Ultrasonic enhancement of the simultaneous removal of quaternary toxic organic dyes by CuO nanoparticles loaded on activated carbon: central composite design, kinetic and isotherm study

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Abstract

Copper oxide nanoparticles loaded on activated carbon (CuO-NPs-AC) were prepared and fully analyzed and characterized with FE-SEM, XRD and FT-IR. Subsequently, this novel material was used for simultaneous ultrasound-assisted adsorption of brilliant green (BG), auramine O (AO), methylene blue (MB) and eosin yellow (EY) dyes. Problems regard to dyes spectra overlap in quaternary solution of this dyes were omitted by derivative spectrophotometric method. The best pH in quaternary system was studied by using one at a time method to achieved maximum dyes removal percentage. Subsequently, sonication time, adsorbent dosage and initial dyes concentrations influence on dyes removal was optimized by central composite design (CCD) combined with desirability function approach (DFA). Desirability score of 0.978 show optimum conditions set at sonication time (4.2 min), adsorbent mass (0.029 g), initial dyes concentration (4.5 mg L⁻¹). Under this optimum condition the removal percentage for MB, AO, EY and BG dyes 97.58, 94.66, 96.22 and 94.93, respectively. The adsorption rate well fitted by pseudo second-order while adsorption capacity according to the Langmuir model as best equilibrium isotherm model for BG, MB, AO and EY was 20.48, 21.26, 22.34 and 21.29 mg g⁻¹, respectively.

Keywords: Auramine-O, Brilliant green, eosin yellow, central composite design, copper oxide nanoparticle, methylene blue, ultrasound-assisted adsorption

1. Introduction

Organic dyes widely present in wastewater of textiles, paper, plastics, leather, food, antiseptics, cosmetics, fungicides following entrance to the aquatic environment [1-3] cause toxicity, carcinogenicity and mutagenic points [2, 4-6]. Therefore, their removal from wastewater is great demand and achieved by application of conventional physicochemical, chemical and biological principles that classified to coagulation and flocculation [7], adsorption [8], biosorption [9], electrochemical techniques [10] and fungal decolonization [11], while more diversity is possible in adsorption [12]. The simple design, nontoxic and low cost adsorbents, low treatment cost and mild conditions are criterion for selection of best mode and adsorbent in this approach [13]. Growing researches interest and effort lead exporting carbon-based materials that simply were modified by novel nanoscale materials. This combination is associated with enhance in surface area porosity and rate of mass transfer [14-16]. AC as sole adsorbent due to presence of nan-localized π electrons and also fictional reactive centers like OH, COOH, NH_2 and amide group seems to attract various species through π - π , hydrogen bonding and charge electrostatic force deepened on working pH [17, 18]. On the other hands, compounded like CuO nanoparticles eagerly like to bind on AC surface through binding copper center to the functional group or non-localized M-electron through ion dipole interaction, while presence of its oxygen reactive center also favor loading process through hydrogen bonding via hard-hard interaction [18, 19]. Therefore, it seems and expectable that CuO-NP-AC has greater and favorable reactive sites toward AC and/or CuO-NP as sole adsorbent. Probable back distribution of copper (ions and atoms) to environments do not generate harmful problem for living things is related to its high threshold limit suggested by world health organization (WHO) [20-22].

Procedures using ultrasonic waves are very efficient at removing chemicals and eliminating toxic contamination. Therefore, techniques using hybrid ultrasonic waves, together with other methods such as adsorption process are the most common uses of ultrasonic waves [23-25]. In this case the using of ultrasound waves its well-known to accelerate chemical process due to the phenomenon of acoustic cavitation, that is, the formation, growth and collapse of micrometrical bubbles, formed by the propagation of a pressure wave through a liquid [26]. As well as, ultrasound waves and its secondary effect, cavitation (nucleation, growth and transient collapse of tiny gas bubbles) improve the mass transfer and breaking the affinity between adsorbate and adsorbent through convection pathway that is emerged from physical phenomena without significant change in equilibrium characteristics of the adsorption/desorption system [27-29].

Simultaneous removal of dyes due to their absorption peak overlap is big problem that limit the simultaneous clean up procedures. The derivative spectrophotometric are good choice that cope with these problems [30, 31].

Experimental design methods widely used as the efficient way for modeling, analyzing and interpreting experimental data. This method permits efficient optimization and give useful subject about individual and cooperation contribution as main and interaction on response. As well as, improve characteristics performance with at least number of experiments while minimize error of experiments [32, 33].

In this work, the Copper oxide nanoparticles loaded on activated carbon (CuO-NPs-AC) synthesized and characterized via FE-SEM, XRD and FT-IR. Subsequently, simultaneous ultrasonic assistant removal performance of prepared adsorbent was investigated for BG, MB, EY and AO dyes at various operating conditions by bath method. Central composite design was used for optimization of variables (sonication time, initial dyes concentration and amount of adsorbent) and dyes spectra overlap in quaternary solution was resolved following application of first and second order derivative spectrophotometry. Kinetics and equilibrium study of adsorption reveal suitability of second order kinetic model and Langmuir model for good and efficient prediction of experimental data.

2. Experimental method

2.1. Synthesis of CuO nanoparticles loaded on AC

NH₄OH solution was purchased from Chem. lab company, (Cu(CH₃COO)₂·2H₂O), and activated carbon (AC) were purchased from Merck company, Dernasdat Germany. The reaction solution for CuO nanoparticles preparation is as follows: 5.0 mmol copper acetate solutions were mixed with 5.0 ml of fresh NH₄OH solution at pH= 10.4-10.7. Then, deionized water was added to the above solution to make total volume of 250 ml in a volumetric flask and 10.0 gr activated carbon (AC) was added to the mixture in Erlenmayer flask. CuO-NPs was homogenously loaded on AC after 3.0 hours stirring at 55-60°C. After 3 hours, CuO-NPs-AC were filtered and several time was washed with deionized water and dried at 70°C for 48 h.

