Supplementary Information

TABLES

Table SI Molecular structure and chemical properties of the Malachite Green (MG) dye

Dye name	Molecular structure	Chemical properties	
MG	H_3C N CI^- H_3C N^+ CH_3 CH_3	Chemical name:	4-{[4- (Dimethylamino)phenyl](phenyl)methylidene}- N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride
		Chemical formula	C ₂₃ H ₂₅ CIN ₂
		Molar mass:	364.911 g/mol (chloride)
		Colour Index Number:	42000
		Dye class:	Azo dyes
		λ_{max} :	617 nm
		Melting point:	112°C
		Boiling point:	Not available, it decomposes. When there are
			a lot of branching in a compound the boiling
			point goes away

TEXT

Text-SI

The chemicals such as sodium alginate (SA) powders (Sinopharm Chemical Reagent Co., Ltd. China), poly-vinyl alcohol (PVA) having MW 146,000-186,000, (Sigma-Aldrich, 99% hydrolyzed), glutaraldehyde (GA) (Aladdin Reagents Co., Ltd. (China), 50.0% vol in H₂O), and boracic acid (H₃BO₃) (Sinopharm Chemical Reagent Co., Ltd. China), anhydrous calcium chloride (CaCl₂) (Sinopharm Chemical Reagent Co., Ltd. China), hydrochloric acid (HCl) (Sinopharm Chemical Reagent Co., Ltd. China) and malachite green (C₂₃H₂₅ClN₂) (Aldrich, 99%) were employed in the present study. All the chemicals and regents were analytically pure and used without further purifications and ultra-pure distilled water was obtained from Qingdao water purification agency having resistivity of 18 MΩ cm to make all aqueous solution. The pH of the solution was adjusted using 0.1 mol/L NaOH and HCl aqueous solutions throughout all the experiments depending on requirements.

Various types of instruments such as UV-vis spectrophotometer (T80, P.G. Instrument Ltd., UK), pH meter (mV/ORP METTLER TOLEDO), Atomic Absorption Spectrometry (Solar M6, Thermo Elemental, USA), rotary shaker (THZ-92A, China), thermostatic water bath shaker (Max Q 7000, Thermo Scientific), centrifuge machine (model C-30BL), magnetic stirrer (MS-M-S10, Biobase Biodustry, Shandong Co., Ltd), Elemental analyzer (EA, Vario EL cube, German), Brunauer-Emmet-Teller (BET) analyzer (Micromeritics'ASAP2020; Cell Type: 9mm; Analysis gas: Nitrogen;), fourier transforms infrared spectroscopy (FTIR, Bruker Vertex 70; KBr powder used as blank), transmission electron microscopy (TEM, JEM-2100HR, Japan), Vibrating sample magnetometer (VSM, VSM600), Scanning Electron Microscope with integrated energy dispersive X-ray system (SEM-EDX, JSM-6610 LV, Japan Electronics), X-ray photoelectron spectroscopy (XPS, ESCALAB 250, German), X-ray diffractometer (XRD, Philips Electronic Instruments), Thermo-gravimetric analyzer (TGA, NETZSCH TG 209F3; Detector Type: DTG-60H; Detector Serial No: C30574300136TK; Atmosphere: Nitrogen; Gas Flow: 50[ml/min]), weighing balance (Sartorius Entris 64-15, German), syringe pump, syringe, volumetric flasks and Erlenmeyer flasks (JOAN Lab Pyrex Glass Erlenmeyer Flask, Ningbo Yinzhou Joan Lab Equipmennts, china) were utilized for the fabrication, characterization and to conduct adsorption experimental studies of BMMCs.

Text-SII

Sorption isotherm Models

The following equations of these models were used to fit the experimental data:

Langmuir Model

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}}$$

Where, $q_e (mg/g)$ and $C_e (mg/L)$ are the amount adsorbed and concentration of the MG in solution at equilibrium. The $q_{max} (mg/g)$ and $K_L (L/mg)$ are the monolayer sorption capacity of the adsorbent and Langmuir equilibrium constant relating to the free energy of the adsorption. The Langmuir model is based upon the assumption of monolayer adsorption process where pollutant sorbed onto the homogenous sites of the adsorbents without any interaction between sorbed ions. The values of the Langmuir equilibrium constant or dimensionless constant/ separation factor (K_L) were determined by the following equation:

$$K_L = \frac{1}{1 + bC_e}$$

Where, b (L/mg) is another Langmuir constant related to binding energy of the pollutants onto the active sites of the adsorbent. The values of q_{max} give hint about active sites while b about driving force at equilibrium. The values of q_{max} and b were determined from slope and intercept of a straight line by plotting graph $1/C_e$ vs $1/q_e$. The favorability of the sorption isotherm depends upon on the K_L value. If K_L> 1 sorption isotherm is unfavorable, if K_L = 1 sorption isotherm is liner, if K_L = 0 sorption is irreversible isotherm and if $0 < K_L < 1$ then sorption is favorable.

