb several ions from one active site (Sellaoui et al. 2016).

All the $n$ values measured were less than 1 as a function of temperature, which showed the horizontal geometry of the adsorbed Pb-FeONPs. Following Figure 9(a), due to thermal collisions, the number of molecules per site increases as the temperature increases. It is fact that the $n$ value never exceeds 1 (at low temperatures), which suggests that there is no dimerization and trimerization until adsorption. As regards the NM parameter, it was observed that the number of active Pb-FeONPs sites contributing to CR capture decreases as the solution temperature increases (Table 4) (Figure 9(b)). It was also found that $N_M$ density decreases as a function of temperature. Additional receptor sites were uncovered at high temperatures that are obscured at low temperatures. This depends primarily on the quantity of bonded CR dye per receptor site, the density of the receptor site, and the average number of adsorbed layers (i.e. for the single-layer model, $Q_{sat} = n^2 N_M$ and the double-layer...
The effect of temperature on the capacity of adsorption at saturation is shown in Figure 9(c). The value of $Q_{\text{sat}}$ at 298, 308, and 318 K were 438.46, 66.08, and 34.63 mg/g, respectively. The lower interaction between CR molecules and Pb-FeONPs was confirmed by the decrease in the $Q_{\text{sat}}$ values with the change in the temperature. This parameter illustrates the exothermic phase in the adsorption mechanism of CR on to the Pb-FeONPs. It was further confirmed by the absorption energetic interpretation (Selim et al. 2019).

**Energetic interpretation**

Equations can be used to determine the interactions between the CR and the Pb-FeONPs (Li et al. 2019):

$$
\varepsilon_1 = RT \ln \left( \frac{C_s}{C_1} \right)
$$

(17)

$$
\varepsilon_2 = RT \ln \left( \frac{C_s}{C_2} \right)
$$

(18)

in which $C_s$ is the solubility of the PCE molecule.

In Figure 9(d), the evolution of the $\varepsilon_1$ and $\varepsilon_2$ adsorption energies is shown as a function of temperature. The values of adsorption energies are less than 40 kJ mol$^{-1}$. This means that physisorption is the adsorption of CR on to Pb-FeONPs. It can also be seen from Figure 9(d) that in the first adsorbed layer, the maximum adsorption energy was observed, as the affinity of the receptor sites on that layer is more important. Compared to adsorbate and adsorbent, this results in less contact between the adsorbate and the adsorbate. Moreover, the energy of adsorption increases as a function of temperature. Therefore, more energy was required to transfer the CR molecules from the liquid phase to the adsorbent surface at elevated temperatures (Dil et al. 2019; Massoudinejad et al. 2019; Ahmad et al. 2020; Baig et al. 2020; Nithya et al. 2020).

**REGENERATION AND INDUSTRIAL APPLICATION**

The reusability of the Pb-FeONPs was performed in replicate ($n = 5$). A 0.1 M HCl was used for desorption of CR from the surface of Pb-FeONPs. It was verified that Pb-FeONPs adsorption potential remains greater than 93% after the fifth cycle of the adsorption-desorption process as shown in Figure 10 (Azeez et al. 2019; Rahdar et al. 2019; Li et al. 2020a, 2020b). To evaluate the adsorption efficiency of the Pb-FeONPs, wastewater samples were used to remove CR. The obtained results indicate that 94% of CR was removed, as shown in Table 5 (Azeez et al. 2019; Ojemaye & Okoh 2019; Dhaif-Allah et al. 2020). The comparison table of the adsorption potential of several recorded adsorbents against CR dye is shown in Table 6.
CONCLUSION

A cost-effective Pb-FeONPs was prepared. Complete CR adsorption was achieved at pH 6.5 with an adsorption time of 40 min using an adsorption dose of 200 mg. The adsorption process showed that Langmuir with Qmax at 500 mg/g was the second-order of the kinetic and best-fitted isothermal model. The adverse value of G° confirms the spontaneity of the adsorption process. It was checked that the adsorption potential of Pb-FeONPs was still greater than 93 percent after the fifth adsorption-desorption period. The n values obtained from the double-layer model of

### Table 4 | Parameters of the double-layer model with two energies

| Temp. in Kelvin | n   | N_max (mg/g) | Q_max (mg/g) | C1     | C2     | E1     | E2     |
|----------------|-----|--------------|--------------|--------|--------|--------|--------|
| 298            | 0.599 | 366.238      | 438.465      | 43.793 | 1,988.182 | 12.561 | 3.108  |
| 308            | 0.593 | 55.732       | 66.084       | 1.623  | 367.043 | 21.420 | 7.538  |
| 318            | 0.565 | 30.633       | 34.633       | 0.346  | 363.335 | 26.201 | 7.810  |

### Figure 9 | Evolution of the physicochemical parameters (a) n, (b) N_max, (c) Q_max, and (d) adsorption energy as a function of temperature.
statistical physics were 0.599, 0.593, and 0.565, which were less than 1, demonstrating the multi-docking process. Pb-FeONPs are regenerated up to 5 cycles and have been successfully used for laboratory and industrial-scale removal of CR dye from wastewater.

