Electronic Supplementary Information (ESI) for New Journal of Chemistry

Xerogel activated diatom as an effective hybrid adsorbent for the efficient removal of malachite green

Ganesan Sriram,[a] U.T. Uthappa,[a] Madhuprasad Kigga,[a] Ho-Young Jung,[b] Tariq Altalhi,[c] Varsha Brahmkhatri[a]* and Mahaveer D. Kurkuri[a]*

[a] *Centre for Nano and Material Sciences, JAIN (Deemed-to-be-university), Jain Global Campus, Bengaluru, 562112, Karnataka, India*

[b] *Department of Environment and Energy Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, Republic of Korea*

[c] *Department of Chemistry, Faculty of Science, Taif University, Taif, Saudi Arabia*

* Corresponding authors.

Email addresses: mahaveer.kurkuri@jainuniversity.ac.in (Mahaveer D. Kurkuri)

b.varsha@jainuniversity.ac.in (Varsha Brahmkhatri)

Adsorption Isotherms. The dye (adsorbate) interact with XDE (adsorbent) can be determined by adsorption isotherms i.e. Langmuir isotherm and Freundlich isotherm. The interaction of adsorbate on adsorbent sites by a monolayer or homogeneous is Langmuir isotherm.[1] The interaction of adsorbate on adsorbent sites by multilayer or heterogeneous is Freundlich isotherm.[2] After dye adsorption studies all the materials were isolated and characterized by various physicochemical studies to understand the nature of the adsorption process.

The following linearized equations can be used to perform the isotherm model for the experiment:

For Langmuir isotherm,

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

Where q_m (mgg^{-1}) denotes the maximum adsorption capacity of adsorbent and K_L (Lmg^{-1}) denotes Langmuir constant related to the affinity of binding sites and adsorption energy. The Langmuir isotherm can be stated dimensionless separation factor,[3] R_L which can describes the type of isotherm process either favorable$(0 < R_L < 1)$, unfavorable $(R_L > 1)$, linear $(R_L = 1)$ or irreversible process $(R_L = 0)$, which can be expressed in Eq. (4):

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{(S2)}$$

For Freundlich isotherm,

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad \text{(S3)}$$

Where K_F (mgg^{-1}) and n are the Freundlich constants of adsorption capacity and adsorption tendency respectively. K_F denotes an adsorption or distribution coefficient i.e. the amount of adsorbate adsorbed on an adsorbent sites. The n can be expressed how favorable the adsorption process. The $1/n$ value is expressed energy distribution of adsorbent sites i.e. a value between 0 and 1 is adsorbent surface is heterogeneity. The surface is become more heterogeneous if the value is nearly zero.[4]

Batch Kinetic Studies. For the adsorption process, it is a very essential parameter to determine the rate of time at adsorbate is removed from aqueous solution using the unit mass of adsorbent.

The concentration of adsorbate in aqueous solution can be measured at the certain time, q_t (mgg^{-1}), was determined by Eq. (6):

$$q_t = \frac{C_0 - C_t}{M} \times V \quad (S4)$$

Where C_t (mgL^{-1}) is a concentration of adsorbate in aqueous solution at a certain time t (h).

The kinetic models pseudo-first-order, pseudo-second-order and intra-particle diffusion were used to determine the adsorption kinetics of adsorbate onto adsorbent sites. The following equations were used for fitting the adsorption kinetics: [5]

For pseudo-first-order kinetic model,

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (S5)$$

For pseudo-second-order kinetic model,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (S6)$$

For intra-particle diffusion,

$$q_t = K_{int} t^{1/2} + C \quad (S7)$$

Where K_1 (min^{-1}) and K_2 ($g^{-1}mg^{-1}min^{-1}$) are the adsorption rate constant of pseudo-first-order and pseudo-second-order adsorption kinetics, respectively. q_e (mgg^{-1}) and q_t (mgg^{-1}) are the amounts of adsorbate adsorbed at equilibrium and time *'t'*, respectively. K_{int} ($mgg^{-1}min^{-1/2}$) denotes intra-particle diffusion rate constant and C (mgg^{-1}) was the thickness of the boundary layer of adsorbate onto adsorbent sites.

Adsorption Thermodynamics. The thermodynamic parameters were obtained by van't Hoff equation:

$$\Delta G^\circ = -RT \ln K_d \quad (S8)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (S9)$$

$$K_d = \frac{q_e}{C_e} \quad (S10)$$

Where R (8.314 J $mol^{-1}K^{-1}$) is the universal gas constant, T (K) is the absolute temperature, K_d ($Lmol^{-1}$) is the distribution coefficient, q_e (mgg^{-1}) means the amount of dye adsorbed on adsorbent at equilibrium and C_e (mgL^{-1}) is the equilibrium concentration of dye in aqueous solution.[6]

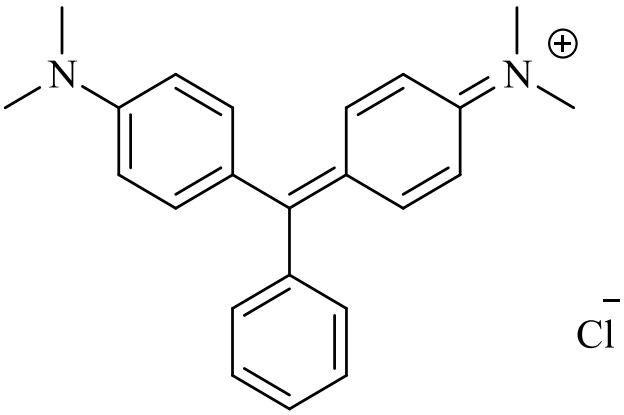


Fig. S1. Chemical structure of malachite green (MG) dye.

