Supporting information

Magnetized Cubic Zinc MOFs for Efficient Removal of Hazardous Cationic and Anionic Dyes in Water

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Instruments

The surface properties of nanocube Zn-MOFs and MDLZ including the specific surface area and the pore structure were determined by N_2 adsorption-desorption isotherms which were measured by applying the Barrett–Joyner–Halenda (BJH) method. The pore size distribution was determined from the adsorption isotherms by using nonlocal density functional theory. Specific surface area (SBET) was calculated using multi-point adsorption data from linear segment of the N_2 adsorption isotherms using Brunauer-Emmett-Teller (BET) theory. Before the N_2 isothermal analysis, all samples pre-treated at 80^{o}C for 6h and calibrated to 10^{-3} Torr. Small- and wide-angle powder X-ray diffraction patterns were measured by using with monochromated CuKα (λ = 1.54060 Å) radiation with diffraction reflections recorded for 2 angles between 5◦ and 10◦ corresponding to d- and WAXRD of nanocube Zn-MOFs and MDLZ scanned from 4° to 80°. Prior to analysis, the samples were outgassed at 80 °C for 24 h. The Field emission scanning electron microscopy (FESEM) images of Zn-MOFs and MDLZ were used to investigate the morphologies and obtained by Zeiss Leo Supra55 microscope. Moreover, to record the SEM micrographs, the scanning electron microscope was operated at 20 keV. The samples for FESEM observations. The absorbance spectrum of the CR, CV and NR dyes were measured by a Shimadzu UV-2600 solid-state UV–vis spectrophotometer. FT-IR spectra were measured in a Nicolet iS10 system. Samples were grinded with KBr for FT-IR measurements in the wave number range of 4000-400.

Preparation of Zn-MOFs

The Zn-MOFs were prepared via a simple and green approach using methanol in room temperature under stirring. First, 3.672 g (0.012 mol) of Zn $(NO_3)_2 6H_2O$ dissolved in 50 mL of methanol (Soln 1), and 4.053 g (0.049 mol) of 2-MIM dissolved in 50 mL of methanol (Soln 2), then add (Soln1) to (Soln2) and was stirred for 24 h at room temperature. The Zn-MOFs formed was creamy white in color and separated from the solution via centrifugation Then washed by methanol. The obtained powder was dried at 50 °C overnight. The chemical structure and morphology of the obtained Zn-MOFs was investigated.

Fabrication of Fe_3O_4 NPs

The preparation of Fe_3O_4 was conducted as previously reported method [1]. Briefly, 6.1 g of $FeCl_3.6H_2O$ and 4.2 g of $FeSO_4.7H_2O$ were dissolved in 100 mL distilled water, heated to 90 °C and then 10 mL of ammonium hydroxide (25%) was added. The mixture was stirred at 90 °C for 30 min and then cooled to room temperature. The precipitate was collected by an external magnet, washed with acetone, and dried in a drying oven for 24 h at 50 °C.

Preparation of Fe_3O_4@PAM

Synthesis of Fe_3O_4@Acr: 1.5 g Fe_3O_4 and 1.0 g acrylamide were dissolved in 100 mL aqueous solution. Then, 0.1 g $(NH_4)_2S_2O_8$ was added portion-wise into the beaker under vigorous stirring. After 24 h stirring, the synthesized composites were separated by a magnet and washed thoroughly with Milli-Q water, and then dried in vacuum at 50 °C [2].

Calculation of adsorption capacity

The adsorption capacity (Q, mmol g^1) of the nanocube Zn-MOFs at saturation was deduced by the following equation;

$$Q_e = \frac{(C_o - C_e)\, V}{m} \qquad \text{(S1)}$$

Where Q_e is the adsorbed amount at saturation time t, V is the solution volume (L), m is the mass of nanocube Zn-MOFs adsorbent, C_0 (mg/L) is the initial concentration of adsorbate in the solution, and C_e (mg/L) is the concentration of adsorbate in the solution. The removal efficiency, R (%), and adsorption capacity for MG, q (mg/g), are respectively expressed using the following equations:

$$R(\%) = \frac{C_0 V - C_t V}{C_0 V} \times 100 \qquad \text{(S2)}$$

For evaluating the Langmuir isotherm, the equation (S3) was used

$$Ce/qe = 1/q_m K_L + Ce/q_m \quad (S3)$$

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), q_m is the maximum adsorption capacity of the adsorbent, K_L is the equilibrium constant, also known as the Langmuir constant or adsorption coefficient. The constants q_m and K_L are calculated by the plot of Ce/qe vs. Ce with slope $1/q_m$ and intercept $1/(q_m K_L)$.

