Supporting information

Magnetically Recyclable Adsorption of Anionic Pollutants from Wastewater using 3,5-Diaminobenzoic Acid-Functionalized Magnetic Iron-Oxide-Nanoparticles

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Evidence for CR-adsorption on Fe$_3$O$_4$@DABA

FTIR spectrum of CR-adsorbed Fe$_3$O$_4$@DABA nanoadsorbent particles is shown in Figure S1. The spectrum of CR-adsorbed Fe$_3$O$_4$@DABA (Fe$_3$O$_4$@DABA@CR) shows some significant changes as compared to the spectrum of bare-Fe$_3$O$_4$@DABA adsorbent. For example, the characteristic stretching vibration band of azo group (-N=N-) was found at 1507 cm^{-1} that is identifiable between 1504 to 1555 cm^{-1}, aromatic ring stretching appeared at 1355 and 1236 cm^{-1} while the asymmetry stretching vibration of S-O band in -SO$_3^-$ groups was appeared at 1165 cm^{-1}, which are confirming the presence of adsorptive-CR on the surface of Fe$_3$O$_4$@DABA.[1] Additionally, the N-H stretching vibration peak at 3600-3200 cm^{-1} was significantly reduced due to co-ordination with protons via electrostatic interactions and hydrogen bonding with the CR molecules. In addition, in the spectrum of Fe$_3$O$_4$@DABA@CR others peak of Fe$_3$O$_4$@DABA were observed in slightly shifted region with some variation of the peak intensity. All these changes indicate the interactions between the functional groups of the Fe$_3$O$_4$@DABA nanoadsorbent with CR azo dye molecules.[1]
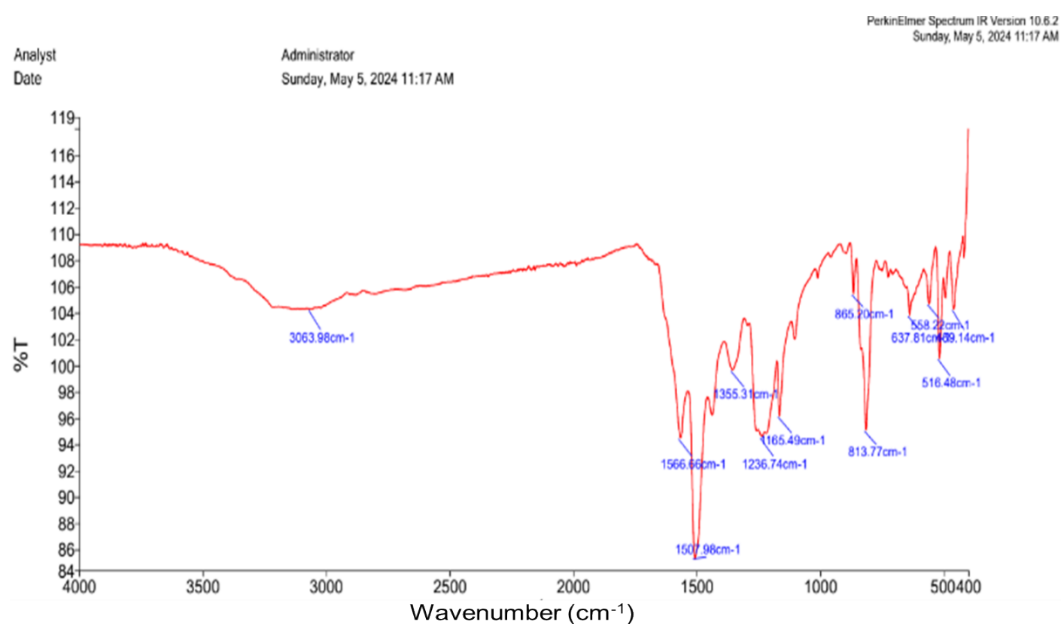

Figure S1: FTIR spectrum of CR-adsorbed Fe$_3$O$_4$@DABA nanoadsorbent particles taken in an ATIR mode under ambient conditions.