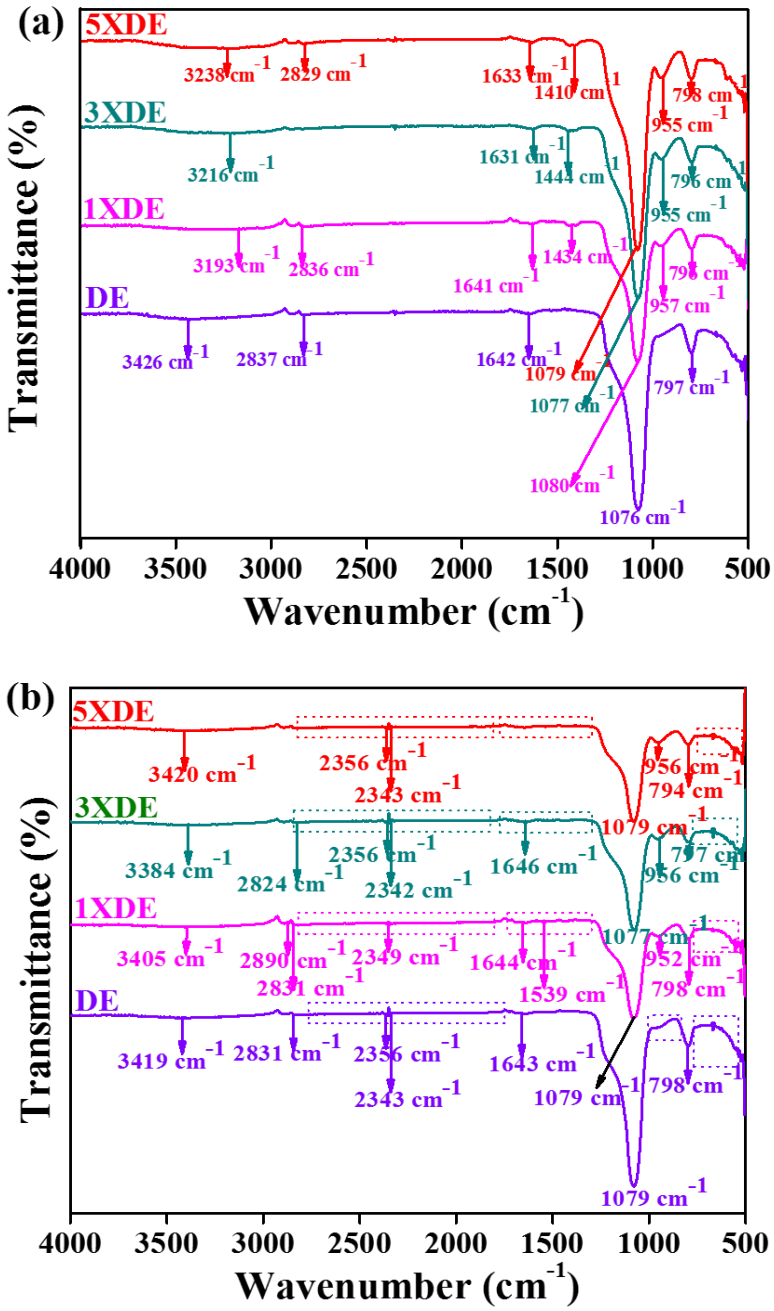


Fig. S2. ATR-IR spectra of DE, 1XDE, 3XDE, 5XDE shows (a) before MG adsorption and (b) after MG adsorption.

