Electronic Supplementary Information

Novel *Averrhoa carambola* extract stabilized magnetite nanoparticles: A green synthesis route for the removal of chlorazol black E from wastewater

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2. Materials and methods

2.3 Characterization tools and techniques

The spectrophotometer was first calibrated with a 7 point calibration curve (correlation co-efficient=0.999), obtained from standard solutions (1−7 mg L^{-1}) of the dye in ultrapure water; analysed at wavelength of maximum absorbance (λ_{max}) of 550 nm. When the dye samples had higher concentration, which showed absorbance beyond the range of the calibration curve, they were diluted with ultrapure water, for the accurate determination of the CBE concentration

The percentage removal and the sequestration capacity of the nanoparticles were estimated from mass-balance equations.

Percentage removal of the dye is predicted by:

$$\%\, removal = \frac{(C_o - C_e)}{C_o} x100 \qquad (S1)$$

Sequestration capacity of the nanoparticle is estimated by:

$$q_e = \frac{(C_o - C_e)\, x\ V}{m} \qquad (S2)$$

where C_o and C_e (mg L^{-1}) are the initial and equilibrium liquid phase concentration of CBE, V (L) is the volume of the dye sample, and m (g) is the weight of the nanoparticles.

2.4 Removal of CBE in batch assay

The effect of pH_o on CBE removal was considered over a pH range 2−10, adjusted using 0.1M HCl and 0.1M NaOH. Optimum adsorbent load (m) was determined by contacting different amounts of adsorbent (0.25−6 g L^{-1}) with 20 mL CBE solution of known Co (100 mg L^{-1}) till the attainment of equilibrium. To study the temperature dependent characteristics, the batch operation was performed at 293K, 303K, and 313K, under optimum m and t.

Adsorption kinetics was studied by analyzing the CBE retention at different time intervals starting from more frequent to greater time periods. For adsorption isotherm, CBE samples of C_O (50−400 mg.L^{-1}) were contacted with optimum adsorbent load (m) until equilibrium is reached.

2.5 Regeneration of dye-loaded nanoparticles and their reusability studies

The regeneration efficiency (η_L) of the dye-loaded nanoparticles were determined using the following equation:

$$\eta_L = \left(\frac{C_d.V_d}{m.q_e}\right)X100 \qquad (S3)$$

where, C_d is the concentration of CBE (mg L^{-1}) in the solvent, V_d is the volume (L) of the desorbing solvent, q_e is the sequestration capacity (mg g^{-1}) of the nanoparticles, and m is the mass (g) of the CBE-loaded nanoparticles.

3. Results and discussions

3.1 Characterization of magnetite nanoparticles

Scherrer's equation is given by:

$$D = \frac{K\,\lambda}{\beta}Cos\theta \qquad (S4)$$

where D is the average crystallite size, β is the FWHM of the most intense peak, λ is the wavelength of X-ray used (0.154 nm), K is a constant (0.9), and θ is the diffraction angle.

3.3 Kinetics, isotherm, and thermodynamics of dye removal

Pseudo-first-order kinetics is followed when adsorption pave the way by diffusion through a boundary. Lagergren proposed pseudo-first-order kinetic equation based on solid capacity represented in the form of:

$$log\,(q_e - q_t) = log\,q_e - \left(\frac{k_1}{2.303}\right)t \qquad (S5)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the sequestration capacities at equilibrium and at time 't', respectively; k_1 is the rate constant of pseudo-first-order equation. Ho and McKay proposed the pseudo second-order kinetic equation based on the sequestering behaviour over the whole range and is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \left(\frac{1}{q_e}\right)t \qquad (S6)$$

where k_2 (g mg^{-1} h^{-1}) is the rate constant of pseudo-second-order equation. To ascertain the adsorption mechanism and rate controlling step of adsorption, Weber-Morris intraparticle diffusion model is applied to the equilibrium data. The intraparticle diffusion model is given as:

$$q_t = k_{ip}\, t^{1/2} + C \qquad (S7)$$

where k_{ip} is the intraparticle diffusion rate constant and values of C give an idea about thickness of the boundary layer. The non-linear kinetics of mass transfer is ascertained from the mode of diffusion, which is determined from the transport number (n) with the help of the following:

$$\frac{Q_t}{Q_e} = kt^n \qquad (S8)$$

where Q_t and Q_e are the weight of the nanoparticles with the CBE at time t and at equilibrium, respectively. k is the dye–nanoparticle interaction coefficient. The various kinetic models are validated by the normalized standard deviation (Δq %) given by:

$$\Delta q(\%) = 100 \sqrt{\frac{\sum\left[\frac{(q_{exp} - q_{cal})}{q_{exp}}\right]^2}{(N-1)}} \qquad (S9)$$

where q_{exp} and q_{cal} (mg g^{-1}) are the experimental and calculated sequestration capacities respectively. N is the number of data points in the graph, which corresponds to the kinetic equation.

The Langmuir isotherm model is based on the assumption of monolayer, uniform adsorption, with finite number of active sites, and with no lateral interaction as well as steric hindrance between the adsorbed molecules (even on the adjacent sites). Langmuir isotherm in linear form can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{a_L b_L} + \frac{C_e}{a_L} \qquad (S10)$$

where C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate, q_e (mg g^{-1})is the adsorptive uptake per unit weight of the adsorbent; a_L (mg g^{-1}) and b_L (L mg^{-1}) are Langmuir constant related to monolayer adsorption capacity and energy of adsorption, respectively. Freundlich isotherm is an empirical model relating to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface of the adsorbent. The linearized expression of Freundlich isotherm is given as:

$$log\ q_e = log\ K_F + \frac{1}{n} log\ C_e \qquad (S11)$$

where K_F (L mg^{-1}) and $1/n$ are the Freundlich adsorption constant and a measure of adsorption efficiency, respectively. The feasibility and vital characteristics of the Langmuir isotherm is ascertained with dimensionless separation factor (R_L), which is given by:

$$R_L = \frac{1}{1 + b_L C_o} \quad (S12)$$

For the error analysis of the fit of the isotherm equations, Marquardt's percent standard deviation (MPSD) error function is used and is given as:

$$MPSD = 100 \sqrt{\left(\frac{1}{n-p}\right) \sum_{i=1}^{n} \left(\frac{q_{e,\ exp} - q_{e,\ cal}}{q_{e,\ exp}}\right)_i^2} \quad (S13)$$

where n is the number of data points and p is the number of parameters in the isotherm equation.

The thermodynamic parameters for the sequestration of CBE can be calculated from the following thermodynamic equations:

$$K_{ad} = \frac{C_s}{C_e} \quad (S14)$$

$$\Delta G = \Delta H - T\Delta S \quad (S15)$$

$$lnK_{ad} = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (S16)$$

where K_{ad} is the adsorption equilibrium constant, C_s and C_e (mg L^{-1}) are the equilibrium adsorbate concentration in the solid and liquid phase, respectively. ΔG (kJ mol^{-1}) is the change in free energy, ΔH (kJ mol^{-1}) is the enthalpy change, and ΔS (kJ mol^{-1} K^{-1}) is the entropy change of the system. T (K) is the temperature of the reaction in the absolute scale and R (8.314 J mol^{-1} K^{-1}) is the universal gas constant.