2.2. Ultrasonic assisted dyes adsorption experiment

The simultaneous ultrasonic assisted adsorption of BG, EY, MB and AO (these dyes were purchased from Sigma Aldrich company) in quaternary solution onto CuO-NPs-AC was carried out in a batch method as follow: 50 mL of 4.5 mg L⁻¹ of dyes solution at pH 6.0 (The pH/Ion meter model-686 (Metrohm, Switzerland, Swiss) was used for pH

adjustment) was mixed thoroughly with 0.03 g of CuO-NPs-AC in erlenmayer flask and immersed in an ultrasonic bath (ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System) at 40 kHz of frequency and 130 W of power was used for the ultrasound-assisted adsorption) for 4.5 min at room temperature. Finally, the sample was centrifuged and the spectrum of dyes in the effluent solutions was record by Jasco UV-Vis spectrophotometer model V-530 (Jasco, Japan). All of experimental was performed 2.0 time. Then dyes removal percentage (R %) and adsorption capacity (Qe) was calculated according to below equations [14-16]:

$$R\% = \frac{C_{0i} - C_{ei}}{C_{0i}} \times 100 \quad (1)$$

$$q_i = \frac{V(C_{0i} - C_{ei})}{M} \quad (2)$$

where $C_{0,i}$ and $C_{e,i}$ are the initial and final concentrations (mg L^{-1}) of dye i in the ternary solution, respectively, V is the volume (L) of dyes solution used for the adsorption experiments, and M is the mass (g) of adsorbent [3, 28].

Equilibrium adsorption isotherm studies are required to give useful information about mechanism, confirm the accuracy of our results, calculate the theoretical maximum adsorption capacity and tendency of adsorbent toward each operating adsorb [25]. As well as, adsorption kinetics is an important step to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction [34, 35]. Therefore, the adsorption kinetics and isotherms of understudy dyes removal on this adsorbent at optimal condition was investigated and its applicability for treatment of wastewater and these dyes removal was investigated.

2.3. Analytical measurements

Concentrations of dyes were determined by finding out the absorbance at the characteristic wavelength using a Jasco UV-Vis spectrophotometer model V-530 (Jasco, Japan). A standard solution of the dye was taken and the absorbance was determined at different wavelengths after analysis of derivative spectrophotometric method. This wavelength was used for preparing the calibration curve between absorbance and the concentration of the dye solution. The calibration plot showed a linear variation up to 10 mg L^{-1} of each dyes.

2.4. Central composite design

The simultaneous optimization as must useful way is superior to one variable at a time in term of lower number of experiments and cost while able to estimate the main effect and variables interaction. Therefore, central composite design method as a simultaneous optimization method using STATISTICA 10.0 software consists of $2f$ factorial points, $2f$ axial points (f is the number of factors) and N_C central points was used to evaluate the optimization conditions, interaction and main effect of studied variables. In this case, the center points are usually repeated to get a good estimate of experimental error (pure error) and the reproducibility of the data and the axial points are located at distance of α from center and make the design [36]. Present central composite design is based on various parameters including sonication time (X_1), adsorbent dosage (X_2), concentration of MB (X_3), concentration of AO (X_4), concentration of EY (X_5) and concentration of BG (X_6), into five levels (low, central and high) with coded value (-1, 0, 1) and the starting points of +2.37 and -2.37 for $+\alpha$ and $-\alpha$, respectively, are shown in Table 1. The design matrix and the responses for the four dyes are shown in the Table 2. The analysis of variance (ANOVA) related to CCD (statistical technique) is efficient to evaluate the significance levels of parameters, multiple correlation coefficient R^2 , adjusted and predicted R^2 values and F- value of model. Subsequently, the second-order polynomial model consists of all main effects, all two-factor effects and all curvature effects were fitted as follow [37]:

$$R = \beta_0 + \sum_{i=1}^6 \beta_i X_i + \sum_{i=1}^6 \sum_{j=1}^6 \beta_{ij} X_i X_j + \sum_{i=1}^6 \beta_{ii} X_i^2 \quad (3)$$

where R is the response; X_i 's and X_j 's are the independent variables; β_0 is the model constant; β_i is the linear coefficient; β_{ii} is the quadratic coefficient and β_{ij} is the cross-product coefficient, while three-dimensional (3D) plots permit quantification of interpretation of the interactions of variable and determination of the best operating process conditions. As well as, diagram for predicted values and desirability based on desirability function approach in central composite design gives information about the quality and acceptance of the process. It is easy to understand and use. Moreover the desirability profile is able to obtain qualitative and quantitative response by simple and rapid transformation for each measurement [38, 39].

Table 1. &Table 2.

3. Results and discussion

3.1. Physicochemical characterization of adsorbent

The morphology of the nanoparticles was observed by field emission scanning electron microscopy (FE- SEM: Hitachi S- 4160) under an acceleration voltage of 15 KV. Fourier transform infrared (FT-IR) spectrum was recorded using a Perkin Elmer-Spectrum RX-I FTIR spectrometer in the range of 300–4000 cm^{-1} and X-ray diffraction (XRD) pattern was recorded by an automated Philips X'Pert X-ray diffractometer (40 kV and 30 mA) for 2θ values over 20–60°.

FT-IR spectrum of CuO-NPs-AC in the range of 300–4000 cm^{-1} (Fig. 1a) was recorded and it was seen that exhibits a large broad band at 3000–3400 cm^{-1} correspond to O–H bond stretching of surface active carbon and the presence of peak at around 1100 cm^{-1} corresponds to the vibrational mode of H–O–H and at around 1600 cm^{-1} is due to H–O–H bending [40]. The vibration peak of the Cu–O bond was observed at 445 and 524 cm^{-1} that this peak indicates successful synthesis of under study adsorbent. The broad and weak absorption peaks in the range of 1500–3500 cm^{-1} as could be related to the stretching and bending vibration modes of trace amounts of adsorbed H_2O in CuO lattice [41].

The structural analysis of CuO-NPs-loaded on AC over diffraction angle 2θ from 10° to 80° was shown in Fig. 1b. As it was found, two diffraction peaks at about $2\theta = 35.54^\circ$, and 38.74° are correspond to the (002), and (111) lattice planes of the monoclinic structure of CuO particles has good agreement with (JCPDS, no. 45-0935) [40]. The observed broad peak at $2\theta = 20\text{--}27^\circ$ as well as a broad peak at $2\theta = 43^\circ$ is related to the amorphous nature of activated carbon particles as good support for loading CuO nanoparticles. Insertion of full width at half-maximum (FWHM) of (111) peak to the Debye-Scherrer equation [42] suggest the average size of CuO nanoparticles was about 11.5 nm that confirm polycrystalline grain each feature in FE-SEM of Fig.1b. The surface morphology and size of the CuO-NPs-AC with FE-SEM (Fig. 2) reveals approximated that the particles are almost spherical in nature which is free from agglomeration. Further it is observed that nano structure with size in the range of 50–100 nm while SEM image of CuO-NPs loaded on AC (Fig.2b) shows a homogeneous distribution of CuO nanoparticles on to surface of activated carbon.