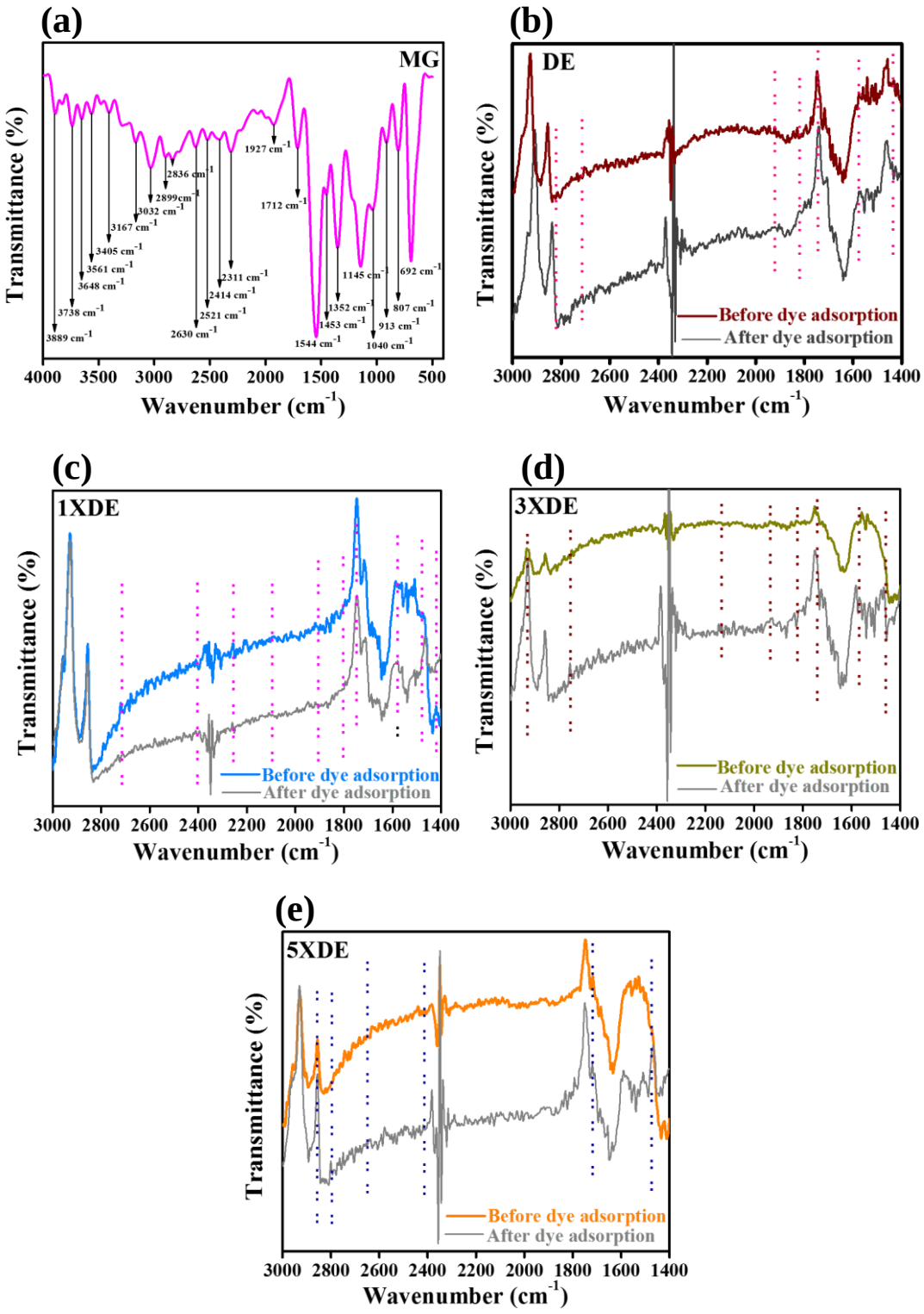
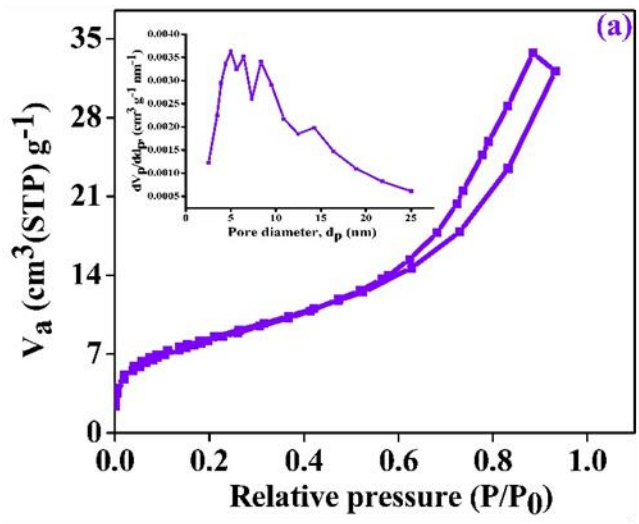
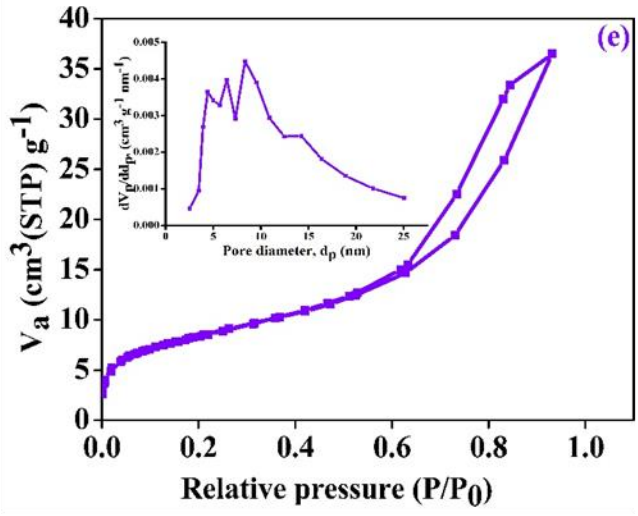
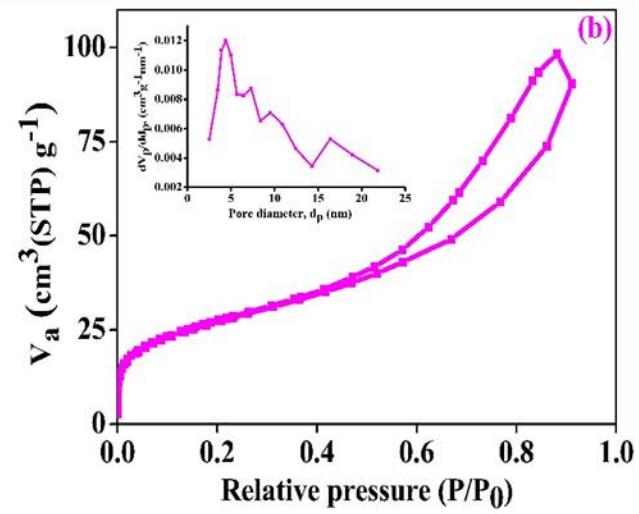
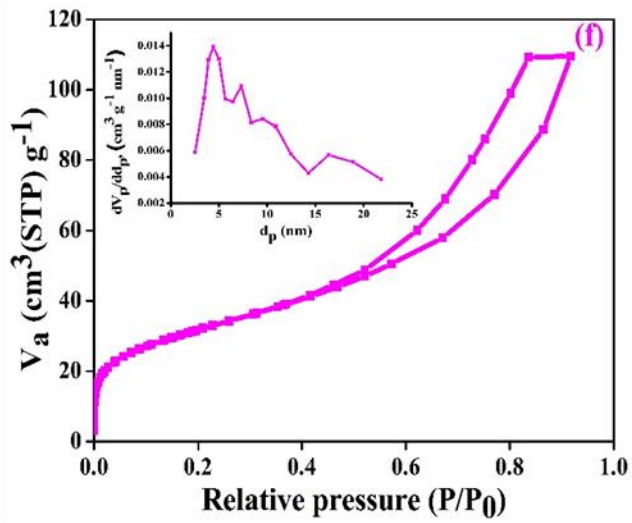