For calculating the Freundlich isotherm, the equation (S4) was used

$$\ln q_e = \ln K_F + 1n \ln Ce \quad (S4)$$

K_F is the Freundlich constant or adsorption capacity, n is the Freundlich exponent, representing surface heterogeneity. K_F and n can be calculated from a linear plot of ln q_e vs. ln C_e.

The Temkin isotherm was determined using the equation (S5) was used

$$q_e = \beta_T . \ln K_T + \beta_T \ln Ce \quad (S5)$$

Where β_T and K_T is a Temkin isotherm constant. The parameters β and K_T can be determined by the plot of q_e *vs*. ln Ce

$$\log(q_e - q_t) = \log(q_e) - k_1.t /2.303 \quad (S6)$$

Where qe is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium. qt is the amount of adsorbate adsorbed per unit mass of adsorbent at time t. k1 is the rate constant of the pseudo-first-order adsorption process. The plot of log (q_e - q_t) against t gives a straight line with the slope K_1 and intercept ln q_e.

$$t/qt = 1/K^2 qe^2 + t/qe \quad (S7)$$

Values of K_2 and q_e for different initial concentrations of dye were calculated from the slope and intercept of the linear plot of t/q_t *vs.* t

To explore the adsorption process of MDLZ for CR, NR, and CV dyes in different environments, the effect of pH, initial concentration of dye (20-1000 mg/L), MDLZ dose (5-50 mg), temperature (293-333 K), on the adsorption capacity were evaluated.

$$Kc = Ce/qe \qquad \text{(S8)}$$

Kc is Three control groups were established in all the experiments to ensure the reliability of the experimental data. (i.e., the standard enthalpy change, ΔH^o, the standard free Gibbs energy, ΔG^o, and the standard entropy change, ΔS^o).

$$\Delta G^o = - RT \ln K_c \qquad \text{(S9)}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad \text{(S10)}$$

Therefore, the van't Hoff equation becomes:

$$\ln K_c = - \Delta H^o/RT + \Delta S^o/RT \qquad \text{(S11)}$$

The value of standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) for the adsorption process are thus determined from the slope and intercept of the plot of $\ln K_c$ *vs.* 1/T.

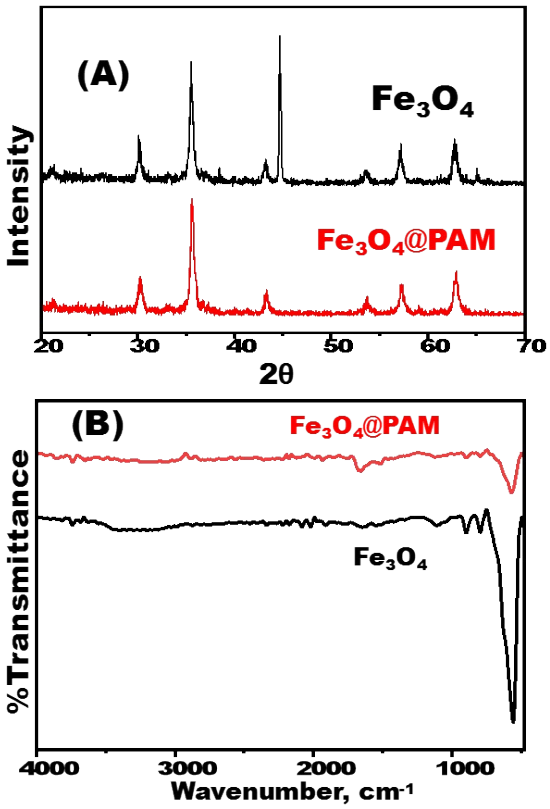

Figure S1. The magnetite Fe_3O_4 and Fe_3O_4@PAM (A) PXRD diffraction patterns . B) FTIR spectra of magnetite Fe_3O_4 and Fe_3O_4@PAM.