Freundlich Model

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log k_F$$

Where, k_F (mg/g) and n are the empirical constants/ Freundlich constants, related to adsorption capacity and adsorption intensity of the adsorbent. The Freundlich isotherm model is based upon the assumption of heterogeneous adsorption process where pollutant sorbed onto the miscellaneous sites of the adsorbents with different binding energy. The values of n and k_F were calculated from intercept and slope of the graph plotted logC_e vs logq_e. Moreover, the value of 1/n varies with the heterogeneity of the material. The value of 1/n between 0 and 1 showed that the adsorption of pollutant onto the surface of adsorbent was favorable at experimental conditions.

Temkin Model

$$q_e = \left(\frac{RT}{B_T}\right) \log C_e + \left(\frac{RT}{B_T}\right) \log K_T$$

Where, $K_T(L/g)$ is the equilibrium binding constant presenting maximum binding energy. $B_T(KJ/mol)$ is the constant related to the heat of adsorption.R is the ideal gas constant (8.314J/mol. K). T is the temperature Kelvin. The values of K_T and B_T were determined from the intercept and slope of graph plotted log C_e vs q_e .

Dubinin-Radushkevich model

$$\ln q_e = \ln q_m - \beta \varepsilon^2$$

Where, qe (mg/g) is the quantity of the CV ions adsorbed on per unit weight of adsorbent, q_m (mg/g) is the maximum sorption capacity, β (mol²/J²) is the activity coefficient related to average sorption energy per mole of adsorbate and ϵ is the Polanyi potential. The values of q_m and β were estimated from intercept and slope of the straight line plotted $\epsilon^2 vs \ln q_e$. While, the values of ϵ were calculated by using this formula:

$$\varepsilon = \operatorname{RTln}\left(1 + \frac{1}{C_e}\right)$$

In addition, the values of sorption mean free energy (E) gives hint about nature of adsorption i.e. physical or chemical and it can be calculated by using this formula:

$$E = \frac{1}{\sqrt{(2\beta)}}$$

Sorption Kinetics Models

The sorption kinetics was calculated by the following equations:

Pseudo-First-Order Kinetic

$$\log\left(q_e - q_t\right) = \log q_e - \frac{tk_1}{2.303}$$

Where, $q_t (mg/g)$ is the adsorption capacity at time (t). while $k_1 (min^{-1})$ is the Pseudo first order rate constant for the kinetic model and it can be measured from the slope of straight line plotted t vs $log(q_e-q_t)$. For calculating q_t and q_e , the following equations were employed:

$$q_e = \frac{(C_o - C_e)}{m}V$$
$$q_t = \frac{(C_o - C_t)}{m}V$$

Where, C_o (mg/L) is the initial concentration of MG dye in solution. While, the C_e (mg/L) and C_t (mg/L) are the concentration of MG dye at equilibrium and time (t).

Pseudo-Second Order Kinetic Model

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$
$$h = k_2(q_e)^2$$

Where h (mg.g⁻¹.min⁻¹) is the initial adsorption rate constant, k_2 is the rate constant and can be calculated from graph plotted t vs t/q_t.

Adsorption and desorption were also discovered by using Elovich's kinetic model.

Elovich's Kinetic Model

$$q_t = \frac{1}{\beta \ln \alpha \beta} + \frac{1}{\beta \ln t}$$

Where, α (mg.g⁻¹.min⁻¹) and β (g/mg) are the adsorption and desorption rate constants. The values of α were calculated by the ratio of q_e/t . whereas the value of β was measured from the slope of graph plotting between Int vs qt.

To check the diffusion mechanism between MG dye and 3-MPA@PMNPs, Weber and Morris kinetic equation was used as.

$$q_t = k_{ipd} t^{0.5}$$

Where, k_{ipd} (mg.g⁻¹.min^{-0.5}) is the intraparticle diffusion rate constant and can be calculated from the slope of the straight line of $t^{0.5}$ vs q_t.

Finally to confirm the film diffusion mechanism, liquid film diffusion kinetic model was employed to experimental data and the applied equation is given below:

$$\ln\left(1-F\right) = -k_{fd}t$$

Where, k_{fd} (g/mg) is the film diffusion rate coefficient. F is the fractional attainment of equilibrium and can be measured by q_t/q_e . The values of k_{fd} were calculated from the slope of the straight line of graph plotted between t vs ln(1-F).