Fig. S3. ATR-IR spectra of (a) malachite green, (b-e) before and after dye adsorption of DE, 1XDE, 3XDE and 5XDE, respectively.


(a)
V_a (cm^3(STP) g^{-1})
Relative pressure (P/P$_0$)
dV$_p$/dd$_p$ (cm^3 g^{-1} nm^{-1})
Pore diameter, d$_p$ (nm)


(e)
V_a (cm^3(STP) g^{-1})
Relative pressure (P/P$_0$)
dV$_p$/dd$_p$ (cm^3 g^{-1} nm^{-1})
Pore diameter, d$_p$ (nm)


(b)
V_a (cm^3(STP) g^{-1})
Relative pressure (P/P$_0$)
dV$_p$/dd$_p$ (cm^3 g^{-1} nm^{-1})
Pore diameter, d$_p$ (nm)


(f)
V_a (cm^3(STP) g^{-1})
Relative pressure (P/P$_0$)
dV$_p$/dd$_p$ (cm^3 g^{-1} nm^{-1})
d$_p$ (nm)

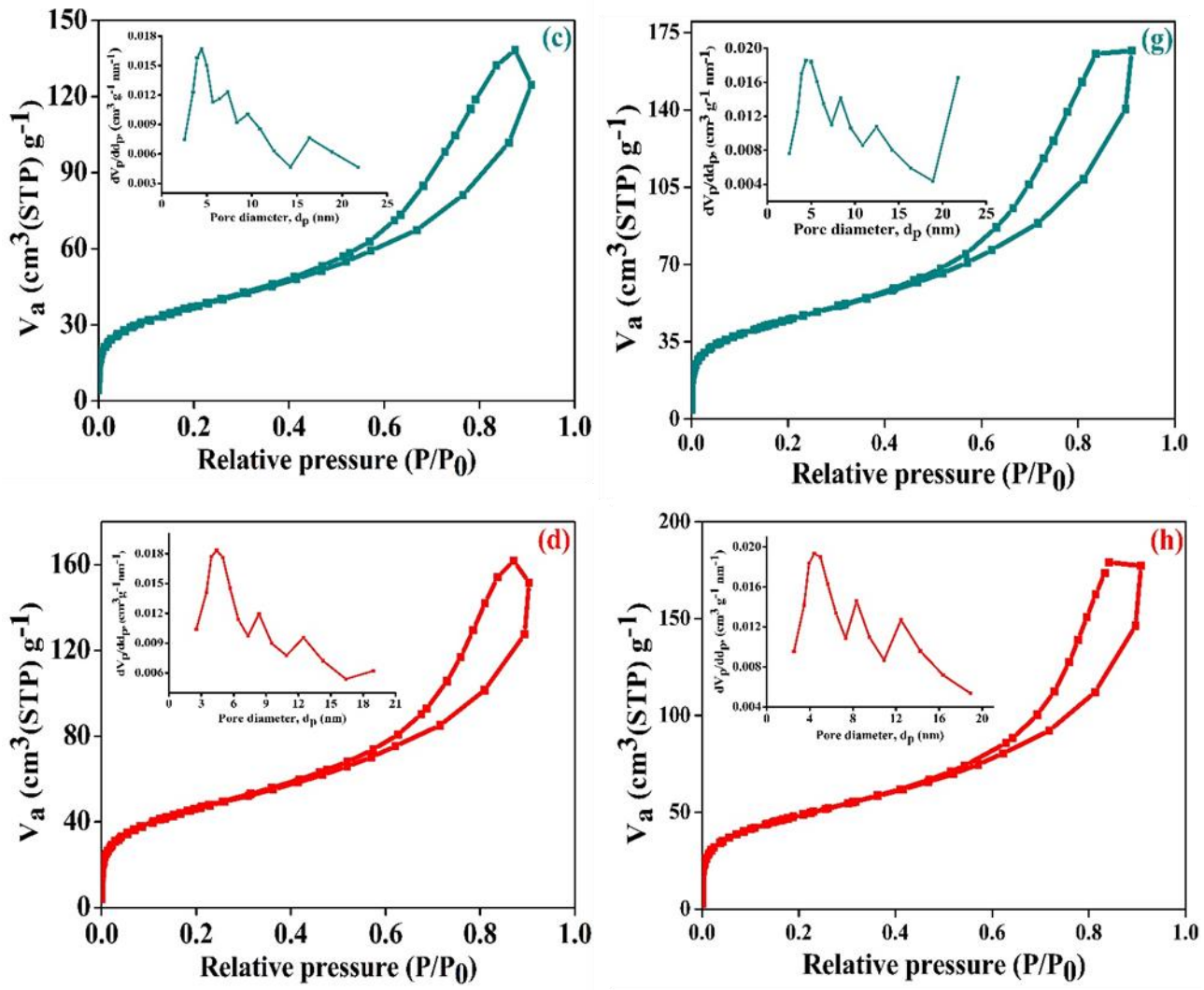


Fig. S4. N_2 adsorption-desorption isotherm of before MG adsorption (a) DE, (b) 1XDE, (c) 3XDE (d) 5XDE and after MG adsorption of (e) DE, (f) 1XDE, (g) 3XDE, (h) 5XDE at 77 K (Inset pictures: Pore size distribution).

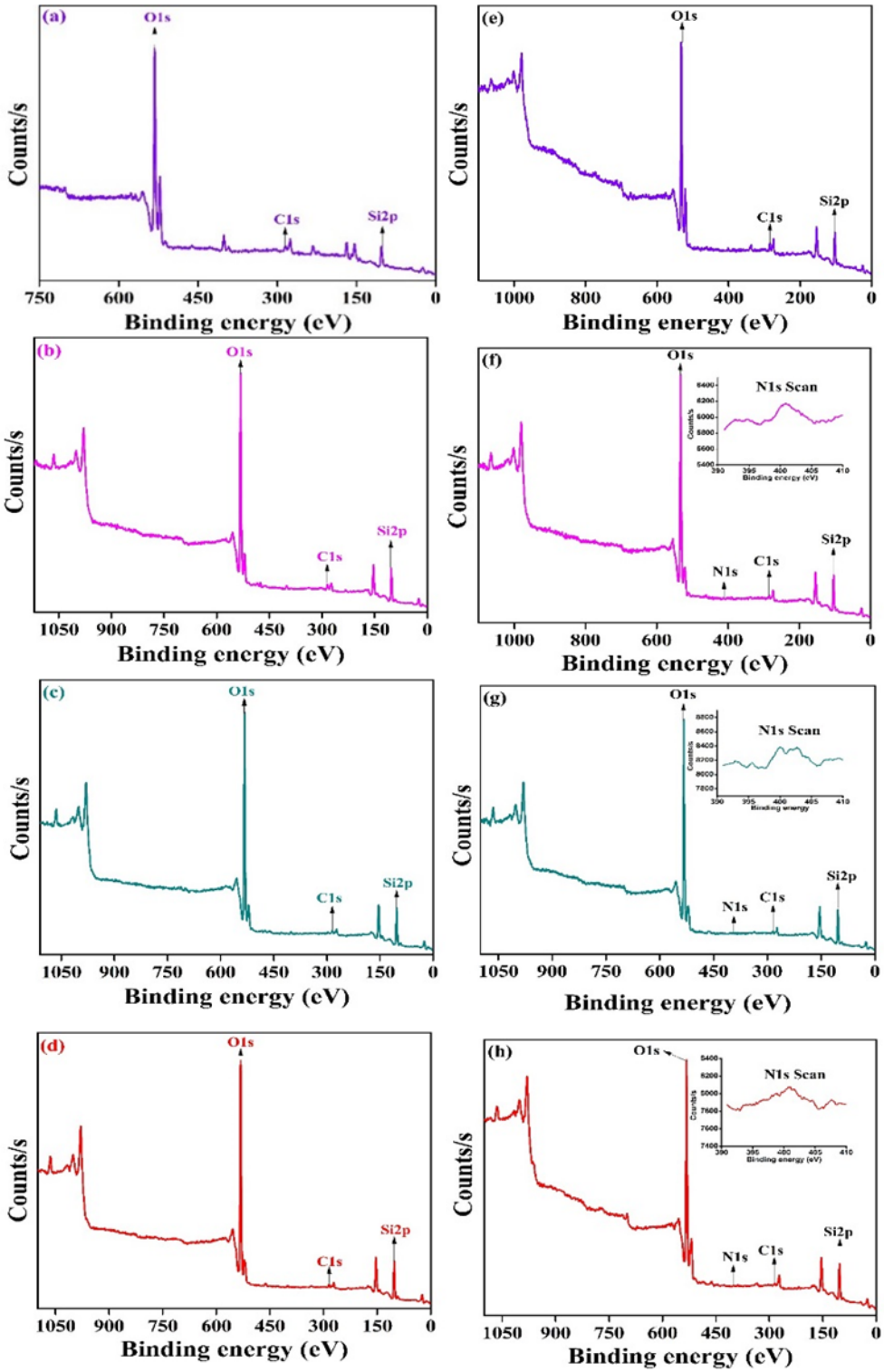


Fig. S5. XPS spectra of before MG adsorption (a) DE, (b) 1XDE, (c) 3XDE and (d) 5XDE. After MG adsorption of (e) DE, (f) 1XDE, (g) 3XDE and (h) 5XDE.