Fig. 1 & 2

3.2. Analysis of quaternary solutions by derivative spectrophotometry

Absorbance spectra of single solutions of BG, AO, EY and MB (all at 10 mg L^{-1}) and their quaternary solution (Fig. 3) show their spectra overlap. The above mention limitation simply can be overcome by to use the derivatives spectrophotometry. Subsequently, the dyes content determination in their mixture solution (after and/or before removal) required construction of preliminary calibration curve. Therefore, first and second order derivative of spectra of individual BG, AO, EY and MB in single solution was drawn (Fig. 4). Then, the proper wavelength which the value of the first and sequined order derivative of three of dyes spectrum is zero was found. Thus, the first and sequined order derivative spectrum of the quaternary solution at these wavelengths would correspond to other dye. According to this explanations (Fig. 4a, first order derivative spectrum) can be observed which at wavelengths of 692 nm value of the first order derivative of BG, AO and EY spectrum is zero. This observation confirm that this wavelength is suitable for the determination of the MB concentration. This protocol was contributed to select best wavelength for accrue monitoring of other dyes at second order derivative (Fig 4b). According to the Fig. 4b, the wavelengths of 391 and 599 nm are suitable for quantification of AO and BG, respectively. Proper wavelength for EY determination was 515 nm, without overlap with other dyes spectrum.

To obtain the appropriate wavelength for dyes content measurements derivatives spectra at different concentrations was undertaken and result is shown in Fig. 5. Subsequently, at suitable wavelength calibration curve was depicted and appropriate correlation coefficient (R^2) shows the efficiency and suitability of each wavelength for dyes quantification.

Fig. 3, 4 & 5

3.3. Effect of pH

The adsorption of dyes is combination of various mechanism vis. ion exchange, hydrogen bonding, Van der Waals force, electrostatic (dye anion and positive support and dyes cation and negative support), soft-soft and dipole-ion interaction [26, 27, 43]. In this work, effects of initial solution pH on the dyes adsorption over CuO-NPs-AC surface were investigated in the range of 2-8 and result are shown in Fig. 6. As seen, at lower pH due to probable protonation of dyes and/or appearance of positive charge on adsorbent via electrostatic repulsive force, hinder and also subsequent mass transfer to the adsorbent surface. In other hand at an acidic pH condition, the hydroxyl and carboxyl groups on the surface of the AC are protonated and they inhibit the binding of the dyes. The excess H^+ ions compete with the dyes for the adsorption sites. The maximum removal was observed at pH of 6.0 and thereafter

simultaneous removal decreases with increase in pH. At pH 6, deprotonating of dyes and surface groups lead to enhance in their mass transfer improvement. While at high pH from 6 to 10, more OH⁻ ions present and compete with the dyes for the adsorption sites of CuO-NPs-AC, thus the available adsorption sites for dyes decrease. Appreciable amount of adsorption in this pH range suggests involvement of physical forces such as hydrogen bonding and Van der Waals force in the adsorption process [44]. Both at high acidic and basic media, expected instability of CuO-NPs lead to reduce in dyes removal percentage and subsequently life time and reusability of adsorbent. Therefore, pH 6 was selected for other experimental.

Fig. 6

3.4. Analysis of central composite design

Analysis of central composite design start with analysis of variance for R₁-R₄ (Table 3). As seen that very low p-value (<0.0001) implied highly significant of model for prediction of data concern to simultaneous removal of BG, AO, MB and EY dyes within 95% confidence interval [45]. The "Lack of Fit F-value" of this model for simultaneous removal of MB, AO, EY and BG is 1.146, 1439, 2.763 and 1.704, respectively, and support that lack of fit is not significant relative to the pure error. Moreover, not-significant lack of fit confirm model efficiency for good prediction of behavior of simultaneous removal of BG, AO, MB and EY dyes on CuO-NPs-AC. The value of multiple correlation coefficient R², adjusted and predicted R² for simultaneous removal of BG is 99.67, 99.18 and 99.12, AO is 99.29, 98.53 and 98.20, MB is 97.87, 94.35 and 94.15 and EY is 98.64, 97.18 and 98.75. "Adeq. Precision" measurement for signal to noise ratio for MB, AO, EY and BG dyes 67.25, 52.97, 25.05 and 33.93, respectively, was greater than 4.0 that its confirm adequate signal [46]. These values confirm high efficiency of quadratic model for best predicting the performance of simultaneous adsorption of BG, AO, MB and EY dyes onto CuO-NPs-AC based on semi-empirical following equations:

$$R_1 = 98.73 + 1.71x_1x_1 + 48346.48x_2x_2 + 0.07x_3x_3 - 0.05x_6x_6 - 55.81x_2x_6 + 0.06x_3x_5 + 0.05x_4x_5 - 0.05x_4x_6 \quad (6)$$

$$R_2 = 14.97 - 7.8x_1 + 0.61x_1x_1 + 0.06x_3x_3 + 1.77x_5 + 0.04x_5x_5 + 2.1x_6 + 0.05x_6x_6 - 183.44x_1x_2 - 0.29x_1x_3 - 0.33x_1x_4 - 0.27x_1x_5 - 152.94x_2x_6 + 0.04x_3x_4 - 0.06x_3x_5 + 0.03x_3x_6 - 0.07x_4x_5 + 0.11x_4x_6 - 0.03x_5x_6 \quad (5)$$

$$R_3 = 88.0 - 10.6x_1 + 0.6x_1x_1 + 2140.6x_2 - 30169.2x_2x_2 - 1.1x_3 - 0.03x_3x_3 - 1.2x_4 - 0.1x_5 - 0.025x_5x_5 - 0.045x_6x_6 + 175.3x_1x_2 + 0.1x_1x_5 + 0.3x_1x_6 - 40.1x_2x_6 - 0.029x_3x_4 - 0.046x_3x_5 + 0.1x_4x_5 + 0.043x_4x_6 \quad (7)$$

$$R_4 = 113.2 - 12.4x_1 - 4.7x_4 + 2.4x_5 - 4.8x_6 + 505.3x_1x_2 - 0.3x_1x_3 + 0.3x_1x_4 - 0.3x_1x_5 + 0.3x_1x_6 - 86.6x_2x_3 + 90.6x_2x_4 - 90.4x_2x_5 + 96.7x_2x_6 + 0.1x_3x_4 + 0.1x_3x_5 + 0.1x_3x_6 + 0.1x_4x_6 - 0.0346x_5x_6 \quad (4)$$

The another convenient expression of Eq. 4-7 was also expressed by comparing simultaneous removal percentage of dyes between experiment and model predicted value (Fig. 7). According to these plots good agreement between experimental and calculated value of dyes adsorption data was found [25].