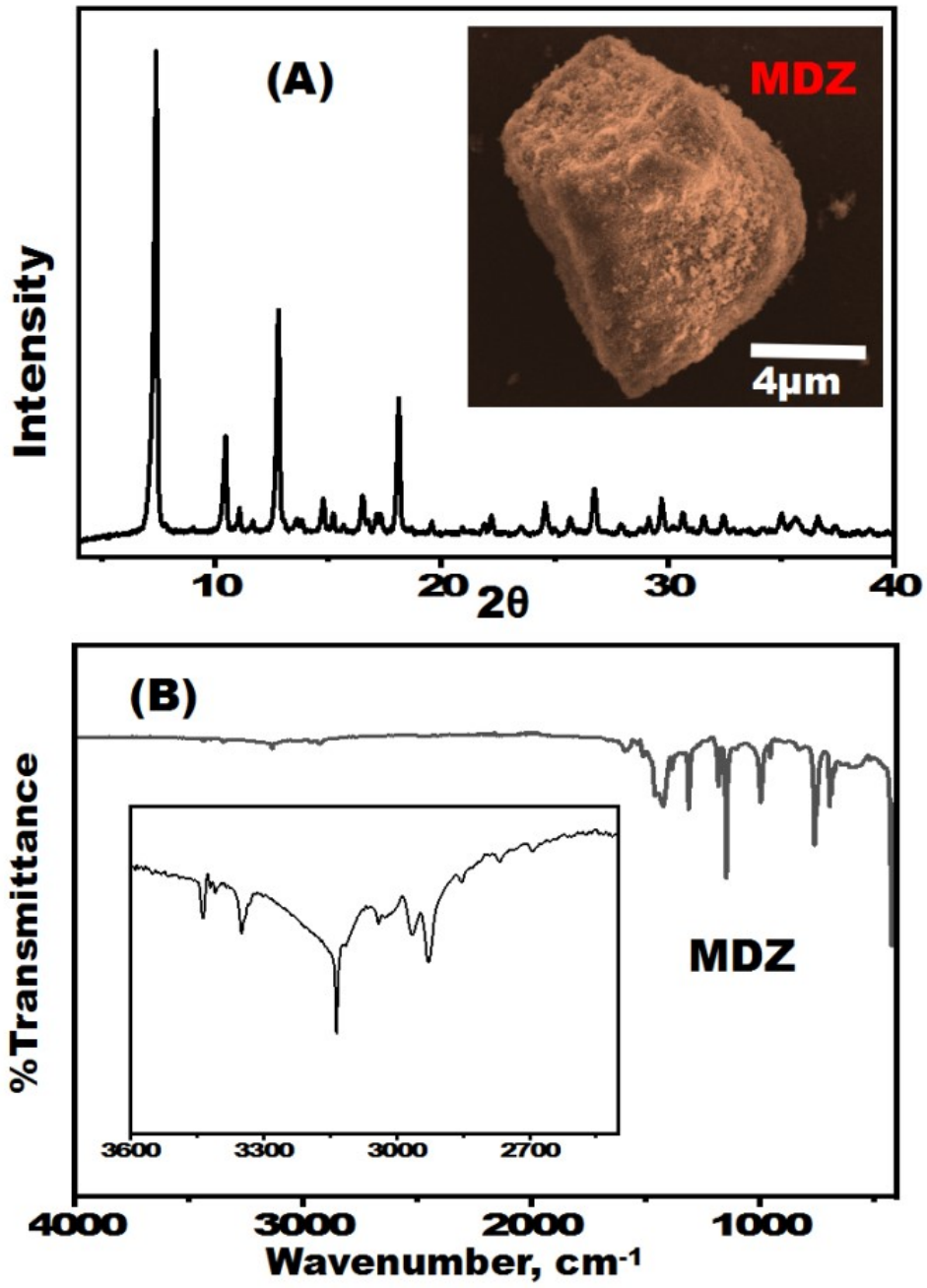

Figure S2. FTIR spectra of the microporous nanocubic Zn-MOFs and magnetite MDLZ adsorbents.