Figure S2 shows the XRD pattern of CR-adsorbed Fe_3O_4@DABA nanoadsorbent particles taken under ambient conditions. In this diffraction pattern two new signals appeared at 2θ values of 21-23° and 24-27.6°, which are relatively broad and plausibly assignable to the densely packed amorphous CR adsorbed onto the surface of Fe_3O_4@DABA nanoadsorbent particles. Other six peaks related to the Fe_3O_4@DABA diffraction were appeared in the slight changes position. This negligible change is plausibly due to the molecular interactions of CR with the crustal facets of the Fe_3O_4@DABA nanoadsorbent particles.[2] However, any additional peak was not appeared related to the undesirable oxidative phase change occurred during the CR-adsorption process on the surface of adsorbent particles. Both the FTIR and XRD data demonstrated that the azo dye molecules were successfully adsorbed on the surface of nanoadsorbent particles.
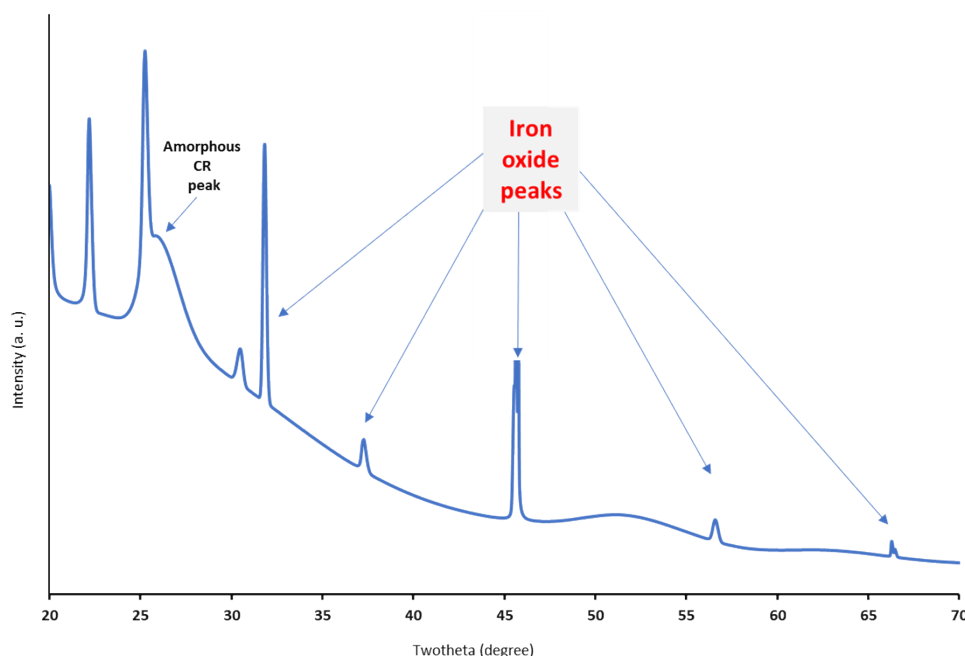

Figure S2: XRD pattern of CR-adsorbed Fe_3O_4@DABA nanoadsorbent particles measured under ambient conditions

Azo dye adsorption isotherm study

Adsorption isotherm models are essential for understanding adsorption mechanisms because they describe the interaction behaviors of adsorbate and adsorbents. Langmuir and Freundlich isotherms are frequently used to describe the interaction between the adsorbent and adsorbate molecules. The Langmuir isotherm assumes that adsorption was a monolayer absorption and adsorption takes place on an almost homogeneous porous surface.[3] The linear form of the Langmuir isotherm equation could be expressed by Equation S1:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad \text{................................. (S1)}$$

Where, q_e (mg/g) is the equilibrium adsorption capacity, C_e (mg/L) is the equilibrium adsorption concentration, q_{max} (mg/g) is the maximum adsorption capacity, and K_L (L/mg) is the adsorption equilibrium constant.

The Freundlich isotherm describes the multilayer adsorption on a heterogeneous surface.[4] The linear form of the Freundlich isotherm equation could be expressed by Equation S2:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. \text{(S2)}$$

Where, K_F is the Freundlich adsorption constant, and n is the non-uniform coefficient.

The experimental data of both CR and EY were best fitted with the Freundlich isotherm model with the values of correlation coefficient, (R^2) are 0.9872 and 0.9776 for CR, and EY respectively. The linear curves of $\ln q_e$ versus $\ln C_e$ for the Freundlich model for CR, and EY adsorption are shown in Figure S3. The best-fitted experimental equilibrium data derived from the Freundlich model suggested multilayer coverage of CR and EY onto the porous Fe_3O_4@DABA nanoadsorbent particles and also revealed that the adsorption was not restricted to a specific number of sites or a monolayer coverage of the adsorbent surface.
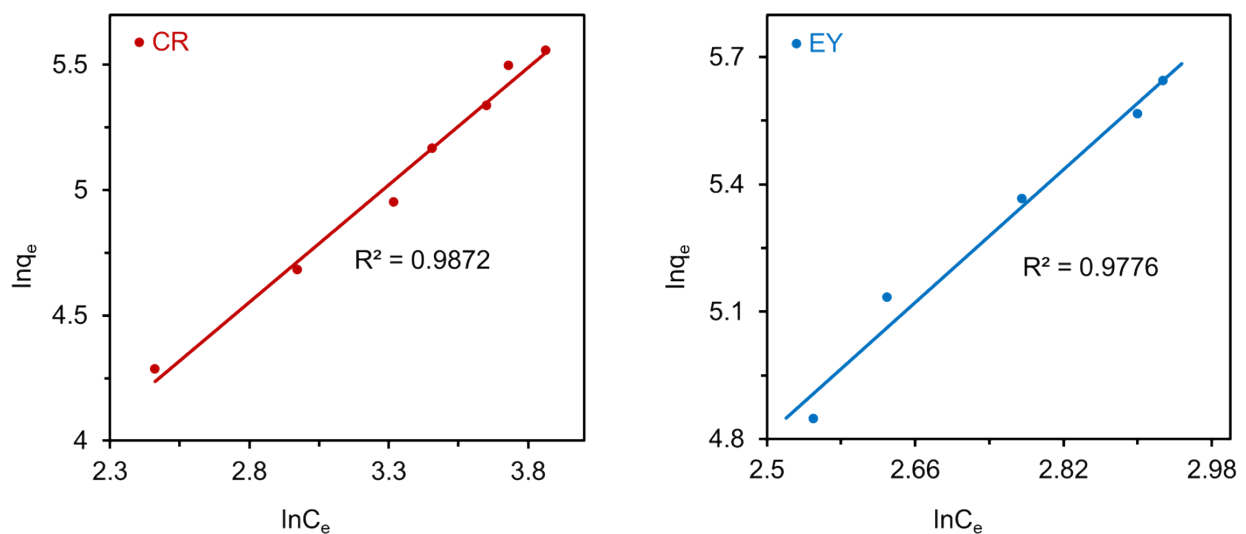