Table 3

Fig. 7

The profile desirable responses for removal percentage of all dyes by assigning predicted values was shows in Fig. 8. In the desirability function method the coded of 0.0 (undesirable), 0.5 (middle desirable) and 1.0 (very desirable) was used [47] which in this work values of this coded (low, middle and high removal percentage for each dye) were obtained of Table 3. Desirability of 1.0 (target value) was use for compression of the overall response (Fig. 8) to obtained the best operation condition. The current level of each variable in the model was depicted at the bottom of Fig. 8. Desirability score of 0.978 show optimum conditions set at sonication time (4.2 min), amount adsorbent (0.029 g), initial dyes concentration (4.5 mg L⁻¹). Under this optimum condition the removal percentage for MB, AO, EY and BG dyes 97.58, 94.66, 96.22 and 94.93, respectively.

Fig. 8

3.5. Effects of variables and interactive variables on removal %

The experimental design based on central composite interactions, contour and 3D surface plots are used for achieved to gust the effect of variables and their interaction [26, 34]. In this work, 3D surface plot was selected for this end and obtained figures are shown in Fig. 9.

Typically the effect of adsorbent dosage on the removal percentage MB (Fig. 9a) show that at lower adsorbent dosage, their removal percentage significantly decreased because of the unbalancing the MB molecules to vacant

sites of CuO-NPs-AC ratio. Enhance in magnitude of adsorbent lead to rapid raising in dyes adsorption and can be attributed to greater specific surface area and availability of more adsorption sites.

Typically the effect of sonication time on the percentage removal of BG in quaternary solution (Fig. 9b) reveal that the maximum adsorption of BG dye could be achieved in short sonication time that strongly support high contribution of ultrasound power in mass transfer. This indicates that rate of adsorption is very fast because of high available surface area and vacant sites of adsorbent is enhanced by ultrasonic power. The mass transfer due to raising diffusion coefficient encounter enhance in rate. These figure also show occurrence of more than 95% of BG removal in the first 4.5 min as short time.

Typically, the effect of initial dyes concentration on the removal percentage of MB, BG and AO (Fig.9a, b and c, respectively) reveal that at lower concentrations of dyes due to low ratio of solute concentrations to adsorbent sites a high removal percentage was observed. The opposite correlation at higher dyes concentrations is emerge the saturation of adsorption sites. This results indicates that the quaternary adsorption of the understudy dyes onto CuO-NPs-AC immensity depends on their initial concentration.

Fig. 9

3.6 Adsorption equilibrium study

The adsorption isotherm indicates how molecules of adsorbate are partitioned between the adsorbent and liquid phase at equilibrium as a function of adsorbate concentration. In this work, equilibrium adsorption isotherm models such as Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin isotherms in different range of adsorbent mass and initial concentration of each dyes while other parameter was concept at optimum conditions were used to obtained useful information about mechanism and accuracy of our results, calculate the theoretical maximum adsorption capacity and tendency of adsorbent toward each adsorbate, and result are summarized in Table 4.

In the linear form of Langmuir isotherm model, values of K_L (the Langmuir adsorption constant ($L\ mg^{-1}$)) and Q_m (theoretical maximum adsorption capacity ($mg\ g^{-1}$)) were obtained from the intercept and slope of the plot of C_e/Q_e versus C_e , respectively (Table 4). This model was applied to describe quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent [3].

In the Freundlich isotherm model, parameters such as n (the capacity and intensity of the adsorption) and K_F (indicator of adsorption capacity ($(mg\ g^{-1})/(mg\ L^{-1})^{1/n}$)) were calculated from the slope and intercept of the linear

plot of $\ln Q_e$ versus $\ln C_e$, respectively. This model was applied to describe the adsorption characteristics for the heterogeneous surface [48].

In the **Temkin** isotherm model, B is the **Temkin** constant related to heat of the adsorption (J mol^{-1}), T is the absolute temperature (K), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and K_T is the equilibrium binding constant (L mg^{-1}). This model was applied until heat of the adsorption and the adsorbent–adsorbate interaction were evaluated [14].

In the D–R isotherm model, $K(\text{mol}^2(\text{KJ}^2)^{-1})$ is a constant related to the adsorption energy, $Q_m(\text{mg g}^{-1})$ is the theoretical saturation capacity, $\mathcal{E}$ is the Polanyi potential. The slope of the plot of $\ln q_e$ versus $\mathcal{E}^2$ gives K and the intercept yields the Q_m value. This model was applied to estimate the porosity apparent free energy and the characteristic of adsorption [49].

According to Table 4, for all adsorbent dosage the lower correlation coefficient (R^2) of the Freundlich, Temkin and Dubinin-Radushkevich models in comparison to Langmuir model (~ 1), suggest that the removal process better modeled by monolayer compare to multilayer adsorption. This means that the adsorption of dyes takes place at specific homogeneous sites and as a mono-layer adsorption onto on the outer surface of CuO-NPs-AC.

Table 4

3.7 Adsorption kinetics study

A kinetic study of adsorption is necessary as it provides the information about the adsorption mechanism, which is crucial for the practicality of the process. In this work, the experimental kinetic data including pseudo first and second-order, Elovich, and intraparticle diffusion models in different range of adsorbent mass and sonication time while other parameter was constant at optimum conditions was applied (Table 5).

In the pseudo-first-order model (Lagergren model) q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg g^{-1}) and k_1 is the rate constant of pseudo first-order adsorption (g min^{-1}). In this model, plotting the values of $\log (q_e - q_t)$ versus t may give a linear relationship that k_1 and q_e values can be determined from its slope and intercept, respectively [50].