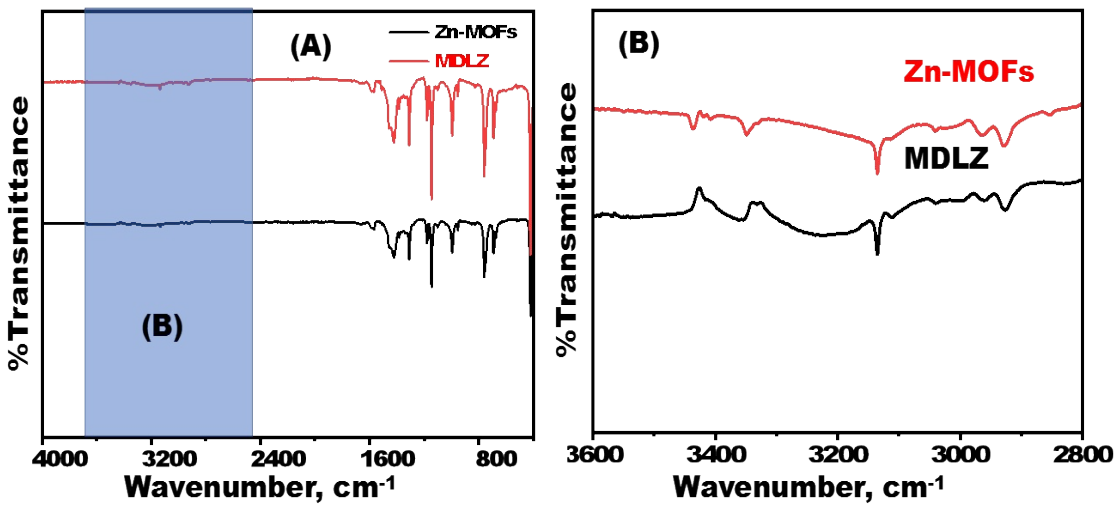

Figure S3. The magnetite doped Zn-MOFs (MDZ) (A) PXRD diffraction patterns MDLZ nanocubes and (Inset) FESEM image of cubic MDZ . B) The full FTIR spectra of the nanocubes MDZ.

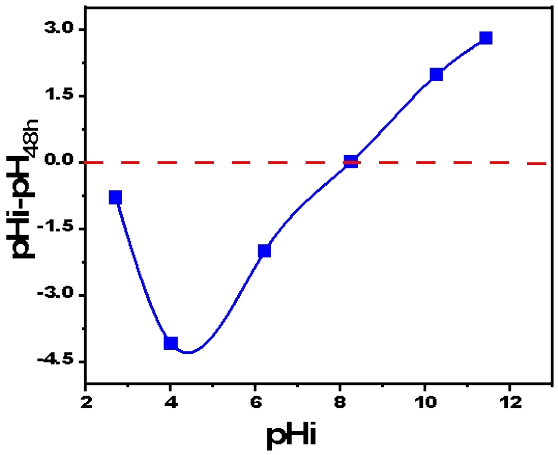

Figure S4. Variations in pH for to identify the isoelectric point of MDLZ magnetic nanocubes adsorbent.