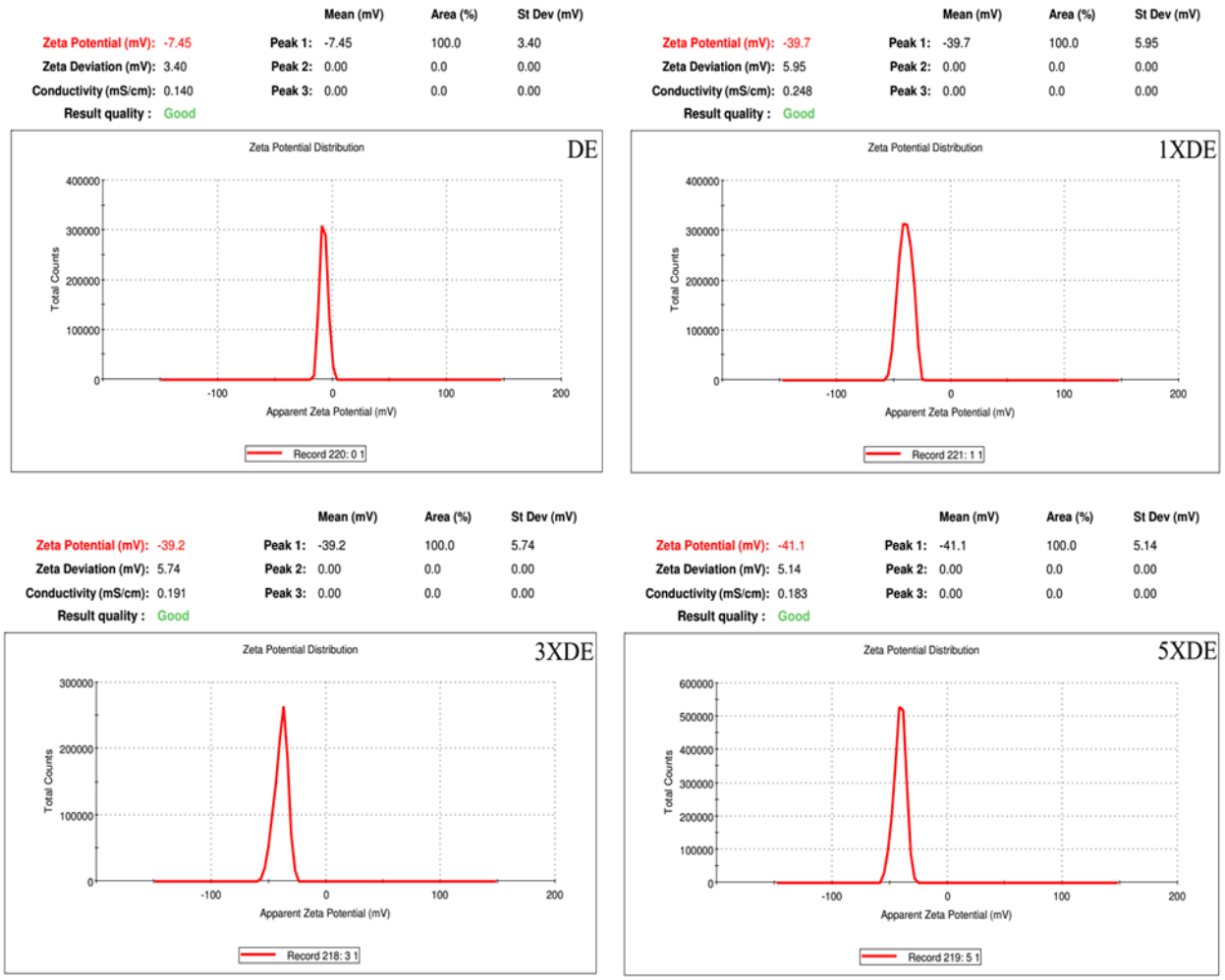


Fig. S6. Zeta potential measurements of DE, 1XDE, 3XDE and 5XDE adsorbents dispersed in water medium at pH 6.0-7.0.