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### DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

### REFERENCES

Ahmad, M. A., Eusoff, M. A., Oladoy, P. O., Adegoke, K. A. & Bello, O. S. 2020 Statistical optimization of Remazol Brilliant Blue R dye adsorption onto activated carbon prepared from pomegranate fruit peel. *Chemical Data Collections* **28**, 100426.

Ahmed, D. N., Naji, L. A., Faisal, A. A. H., Al-Ansari, N. & Naushad, M. 2020 Waste foundry sand/MgFe-layered double hydroxides composite material for efficient removal of Congo red dye from aqueous solution. *Scientific Reports* **10**, 2042.
Albadarin, A. B., Collins, M. N., Naushad, M., Shirazian, S., Walker, G. & Mangwandi, C. 2017 Activated lignin-chitosan extruded blends for efficient adsorption of methylene blue. *Chemical Engineering Journal* **307**, 264–272.

Arshadi, M., Faraji, A. R. & Mehravar, M. 2015 Dye removal from aqueous solution by cobalt-nano particles decorated aluminum silicate: kinetic, thermodynamic and mechanism studies. *Journal of Colloid and Interface Science* **440**, 91–101.

Azeez, L., Lateef, A., Adejumo, A. L., Adeleke, J. T., Adetoro, R. O. & Mustapha, Z. 2019 Adsorption behaviour of rhodamine B on hen feather and corn starch functionalized with green synthesized silver nanoparticles (AgNPs) mediated with cocoa pods extracts. *Chemistry Africa* **3**, 237–250. https://doi.org/10.1007/s42250-019-00115-7.

Baig, U., Uddin, M. K. & Gondal, M. A. 2020 Removal of hazardous azo dye from water using synthetic nano adsorbent: facile synthesis, characterization, adsorption, regeneration and design of experiments. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **584**, 124031.

Crini, G. 2008 Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. *Dyes Pigments* **77**, 415–426.

Dehghanian, N., Ghaedi, M., Ansari, A., Ghaedi, A., Valaei, A., Asif, M., Agarwal, S., Tyagie, I. & Gupta, V. K. 2016 A random forest approach for predicting the removal of Congo red from aqueous solutions by adsorption onto tin sulfide nanoparticles loaded on activated carbon. *Desalination and Water Treatment* **57**, 9272–9285.

Dhaif-Allah, M. A. H., Taqui, S. N., Syed, U. T. & Syed, A. A. 2020 Kinetic and isotherm modeling for acid blue 115 dye adsorption onto low-cost nutraceutical industrial fenugreek seed spent. *Applied Water Science* **10**, 58.

Dil, E. A., Ghaedi, M., Asfaram, A., Mehrabi, F., Bazrafshan, A. A. & Tayebi, L. 2019 Synthesis and application of Ce-doped TiO2 nanoparticles loaded on activated carbon for ultrasound-assisted adsorption of Basic Red 46 dye. *Ultrasonics – Sonochemistry* **58**, 104702.

Duhinin, M. & Radushkevich, L. 1947 Chem. Zentr **1**, 875–889.

El-Gamal, S. M. A., Amin, M. S. & Ahmed, M. A. 2015 Removal of methyl orange and bromophenol blue dyes from aqueous solution using Sorel's cement nanoparticles. *Journal of Environmental Chemical Engineering* **3**, 1702–1712.

Freundlich, H. & Heller, W. 1939 The adsorption of cis- and trans-Azobenzene. *Journal of the American Chemical Society* **61**, 2228–2230.

Jethave, G., Fegade, U., Attarde, S., Ingle, S., Ghaedi, M. & Sabzehei Dani, M. M. 2019a Exploration of the adsorption capability by doping Pb@ZnFe2O4 nanocomposites (NCS) for decontamination of dye from textile wastewater. *Heliyon* **5**, e02412.

Khan, Z. U. H., Khan, A., Chen, Y., Khan, A. u., Shah, N. S., Muhammad, N., Murtaza, B., Tahir, K., Khan, F. U. & Wan, P. 2017 Photo catalytic applications of gold nanoparticles synthesized by green route and electrochemical degradation of phenolic Azo dyes using AuNPs /GC as modified paste electrode. *Journal of Alloys and Compounds* **725**, 869–876.

Langmuir, L. 1918 The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society* **40**, 1361–1405.

Li, Z., Dotto, G. L., Bajahzar, A., Sellaoui, L., Belmabrouk, H., Lamine, A. B. & Bonilla-Petriciolet, A. 2019 Adsorption of indium (III) from aqueous solution on raw, ultrasound- and supercritical-modified chitin: experimental and theoretical analysis. *Chemical Engineering Journal* **375**, 1247–1253.