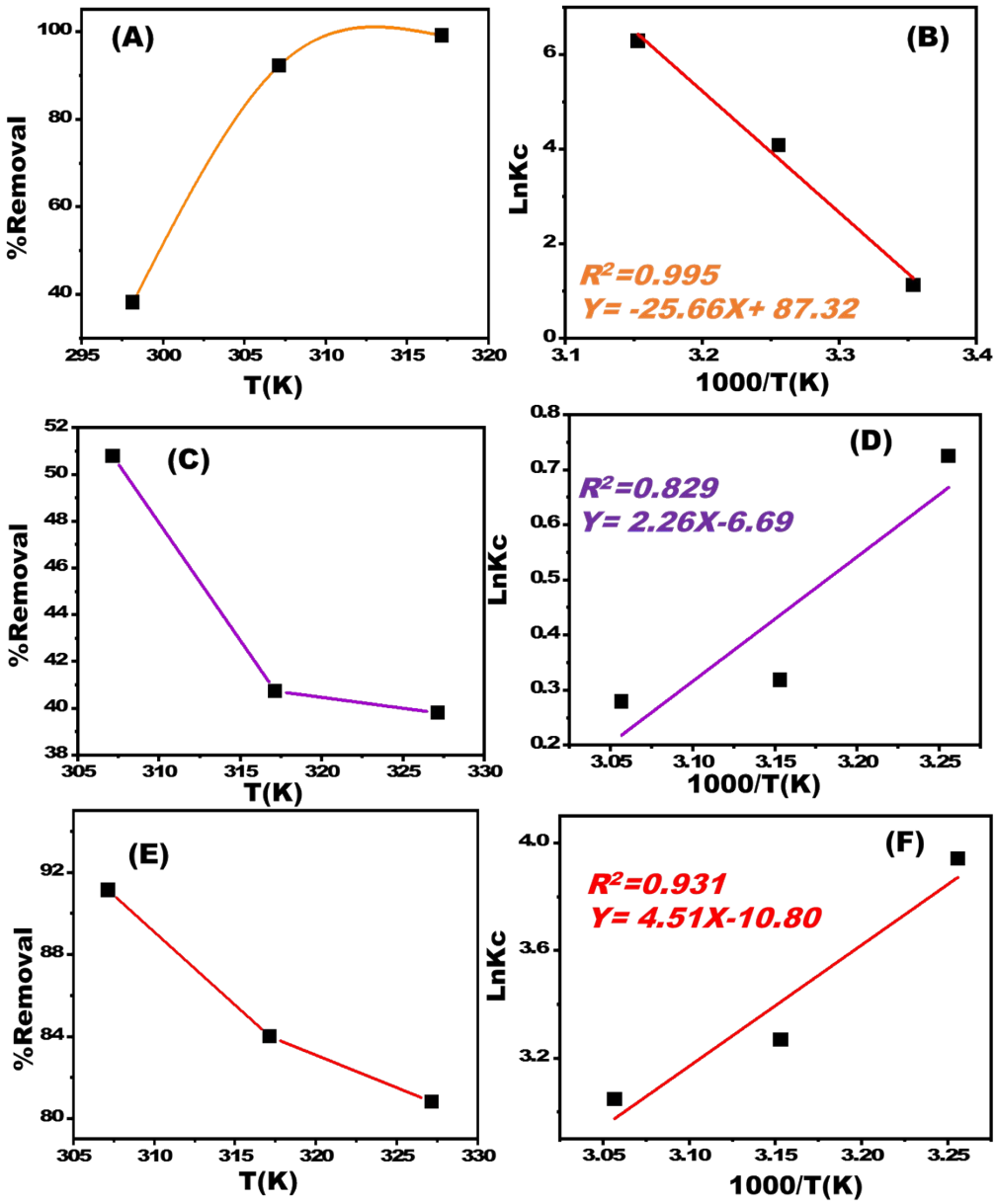

Figure S5. A) Time-dependent dye adsorption of MDLZ nanocubes in different temperature intervals (25°, 40°, and 60°C). Thermodynamic parameters were calculated by plotting ln kc versus 1/T (B) under optimum conditions.