In the pseudo second-order model q_e , q_t , and t , have the same meaning as explained above. k_2 is the rate constants of pseudo second order sorption ($\text{g mg}^{-1} \text{ min}^{-1}$). This model can be followed by plotting the values of t/q_t versus t and probable linear relationship show that q_e and k_2 values can be determined from its slope and intercept, respectively [51].

In the intraparticle diffusion model, C value is related to the thickness of the boundary layer and K_{diff} is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$). In this model, by plotting the values of q_t versus $t^{1/2}$ the values of K_{diff} and C were calculated from the slope and intercept of respective line, respectively [52].

In the Elovich model, the q_t is a linear function of $\ln(t)$ where $1/\beta$ and $(1/\beta) \ln(\alpha\beta)$ would be obtained from the slope and intercept of the plot of the Elovich equation. The correlation coefficient values (R^2 closed to 1), support that the pseudo second order model is best one to analyze the present adsorption kinetic data.

The R^2 value (Table 5) for this model was far from the unity, which shows that the intraparticle diffusion model is not applicable. For all dyes in different adsorbent dosage, the calculated q_e values were mainly closer to the experimental data and the R^2 values for pseudo-second-order kinetic (~ 1) model were larger than that of pseudo-first-order model Elovich, and intraparticle diffusion models. This shows the suitability of the pseudo-second-order kinetic model for the understudy dyes removal over an entire sorption period.

Table 5.

3.8. Comparison of this adsorbent and method with other methods

Comparison of performance of the proposed method and this adsorbent with other methods and some adsorbents are summarized in Table 6. According to the Table 6, the proposed method (simultaneous removal of four dyes) has lower contact time than to the reported methods. On other hand, it was found that the contact time for obtained the higher removal percentage in the absence of ultrasonic waves (other method) is much more than when using ultrasonic power (our work). As well as, adsorption capacity for CuO-NPs-AC in comparison with all of the adsorbents applied in single solution are preferable and superior and shows satisfactory removal performance for all investigated dyes. Finally, the results indicated that the combination of ultrasound waves with CuO-NPs-AC as low cost and ease operated removal method has ability to improve the simultaneous dyes removal efficiency [47, 53, 54]

Table 6

4. Conclusion

In this work, rapid, sensitive and high capacity simultaneous ultrasound-assisted adsorption of BG, AO, MB and EY dyes in quaternary solution was performed onto CuO-NPs-AC. Spectra overlap between four dyes was omitted by

derivative spectrophotometric method. The influences of experimental parameters on the dyes removal percentages was investigated to achieved to the best optimum conditions correspond to adsorption process in quaternary system. Effect of pH was optimized using one-at-a-time method and other variables such as sonication time, adsorbent dosage and initial dyes concentrations was studied by CCD combined with DF. The interaction and main effect of above variables was estimated by ANOVA and 3D surface plots. The isotherm equilibrium data were best described by the Langmuir model. In addition, the kinetics models to describe experimental data points at various initial concentrations of adsorbate shows that successfully fitted to the pseudo-second-order kinetic model. The proposed method was revealed good potential in the efficient removal of this dyes from aqueous solution compared to several other adsorbents and method.

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Figur captions

Fig. 1. FT-IR spectrum of the prepared (a) and XRD patterns (b) of the prepared CuO-NPs-AC.

Fig. 2. FE- SEM images of the CuO (a) and CuO-NPs-loaded on AC (b)

Fig. 3. Absorption spectra of BG, AO, EY and EB in single and quaternary solutions (initial dye concentration for BG, AO, EY and MB was 10, 10, 10 and 10 mg L⁻¹, respectively).

Fig. 4. First (a) and sequined (b) order derivative spectra of BG, AO, EY and EB in single and quaternary solutions (initial dye concentration for BG, AO, EY and MB was 10, 10, 10 and 10 mg L⁻¹, respectively).

Fig. 5. The first (a) and sequined (b) order derivative response versus the BG, AO, EY and EB concentration in the range of 2 to 10 mg L⁻¹ at pH 6.

Fig. 6. Effect of pH on removal of quaternary solution of BG, AO, EY and MB at 10, 10, 10 and 10 mg L⁻¹, respectively, in range of 2–8.

Fig. 7. The Actual values versus the predicted data of normalized simultaneous removal of MB, AO, EY and BG.

Fig. 8. Profile for predicated values and desirability function for simultaneous removal percentage of BG, AO, EY and EB dyes

Fig. 9. Typical response surfaces plot for interaction of variables in responses.

Table 1. Experimental factors and levels in the central composite design.

Factors	unit	Surface factors				
		Levels			Star point	
		(Low)	(Central)	(High)	$\alpha = \pm 2.37$	
		-1	0	+1	$-\alpha$	$+\alpha$
(X ₁) Sonication time	min	3	3.5	4	2.72	4.28
(X ₂) Adsorbent dosage	g	0.023	0.025	0.027	0.022	0.028
(X ₃) Initial MB Concentration	mg L ⁻¹	4	6.5	9	2.6	10.4
(X ₄) Initial AO Concentration	mg L ⁻¹	4	6.5	9	2.6	10.4
(X ₅) Initial EY Concentration	mg L ⁻¹	4	6.5	9	2.6	10.4
(X ₆) Initial BG Concentration	mg L ⁻¹	4	6.5	9	2.6	10.4