Li, Z., Hanafy, H., Zhang, L., Sellaoui, L., Netto, M. S., Oliveira, M. L. S., Seliem, M. K., Dotto, G. L., Bonilla-Petriciolet, A. & Q. 2020 Adsorption of Congo red and methylene blue dyes on an ashitaba waste and a walnut shell-based activated carbon from aqueous solutions: experiments, characterization and physical interpretations. *Chemical Engineering Journal* **388**, 124263.

Li, Z., Sellaoui, L., Gueddida, S., Dotto, G. L., Lamine, A. B., Bonilla-Petriciolet, A. & Badawi, M. 2020b Adsorption of methylene blue on silica nanoparticles: modelling analysis of the adsorption mechanism via a double layer model. *Journal of Molecular Liquids* **319**, 114348.

Massoudinejad, M., Rasoulzadeh, H. & Ghaderpoori, M. 2019 Magnetic chitosan nanocomposite: fabrication, properties, and optimization for adsorptive removal of crystal violet from aqueous solutions. *Carbohydrate Polymers* **206**, 844–853.

Naushad, M., Alqadami, A. A., AlOthman, Z. A., Alsohaimi, I. H., Algamdi, M. S. & Aldawsari, A. M. 2019 Adsorption kinetics, isotherm and reusability studies for the removal of cationic dye from aqueous medium using arginine modified activated carbon. *Journal of Molecular Liquids* **293**, 111442.

Naushad, M., Sharma, G. & Alothman, Z. A. 2019b Photodegradation of toxic dye using Gum Arabic-crosslinked poly(acrylamide)/Ni(OH)2/FeOOH nanocomposites hydrogel. *Journal of Cleaner Production* **241**, 118263.

Nayak, A. K. & Pal, A. 2020 Statistical modeling and performance evaluation of biosorptive removal of Nile blue A by lignocellulosic agricultural waste under the application of high-strength dye concentrations. *Journal of Environmental Chemical Engineering* **8**, 103677.

Nithya, R., Thirunavukkarasu, A., Sivashankar, R. & Rangabhashiyam, S. 2020 Fenalin Yellow G adsorption using surface-functionalized green nanoceria: an insight into mechanism and statistical modeling. *Environmental Research* **181**, 108920.

Ojemeaye, M. O. & Okoh, A. I. 2019 Multiple nitrogen functionalized magnetic nanoparticles as an efficient adsorbent: synthesis, kinetics, isotherm and thermodynamic studies for the removal of rhodamine B from aqueous solution. *Scientific Reports* **9**, 9672.

Rahdar, S., Rahdar, A., Zafar, M. N., Shafqat, S. S. & Ahmad, S. 2019 Synthesis and characterization of MgO supported Fe–Co–Mn nanoparticles with exceptionally high adsorption capacity for Rhodamine B dye. *Journal of Material Research Technology* **8** (5), 3800–3810.

Selim, A. Q., Mohamed, E. A. & Seliem, M. K. 2019 Deep insights into the organic carbon role in selectivity and adsorption
mechanism of phosphate and crystal violet onto low-cost black limestone: modelling and physicochemical parameters interpretation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **580**, 123755.

Sellaoui, L., Knani, S., Erto, A., Hachicha, M. A. & Lamine, A. B. 2016 Equilibrium isotherm simulation of tetrachlorethylene on activated carbon using the double layer model with two energies: steric and energetic interpretations. *Fluid Phase Equilibria* **408**, 259–264.

Shu, J., Wang, Z., Huang, Y., Huang, N., Ren, C. & Zhang, W. 2015 Adsorption removal of Congo red from aqueous solution by polyhedral Cu2O nanoparticles: kinetics, isotherms, thermodynamics and mechanism analysis. *Journal of Alloys and Compounds* **633**, 338–346.

Singh, S., Barick, K. C. & Bahadur, D. 2013 Fe3O4 embedded ZnO nanocomposites for the removal of toxic metal ions, organic dyes and bacterial pathogens. *J. Mater. Chem. A* **1**, 3325–3333.

Sohrabi, M. R., Amiri, S., Masoumi, H. R. F. & Moghri, M. 2014 Optimization of direct yellow 12 dye removal by nanoscale zero-valent iron using response surface methodology. *Journal of Industrial and Engineering Chemistry* **20**, 2535–2542.

Tahermansouri, H., Dehghan, Z. & Kiani, F. 2015 RSC Adv. 5, 44263–44273.

Temkin, M. J. & Pyzhev, V. 1940 Kinetics of ammonia synthesis on promoted iron catalysts. *Acta Physicochimica USSR* **12**, 217–222.

Weber, T. W. & Chakravorti, R. K. 1974 Pore and solid diffusion models for fixed-bed adsorbers. *J. Am. Inst. Chem. Eng.* **209**, 228–238.

Zhou, Q., Gao, Q., Luo, W., Yan, C., Ji, Z. & Duan, P. 2015 One-step synthesis of amino-functionalized attapulgite clay nanoparticles adsorbent by hydrothermal carbonization of chitosan for removal of methylene blue from wastewater. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **470**, 248–257.

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