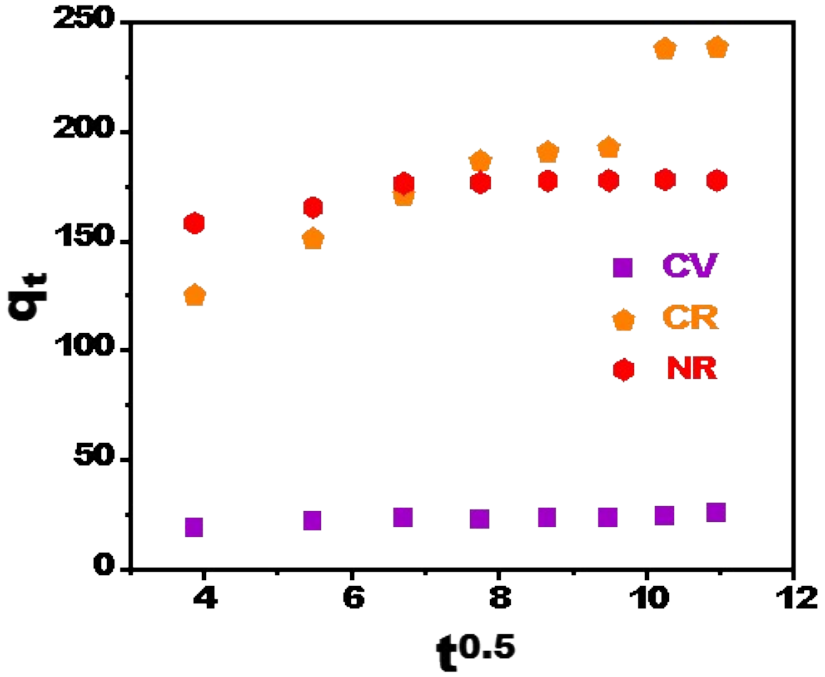

Figure S6. Modeling of uptake kinetics for CV, CR, and NR dyes with simplified model of resistance to intraparticle diffusion (Morris and Weber equation).

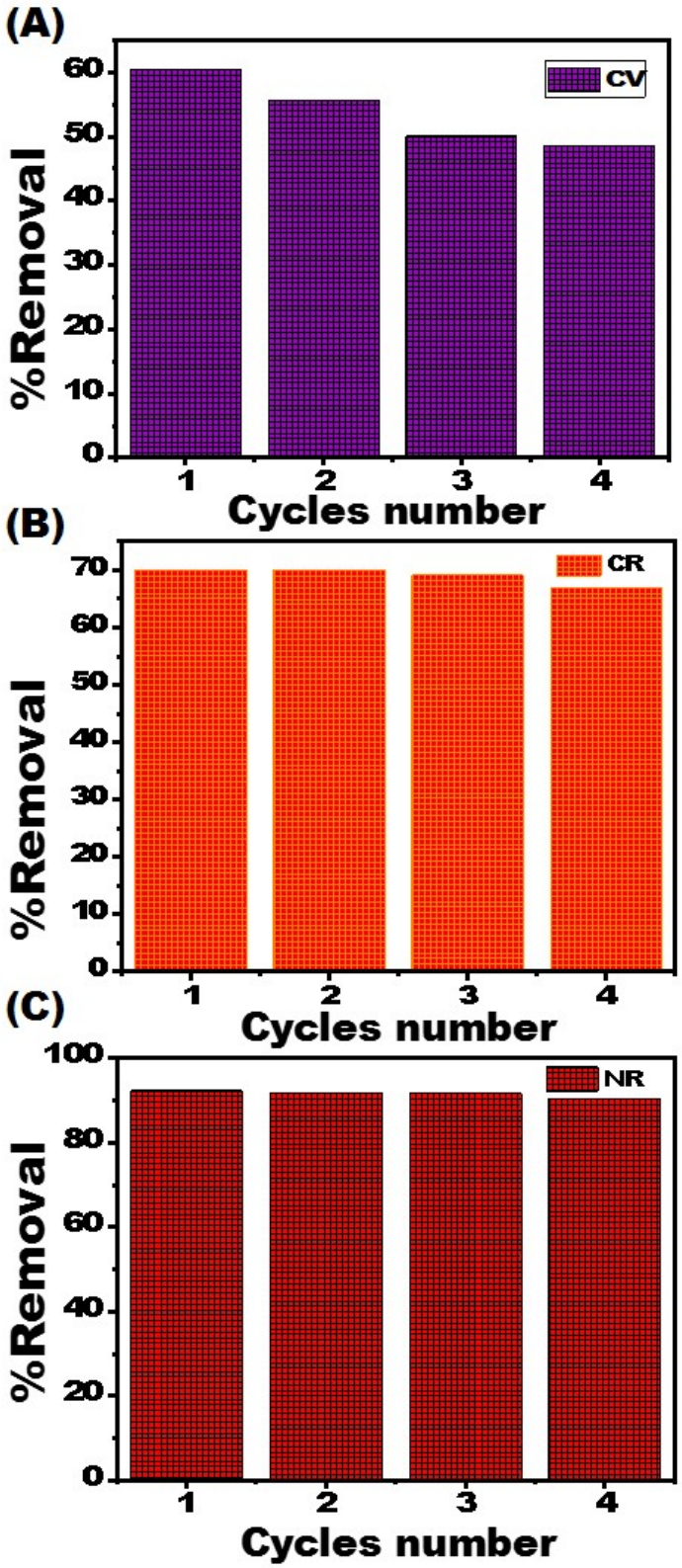

Figure S7. The adsorption, elution and regeneration of nanocubes MDLZ adsorbent for multiple cycles of A) CV, B) CR, and C) NR dyes.