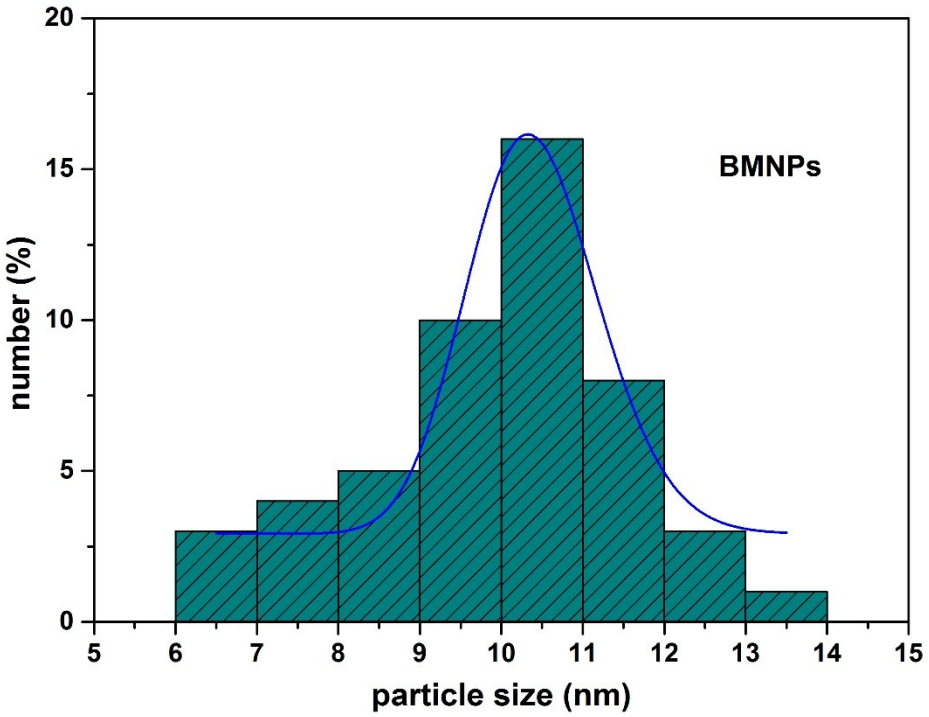

Fig. S1 Particle size distribution of BMNPs as determined from TEM image.

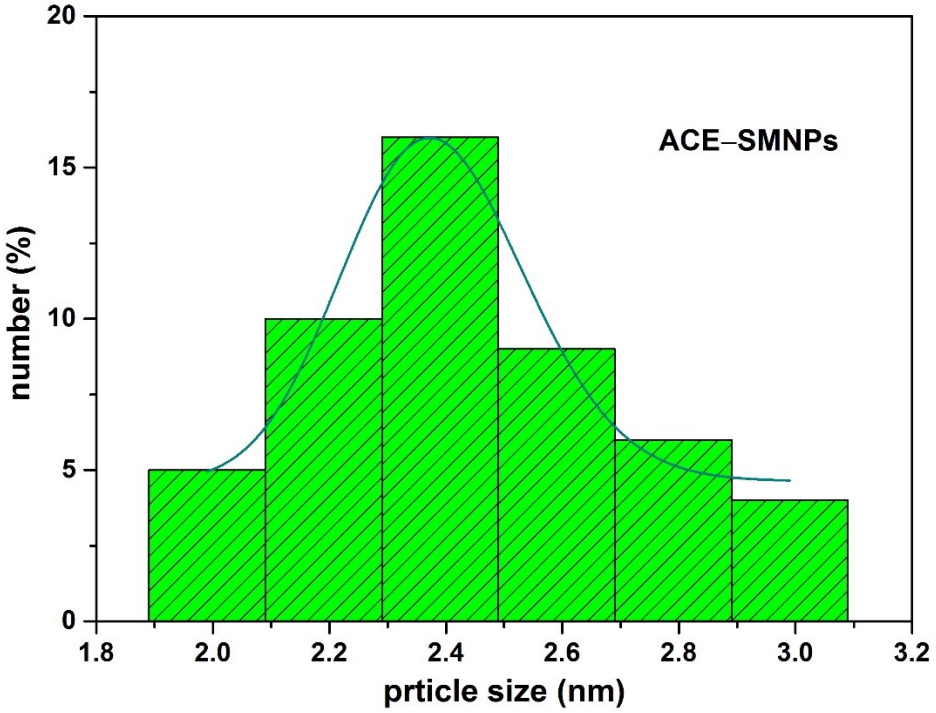

Fig. S2 Particle size distribution of ACE−SMNPs as determined from TEM image.