Runs	Block	X ₁	X ₂	X ₃	X ₄	X ₅	X ₅	R ₁ %	R ₂ %	R ₃ %	R ₄ %
1	1	3	0.023	9	9	9	9	94.35	91.97	92.83	94.62
2	1	3.5	0.025	6.5	6.5	6.5	6.5	99.9	95.3	96.97	98.27
3	1	3.5	0.025	6.5	6.5	6.5	6.5	99.93	95.13	95.55	97.69
4	1	4	0.027	4	9	9	4	107	98.76	99.22	101.5
5	1	4	0.023	9	9	4	9	93.71	94.97	95.31	94.31
6	1	2.3	0.025	6.5	6.5	6.5	6.5	97.82	93.45	97.32	97.38
7	1	4	0.027	9	4	9	4	100.15	103	97.69	102.12
8	1	3.5	0.025	6.5	12.5	6.5	6.5	98.72	91.77	95.24	98.06
9	1	3	0.027	4	9	4	4	104.88	97.14	103.47	99.98
10	1	4	0.023	9	9	9	4	94.53	90.86	94.2	97.29
11	1	3.5	0.025	6.5	6.5	6.5	6.5	99.24	94.91	96.27	97.83
12	1	3.5	0.025	6.5	6.5	6.5	6.5	98.99	95.49	96.19	98.07
13	1	3	0.023	9	4	4	9	91.96	93.18	95.37	93.51
14	1	3	0.027	9	9	4	9	99.21	97.91	98.52	97.17
15	1	4	0.027	9	9	9	9	102.88	95.62	96.04	100.44
16	1	3	0.027	9	9	9	4	99.68	97.79	98.79	102.15
17	1	4	0.023	4	4	9	4	102.29	99.19	94.75	96
18	1	3.5	0.02	6.5	6.5	6.5	6.5	90.5	88.32	90.74	92.41
19	1	3	0.023	9	9	4	4	92.12	91.72	95.68	95.79
20	1	3.5	0.025	6.5	6.5	6.5	6.5	99.87	95.84	95.99	97.44
21	2	3.5	0.025	6.5	0.55	6.5	6.5	101.06	98.59	97.58	97.48
22	2	3	0.023	4	9	4	9	95.02	91.53	95.49	93
23	2	3	0.023	4	9	9	4	98.53	90.87	93.14	96.08
24	2	3.5	0.025	12.4	6.5	6.5	6.5	93.02	96.86	95.84	98.75
25	2	3	0.027	9	4	4	4	99.53	100.87	101.59	102.31
26	2	3	0.027	9	4	9	9	99.48	97.87	97.84	97.11
27	2	3.5	0.025	6.5	6.5	12.4	6.5	101	95.88	91.45	97.42
28	2	4	0.027	9	9	4	4	100.79	99.8	101.03	100.21
29	2	4	0.027	9	4	4	9	100.94	100.03	100.98	98.77
30	2	3.5	0.02	6.5	6.5	6.5	6.5	107.16	101.42	102.14	101.88
31	2	4	0.027	4	4	4	4	110.11	104.24	104.71	102.83
32	2	3	0.027	4	9	9	9	103.15	95.96	98.25	97.43
33	2	4	0.023	4	9	9	9	96.72	93.48	94.63	95.88
34	2	3.5	0.025	6.5	6.5	6.5	6.5	99.57	94.99	95.82	98.13
35	2	4	0.023	9	4	4	4	93.75	96.36	95.87	96.33
36	2	4	0.027	4	9	4	9	109.38	98.07	102	98.36
37	2	4	0.023	9	4	9	9	94.17	95.45	93.09	94.19
38	2	4.7	0.025	6.5	6.5	6.5	6.5	101	98.11	98.21	99.99
39	2	4	0.023	4	4	4	9	99.55	96.97	100.43	95.16
40	3	3.5	0.025	6.5	6.5	6.5	6.5	99.52	95.55	96.05	97.92
41	3	3.5	0.025	6.5	6.5	6.5	6.5	99.52	94.73	95.24	97.28
42	3	3	0.027	4	4	4	9	105.25	96.09	103.26	98.29
43	3	3.5	0.025	0.55	6.5	6.5	6.5	105.54	97.49	99.61	98.74
44	3	3	0.023	9	4	9	4	98.91	94.77	93.2	97
45	3	3.5	0.025	6.5	6.5	0.55	6.5	100.39	96.44	98.97	96.53
46	3	3	0.023	4	4	9	9	97.29	93.61	95.05	93.48
47	3	3	0.027	4	4	9	4	107	103.05	98.79	100.1
48	3	3.5	0.025	6.5	6.5	6.5	0.55	101.35	98.3	97.81	99.92
49	3	4	0.027	4	4	9	9	106.3	100.05	98.85	98.61
50	3	3.5	0.025	6.5	6.5	6.5	6.5	98.93	95.28	95.93	98.25
51	3	4	0.023	4	9	4	4	98.66	92.55	97.21	95.64
52	3	3.5	0.025	6.5	6.5	6.5	12.5	97.98	95.23	96.43	92.5
53	3	3	0.023	4	4	4	4	102	93.42	98.77	98.63

Table 2. The design matrix and the responses

R₁ %= removal percentage of MB

R₂ %= removal percentage of AO

R_3 %= removal percentage of EY

R_4 %= removal percentage of BG

Table 3. The results of ANOVA for the response surface quadratic model for R_1 , R_2 , R_3 and R_4 .