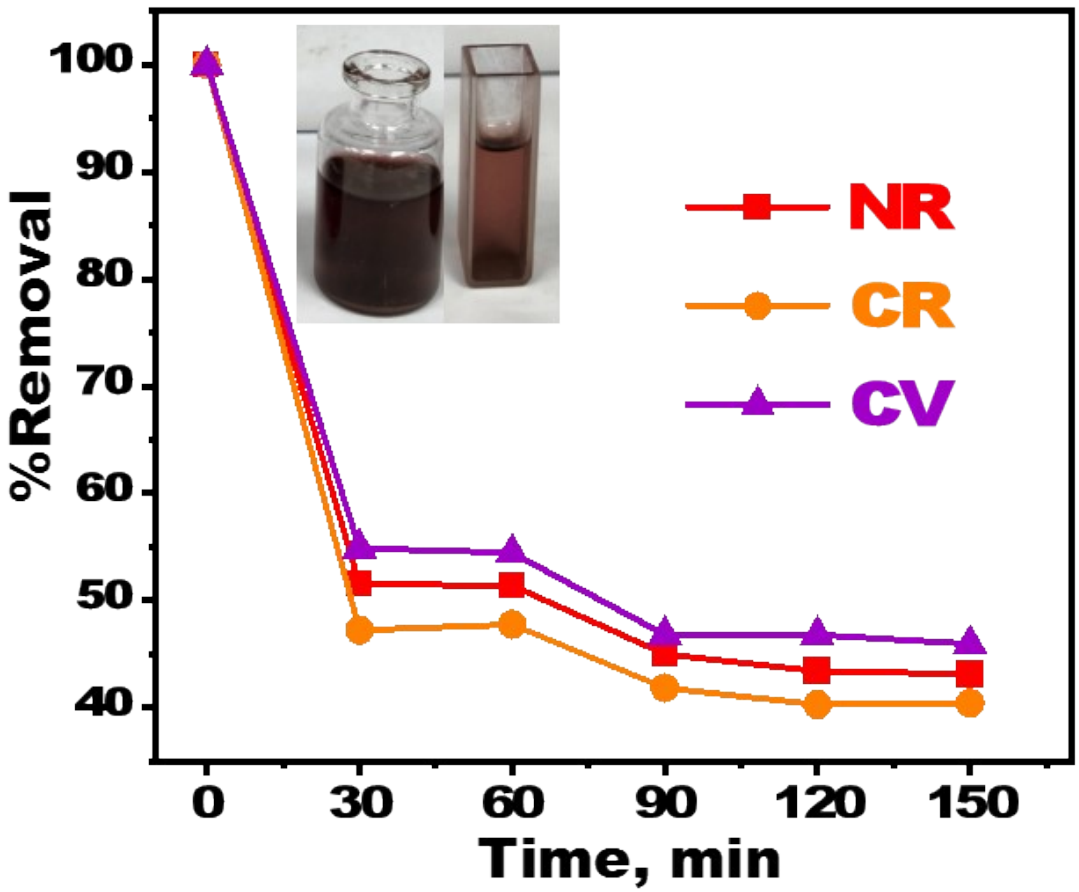

Figure S8. The adsorption of multiple dyes using nanocubes MDLZ adsorbent in simulated solution containing different concentration of cationic and anionic dyes.

References

1. A.H. El-Sheikh, F.S. Nofal, M.H. Shtaiwi, Adsorption and magnetic solid-phase extraction of cadmium and lead using magnetite modified with schiff bases, J Environ Chem Eng. 7 (2019) 103229. https://doi.org/10.1016/j.jece.2019.103229.

2. W. Song, M. Liu, R. Hu, X. Tan, J. Li, Water-soluble polyacrylamide coated-Fe3O4 magnetic composites for high-efficient enrichment of U(VI) from radioactive wastewater, Chemical Engineering Journal. 246 (2014) 268–276. https://doi.org/10.1016/j.cej.2014.02.101.