Figure S3: Linear forms of the Freundlich isotherm model for CR, and EY adsorption onto the porous surface of Fe_3O_4@DABA nanoadsorbent.

Azo dye adsorption kinetics

We have studied the adsorption kinetics to determine the potential stages that could control the rate of adsorption and explain the adsorption mechanism. In predicting the adsorption kinetics onto Fe_3O_4@DABA, the experimental data were applied to the pseudo-first-order and second-order kinetic models. The pseudo-first-order kinetic model was frequently used to examine adsorption behavior in a liquid-solid system.[5] It could be expressed by equation (S3).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. \text{(S3)}$$

Where, q_e (mg/g) is the adsorption amount at equilibrium; q_t is the adsorption amount at time, t (h); and k_1 is the rate constant of pseudo-first-order adsorption.

For the pseudo-second-order kinetic model, it was assumed that the process of adsorption was chemical.[6] The equation could be expressed by equation (S4).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. \text{(S4)}$$

Where, k_2 is the rate constant of pseudo-second-order adsorption; the amount of adsorption at time t, q_t (mg/g), q_e (mg/g), and t (h) is the same as that in the pseudo-first-order equation.

The experimental data of both CR and EY were best fitted with the pseudo-first-order kinetic equation with the values of correlation coefficient, (R^2) were 0.9401 and 0.9739, CR, and EY respectively. The linear curves of ln $(q_e - q_t)$ versus t for the pseudo-first-order kinetic equation of CR and EY adsorptions are shown in Figure S4. The best-fit experimental equilibrium data derived from the pseudo-first-order adsorption model suggested that the rate of CR and EY adsorptions were directly proportional to the initial concentration of dye in the solution. It also revealed that the rate of adsorption was proportional to the number of unoccupied adsorption sites on the surface of Fe_3O_4@DABA nanoparticles.
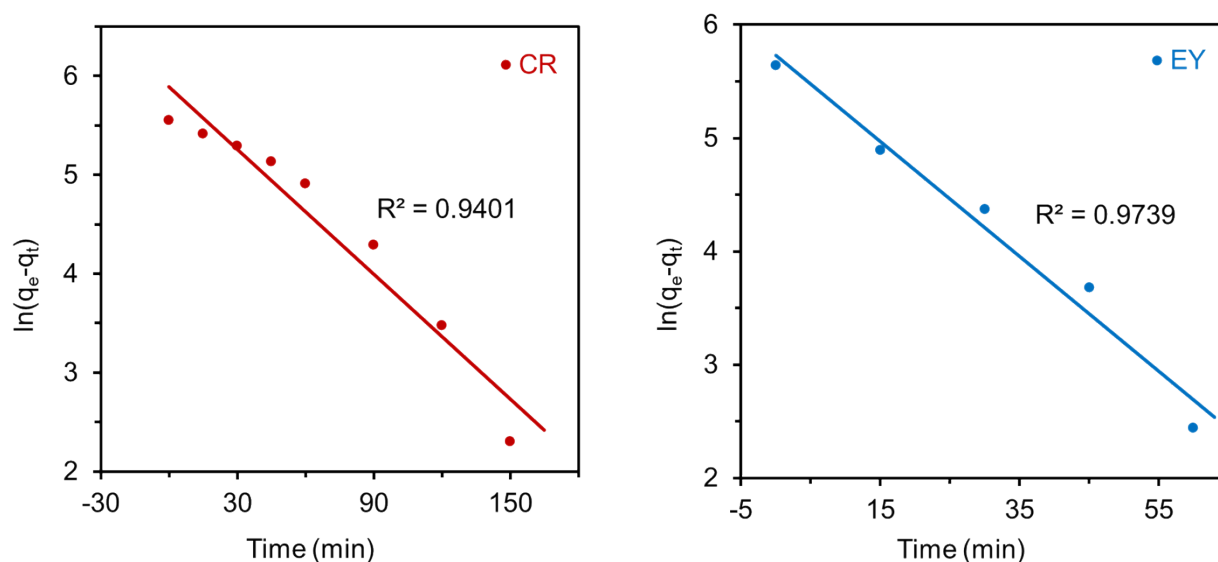

Figure S4: Applications of pseudo-first-order adsorption model for the adsorption of CR, and EY onto the aminated surface of Fe_3O_4@DABA nanoadsorbent particles.

References

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