Source variation	DF ¹	R ₁				R ₂				R ₃				R ₄			
		SS ²	MS ³	F-value	P-value	SS	MS	F-value	P-value	SS	MS	F-value	P-value	SS	MS	F-value	P-value
X ₁	1	20.9638	20.9638	147.114	0.000002	42.1609	42.160	348.79	0.000000	1.5098	1.5098	6.460	0.034627	6.8283	6.8283	55.672	0.000072
X ₁ X ₁	1	0.0551	0.0551	0.387	0.551261	1.3953	1.3953	11.543	0.009394	10.8569	10.8569	46.449	0.000136	1.3638	1.3638	11.120	0.010314
X ₂	1	531.968	531.968	3733.11	0.000000	313.386	313.38	2592.6	0.000000	245.523	245.523	1050.43	0.000000	199.65	199.6552	1627.8	0.000000
X ₂ X ₂	1	0.3083	0.3083	2.164	0.179524	0.0034	0.0034	0.028	0.870932	2.2205	2.2205	9.500	0.015066	0.8647	0.8647	7.050	0.029024
X ₃	1	314.681	314.6818	2208.29	0.000000	0.4286	0.4286	3.545	0.096469	35.0378	35.0378	149.903	0.000002	0.1301	0.1301	1.061	0.333191
X ₃ X ₃	1	0.0033	0.0033	0.023	0.882269	9.4952	9.4952	78.554	0.000021	10.5008	10.5008	44.926	0.000152	1.5614	1.5614	12.730	0.007315
X ₄	1	12.8974	12.8974	90.508	0.000012	98.6602	98.660	816.21	0.000000	9.2308	9.2308	39.492	0.000237	0.2380	0.2380	1.940	0.201133
X ₄ X ₄	1	0.7897	0.7897	5.541	0.046388	0.1325	0.1325	1.096	0.325789	2.1004	2.1004	8.986	0.017132	0.0062	0.0062	0.050	0.828197
X ₅	1	1.1380	1.1380	7.986	0.022288	0.3479	0.3479	2.878	0.128222	117.091	117.091	500.95	0.000000	0.7839	0.7839	6.391	0.035365
X ₅ X ₅	1	3.9409	3.9409	27.655	0.000766	2.8861	2.8861	23.877	0.001215	0.0343	0.0343	0.147	0.711480	1.3489	1.3489	10.998	0.010598
X ₆	1	18.8651	18.8651	132.387	0.000003	19.3252	19.325	159.877	0.000001	4.1779	4.1779	17.875	0.002885	86.692	86.6925	706.81	0.000000
X ₆ X ₆	1	0.3389	0.3389	2.378	0.161613	6.3653	6.3653	52.660	0.000087	5.8390	5.8390	24.981	0.001055	4.8553	4.8553	39.586	0.000235
X ₁ X ₂	1	8.1709	8.1709	57.340	0.000065	1.0768	1.0768	8.908	0.017476	1.1063	1.1063	4.733	0.061281	0.9835	0.9835	8.019	0.022092
X ₁ X ₃	1	3.9270	3.9270	27.558	0.000774	4.2268	4.2268	34.968	0.000356	0.8418	0.8418	3.601	0.094300	0.2794	0.2794	2.278	0.169675
X ₁ X ₄	1	3.7060	3.7060	26.007	0.000930	5.4533	5.4533	45.115	0.000150	0.0294	0.0294	0.126	0.731999	0.4584	0.4584	3.737	0.089274
X ₁ X ₅	1	3.9692	3.9692	27.854	0.000748	3.5179	3.5179	29.103	0.000650	0.7230	0.7230	3.093	0.116666	0.8224	0.8224	6.705	0.032142
X ₁ X ₆	1	5.5361	5.5361	38.850	0.000250	0.0604	0.0604	0.500	0.499780	0.3763	0.3763	1.610	0.240185	3.9410	3.9410	32.132	0.000471
X ₂ X ₃	1	5.9945	5.9945	42.066	0.000191	0.1093	0.1093	0.904	0.369533	0.1445	0.1445	0.618	0.454438	0.5025	0.5025	4.097	0.077565
X ₂ X ₄	1	6.5613	6.5613	46.044	0.000140	0.0226	0.0226	0.187	0.677016	0.0851	0.0851	0.364	0.563008	0.0458	0.0458	0.373	0.558306
X ₂ X ₅	1	6.5432	6.5432	45.917	0.000141	0.0751	0.0751	0.621	0.453348	1.4663	1.4663	6.273	0.036673	0.0124	0.0124	0.101	0.758627
X ₂ X ₆	1	7.4788	7.4788	52.483	0.000089	18.7119	18.711	154.80	0.000002	2.4920	2.4920	10.662	0.011438	1.2840	1.2840	10.469	0.011958
X ₃ X ₄	1	6.8728	6.8728	48.230	0.000119	1.6974	1.6974	14.043	0.005646	1.9850	1.9850	8.493	0.019463	1.0768	1.0768	8.779	0.018065
X ₃ X ₅	1	10.9395	10.9395	76.768	0.000023	4.8594	4.8594	40.202	0.000223	4.4925	4.4925	19.220	0.002336	2.7203	2.7203	22.179	0.001523
X ₃ X ₆	1	7.0782	7.0782	49.672	0.000107	0.8745	0.8745	7.235	0.027507	1.1138	1.1138	4.765	0.060587	0.2000	0.2000	1.631	0.237402
X ₄ X ₅	1	0.0102	0.0102	0.071	0.796277	6.3101	6.3101	52.204	0.000090	3.1941	3.1941	13.666	0.006071	10.294	10.2945	83.932	0.000016
X ₄ X ₆	1	9.0632	9.0632	63.601	0.000045	14.6747	14.674	121.40	0.000004	2.6278	2.6278	11.242	0.010036	2.4035	2.4035	19.596	0.002207
X ₅ X ₆	1	1.5008	1.5008	10.532	0.011784	1.5008	1.5008	12.416	0.007804	0.4442	0.4442	1.900	0.205370	0.2228	0.2228	1.816	0.214670
Lack of fit	17	2.7768	0.1633	1.146	0.442383	2.9577	0.1740	1.439	0.308279	10.9770	0.6457	2.763	0.073398	3.5523	0.2090	1.704	0.224687
Pure error	8	1.1400	0.1425			0.9670	0.1209			1.8699	0.2337			0.9812	0.1227		
Total SS	52	997.059				558.840				472.709				334.66			

¹ degree freedom² sum of square³ mean square

Table. 4 Isotherm constant parameters calculated for the dyes adsorption onto CuO-NPs-AC in pH of 6, 0.023-0.027 g of adsorbent, 4.5 mg L⁻¹ of each dyes and

Isotherm	Parameters	Value											
		MB			BG			AO			EY		
		0.023g	0.025 g	0.027g	0.023g	0.025 g	0.027g	0.023g	0.025 g	0.027g	0.023g	0.025 g	0.027g
Langmuir	Q _m (mg.g ⁻¹)	21.26	18.79	18.97	20.48	17.47	16.70	22.34	20.52	17.67	21.99	19.77	16.91
	K _a (L mg ⁻¹)	1.73	2.26	0.833	1.89	3.145	6.37	0.63	0.68	9.43	5.05	0.05	3.03
	R ²	0.9984	0.9916	0.994	0.9891	0.9963	0.9902	0.9950	0.9984	0.9961	0.9979	0.9963	0.9962
Freundlich	1/n	0.4821	0.4413	0.4115	0.4566	0.3932	0.3086	0.5808	0.5696	0.5516	0.444	0.418	0.3798
	K _F (L mg ⁻¹)	2.99	1.88	2.98	3.005	3.00	3.13	2.49	2.44	2.48	3.58	3.51	3.48
	R ²	0.9927	0.9757	0.9904	0.9942	0.983	0.9983	0.9826	0.9899	0.9884	0.9542	0.982	0.9817
Temkin	B ₁	4.914	4.2219	3.7096	4.67	3.789	3.0442	5.26	4.81	4.46	5.023	4.34	3.68
	K _T (L mg ⁻¹)	7.24	8.24	9.16	7.67	9.32	12.61	4.54	4.78	5.30	10.30	11.09	12.56
	R ²	0.9927	0.960	0.9981	0.9887	0.9953	0.9883	0.9985	0.9995	0.9958	0.9894	0.995	0.9933
Dubinin-	Q _s (mg g ⁻¹)	15.93	12.86	14.03	15.64	14.73	14.54	14.55	13.44	14.54	19.77	17.64	14.54
	B×10 ⁻⁷	-0.5	-0.4	-0.4	-0.5	-0.4	-0.2	-1	-1	-1	-0.3	-0.2	-0.2

1-6 min sonication time.