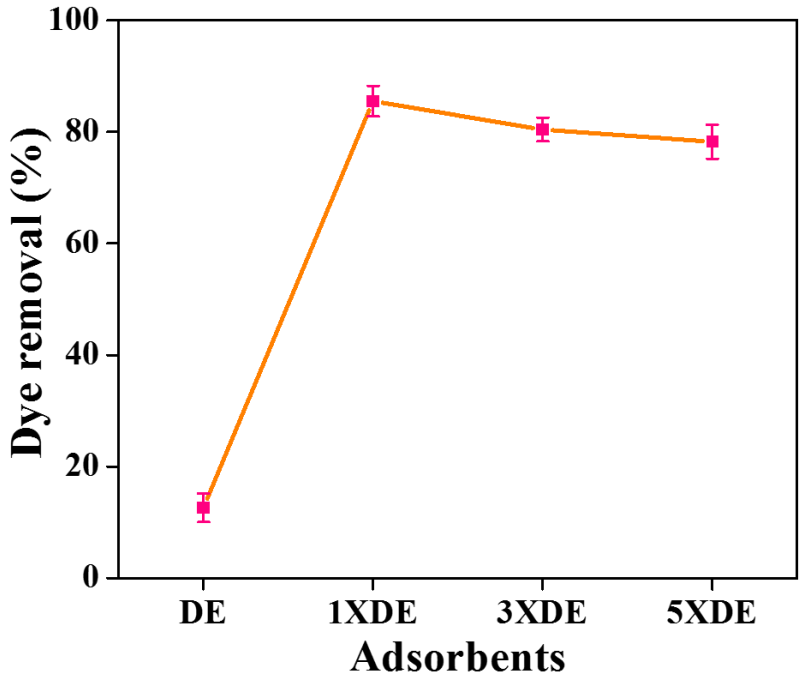


Fig. S7. Effect of adsorbents on dye removal percentage (Adsorbent dosage: 10 mg, dye concentration: 10 mgL^{-1}, pH: natural, working volume: 10 mL, contact time: 1 h, temperature: 30 °C).

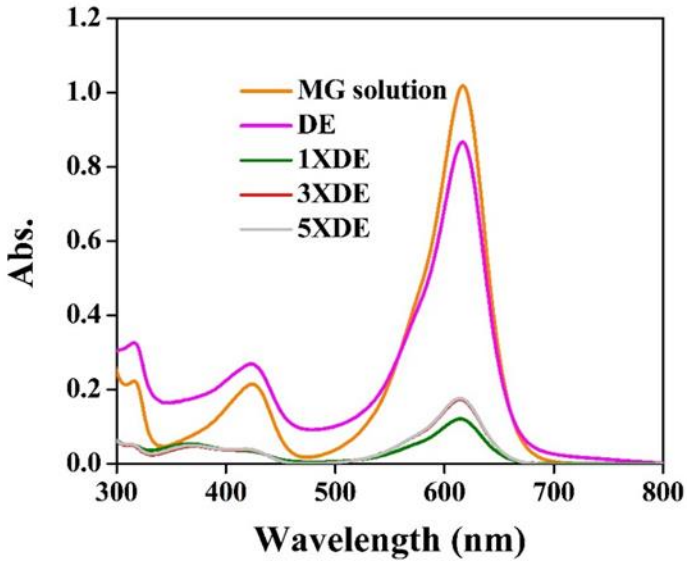


Fig. S8. UV-vis absorbance spectra of as such solution of MG, after MG adsorption of DE, 1XDE, 3XDE and 5XDE (Adsorbent dosage: 10 mg, dye concentration: 10 mgL^{-1}, pH: natural, working volume: 10 mL, contact time: 1 h, temperature: 30 °C).

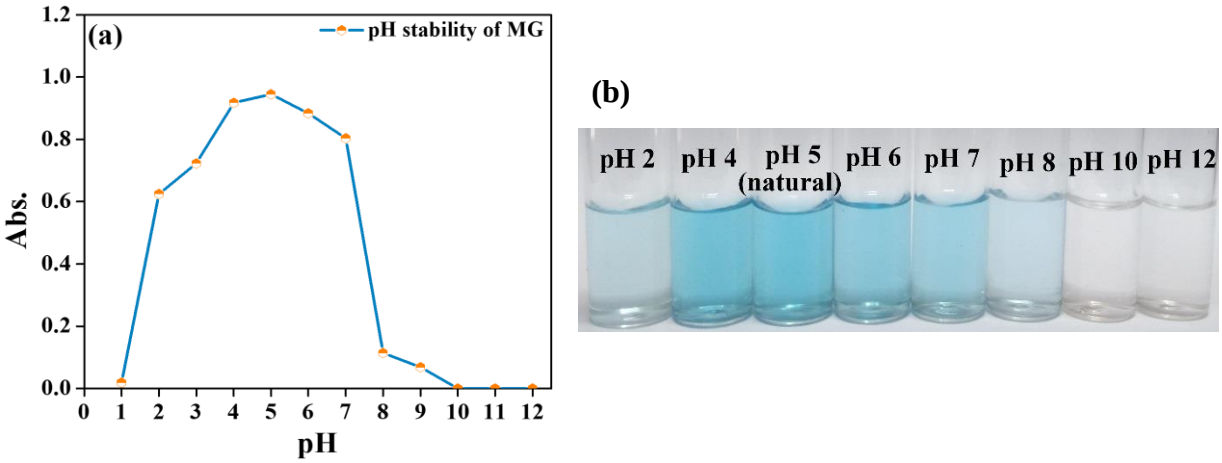


Fig. S9. (a) Stability of MG at different pH and (b) Photo image of MG at different pH (Dye concentartion: 10 mgL^{-1}).