Thermodynamic study

Thermodynamic parameters i.e. change in free energy $\Delta G^{\circ}(kJ/mol)$, enthalpy $\Delta H^{\circ}(kJ/mol)$ and entropy $\Delta S^{\circ}(kJ/mol)$ were estimated by:

$$\Delta G^{\circ} = -RT \ln K_D$$

$$\ln K_D = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$

Where, $\Delta G^{\circ}(kJ/mol)$ is the change in free energy, $\Delta H^{\circ}(kJ/mol)$ is the enthalpy, $\Delta S^{\circ}(kJ/mol)$ is the entropy, R is the universal gas constant (8.314 J/mol.K), T is the temperature (K) and K_D is the distribution coefficient and the value of K_D was calculated by the ratio of q_e/C_e. The values of ΔS° and ΔH° were measured from the slope and intercept of the straight line plotted against 1/T vslnk_D.

Standard deviation (S_D)/ Sum of errors square (SSE)

$$S_D / SSE = \sqrt{\frac{\sum_{t=0}^{n} (X_{exp} - X_{cal})^2}{N}}$$

Where, the subscripts (exp) and (cal) are the experimental and the calculated values of X (variables) respectively and N is the number of measurements/ replications.

Text-SIII

Measurement of Point of Zero Charge

The point of zero charge pH (pHPZC) of the prepared bio-magnetic capsules was calculated using pH drift method employed by (**Ali et al., 2018a**). Briefly, 20 mL of NaCl (0.005 mol/L) solution was added into several 50mL bottles of polystyrene. Initial pH (pHi) values of NaCl solutions were adjusted from 2-13 using drop-wise 0.1mol/L solution of HCl and NaOH. Thereafter, 10 mL of NaCl (0.005 mol/L) solution was further added into each bottle to bring total volume up-to 30mL. The solution (pHi) values were again noted carefully and 0.500 g of bio-magnetic capsules was added in each bottle, which was tightly and instantly covered. The suspensions were shaken at 25°C for 48 h. Thereafter, the suspensions were vacuum-filtered through a 0.22µm filter paper and final pH (pHf) values of the supernatant liquid were noted. The value of pHPZC was estimated by plotting graph between pHi versus (pHf-pHi). In fact, the value of pHPZC is the point where the two curves i.e standard pH (pHi vs pHi) and pHi vs (pHf-pHi) intersect each other.

Text-SIV

Key: q_e (exp.): Experimental q_e (mg/g); q_e (cal.): Calculated q_e (mg/g); I: Intercept; C_o : Initial concentration of the pollutant (mg/L); h: initial adsorption rate constant (mgg⁻¹.min⁻¹); $k_1 \& k_2$: equilibrium rate constants for Pseudo-first and Pseudo second order kinetic models (min⁻¹); R^2 : Regression coefficient; α = adsorption rate constant; β = desorption rate constant; K_{fd} = Film diffusion rate constant (g/mg); k_{ipd} = intraparticle diffusion rate constant (mgg⁻¹.min^{-0.5})

Key: q_{max} : maximum monolayer adsorption capacity of adsorbent; b: constant related to binding energy; K_L : dimensionless constant; n: adsorption intensity; K_f : empirical constants relative adsorption capacities of the adsorbent; K_T : the equilibrium binding constant presenting maximum binding energy; B_T : constant is related to the heat of adsorption; E: average energy; β : activity coefficient; ϵ Polanyi potential

Key: ΔG° : Change in free energy; ΔH° : enthalpy; ΔS° : entropy

FIGURES



Fig. S1 Size mesurment of the prepared BMMCs (a, c) before and (b, d) after the sorption of MG dye



Fig. SII The light absorption results of MG dye (a) before and (b) after the reaction with prepared bio-magnetic capsules at different pH



Fig. SIII Regeneration results of the prepared BMMCs by using different types of regenation solutions



Fig. S1V Effect of different concentration of HCl desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.02g/L, MG initial concentration (C_o) = 25mg/L)



Fig. SV Effect of different concentration of NaCl desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.02g/L, MG initial concentration (C_o) = 25mg/L)



Fig. SVI Effect of different concentration of methanol desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.02g/L, MG initial concentration (C_o) = 25mg/L)



Fig. SVII Effect of different concentration of NaOH desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.02g/L, MG initial concentration (C_o) = 25mg/L)



Fig. SVIII Effect of different concentration of EDTA desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.02g/L, MG initial concentration (C_o) = 25mg/L)



Fig. SIX Effect of different concentration of 1M NaCl salt in methanol desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.02g/L, MG initial concentration (C_o) = 25mg/L)



Effect of temperature on the adsorptive removal and capacity of MG dye by BMMCs (adsorbents dosage = 0.02g/L, MG initial concentration (C_o) = 25mg/L)

Fig. SX