Radushkevich	E	3162.26	3533.57	3533.57	3162.26	3533.57	5000	2237.14	2237.14	2237.14	4081.63	5000	5000
h	R ²	0.9626	0.9768	0.9859	0.9686	0.934	0.92472	0.9912	0.9864	0.9844	0.997	0.994	0.9909

Table. 5 Kinetic parameters for the adsorption of dyes onto CuO-NPs-AC in in pH of 6, 0.023-0.027 g of adsorbent, 3.5 min sonication time and 2-10 mg L⁻¹ of each dyes.

Model	Parameters	Value											
		AO			BG			EY			MB		
		0.023g	0.025g	0.027g	0.023g	0.025g	0.027g	0.023g	0.025g	0.027g	0.023g	0.025g	0.027g
pseudo-First-order kinetic	k ₁ (min ⁻¹)	0.372	0.999	0.622	0.40	0.74	0.60	0.683	0.689	0.554	1.063	0.937	0.695
	q _e (calc) (mg g ⁻¹)	2.10	3.68	1.56	1.31	1.81	1.11	5.73	3.12	2.29	4.30	2.44	1.10
	R ²	0.981	0.971	0.974	0.9703	0.9973	0.9577	0.963	0.903	0.9902	0.971	0.963	0.8538
pseudo-Second -order kinetic	k ₂ (min ⁻¹)	0.25	0.53	0.80	0.399	0.844	1.056	0.167	0.335	0.452	0.448	0.764	1.16
	q _e (calc) (mg g ⁻¹)	13.81	12.90	11.96	14.45	13.11	12.17	13.81	12.59	11.79	14.25	12.95	11.98
	h	48.31	88.49	114.94	83.33	144.93	156.25	31.95	53.19	62.89	90.91	128.20	166.67
	R ²	0.9998	1	1	0.9998	1.0000	1.0000	0.9993	0.999	0.9999	0.9996	0.999	0.999
Intraparticle diffusion	K _{diff} (mg g ⁻¹ min ^{-1/2})	1.5467	0.9597	0.5866	1.1189	0.5583	0.4836	2.30	1.45	0.94	1.26	0.76	0.48
	C (mg g ⁻¹)	9.644	10.448	10.427	11.484	11.645	10.922	7.69	8.89	9.30	11.09	11.16	10.76
	R ²	0.9377	0.8179	0.8884	0.9113	0.9218	0.8289	0.8171	0.7314	0.9137	0.68	0.7696	0.717
Elovich	β (g mg ⁻¹)	0.77918	1.21981	2.027575	1.076	2.145	2.431	0.509	0.798	1.28	0.906	1.65	2.39
	α (mg g ⁻¹ min ⁻¹)	6926.378	776054.8	2.15E+09	635088	9.54E+10	3.89E+11	272.05	4066.6	320888.1	67493.2	1.62E+08	1.67E+11
	R ²	0.9807	0.906	0.954	0.9549	0.9767	0.9111	0.9045	0.8333	0.9696	0.7901	0.8648	0.816

Table. 6 Comparison for the removal of dyes by different methods and adsorbents.

Adsorbent	Dye	Method	Contact time (min)	Adsorption capacity (mg g ⁻¹)	Ref.
Bagasse Fly Ash	AO	Shaker-assisted adsorption	30-240	31.17	[55]
Activated carbon-commercial grade	AO	Shaker-assisted adsorption	120-240	1.5	[55]
activated carbon-laboratory grade	AO	Shaker-assisted adsorption	120-240	12.6	[55]
ZnS: Cu-NP-AC	AO	Ultrasound-assisted adsorption	2.5	123	[34]
CuO-NPs-AC	AO	Ultrasound-assisted adsorption	4.2	22.34	our work
ZnS-NP-AC	BG	Magnetic stirring adsorption	15	333.3	[49]
Bagasse fly ash	BG	Shaker-assisted adsorption	200	65.93	[56]
Watermelon rind	BG	Roto-spin stirring adsorption	50	92.6	[57]
Activated watermelon rind	BG	Roto-spin stirring adsorption	50	186.2	[57]
Graphite oxide	BG	Magnetic stirring adsorption	20	416.7	[58]
CuO-NPs-AC	BG	Ultrasound-assisted adsorption	4.2	20.48	our work
Cu-NPs-ionic liquid based nanoporous organosilica	EY	Magnetic stirring adsorption	14	286	[59]
Ag-NPs-ionic liquid based nanoporous organosilica	EY	Magnetic stirring adsorption	14	250	[59]
Ethylenediamine modified chitosan	EY	Thermostatic stirring adsorption	500	294.1	[44]
Chitosan hydro beads	EY	Shaker-assisted adsorption	800	100	[60]
Chitosan nanoparticles	EY	Shaker-assisted adsorption	100	3.33	[61]
Polypyrrole- wood sawdust	EY	Magnetic stirring adsorption	30	3.148	[62]
Polyaniline- wood sawdust	EY	Magnetic stirring adsorption	30	3.186	[62]
CuO-NP-AC	EY	Ultrasound-assisted adsorption	4.2	21.29	our work
Nitrogen modified TiO ₂ nanoparticles	MB	Shaker-assisted adsorption	100	410.12	[63]
Sulfur modified TiO ₂ nanoparticles	MB	Shaker-assisted adsorption	500	350.66	[63]
Ag-NPs-AC	MB	Magnetic stirring adsorption	15	71.4	[64]
Pd-NPs-AC	MB	Magnetic stirring adsorption	15	75.4	[64]
Graphene oxide	MB	Vortex-assisted adsorption	20	714	[65]
NiS-NP-AC	MB	Magnetic stirring adsorption	5.46	46–52	[15]
Au-NP-AC	MB	Ultrasound-assisted adsorption	1.46	104–185	[47]
Graphene–carbon nanotube hybrid	MB	Shaker-assisted adsorption	50	68.02	[66]
CuO-NPs-AC	MB	Ultrasound-assisted adsorption	4.2	21.26	our work

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9