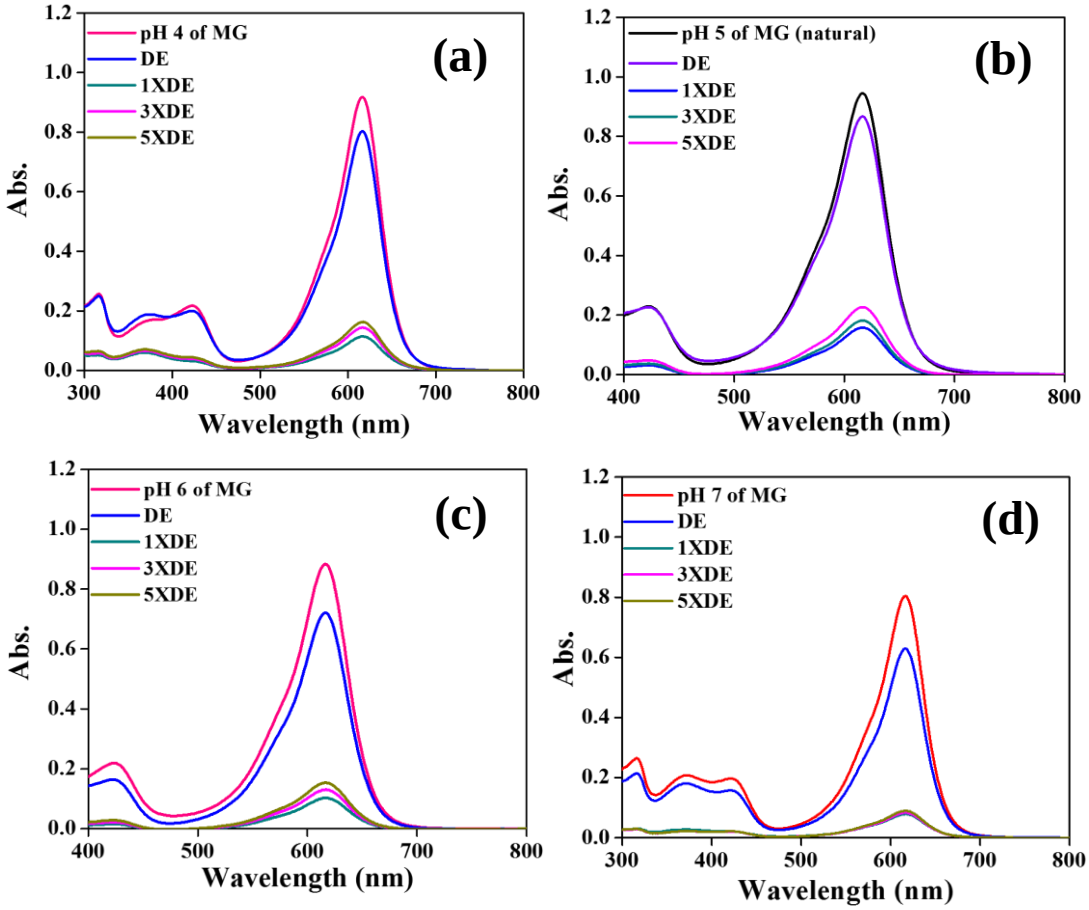


Fig. S10. UV-vis absorbance spectra of effect of pH on adsorption of MG by DE, 1XDE, 3XDE (a) pH 4 (b) pH 5(natural), (c) pH 6 and (d) pH 7 (Adsorbent dosage: 10 mg, dye concentration: 10 mgL^{-1}, working volume: 10 mL, contact time: 1 h, temperature: 30 °C).

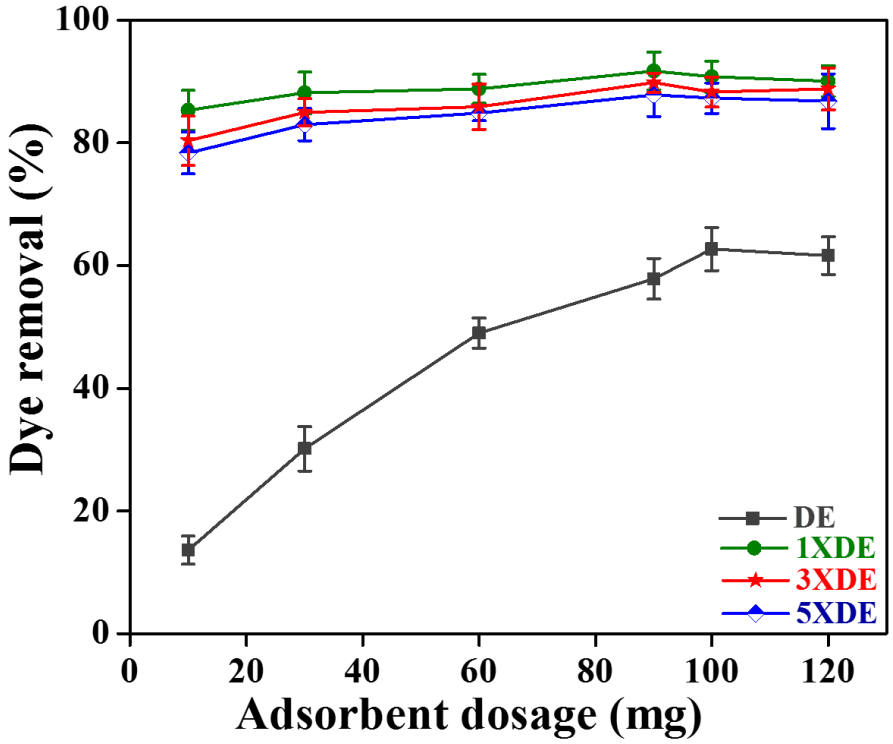


Fig. S11. Effect of adsorbent dosage on dye removal efficiency by DE, 1XDE, 3XDE and 5XDE. (Dye concentration: 10 mgL^{-1}, working volume: 10 mL, pH: natural, contact time: 1 h, temperature: 30 °C).

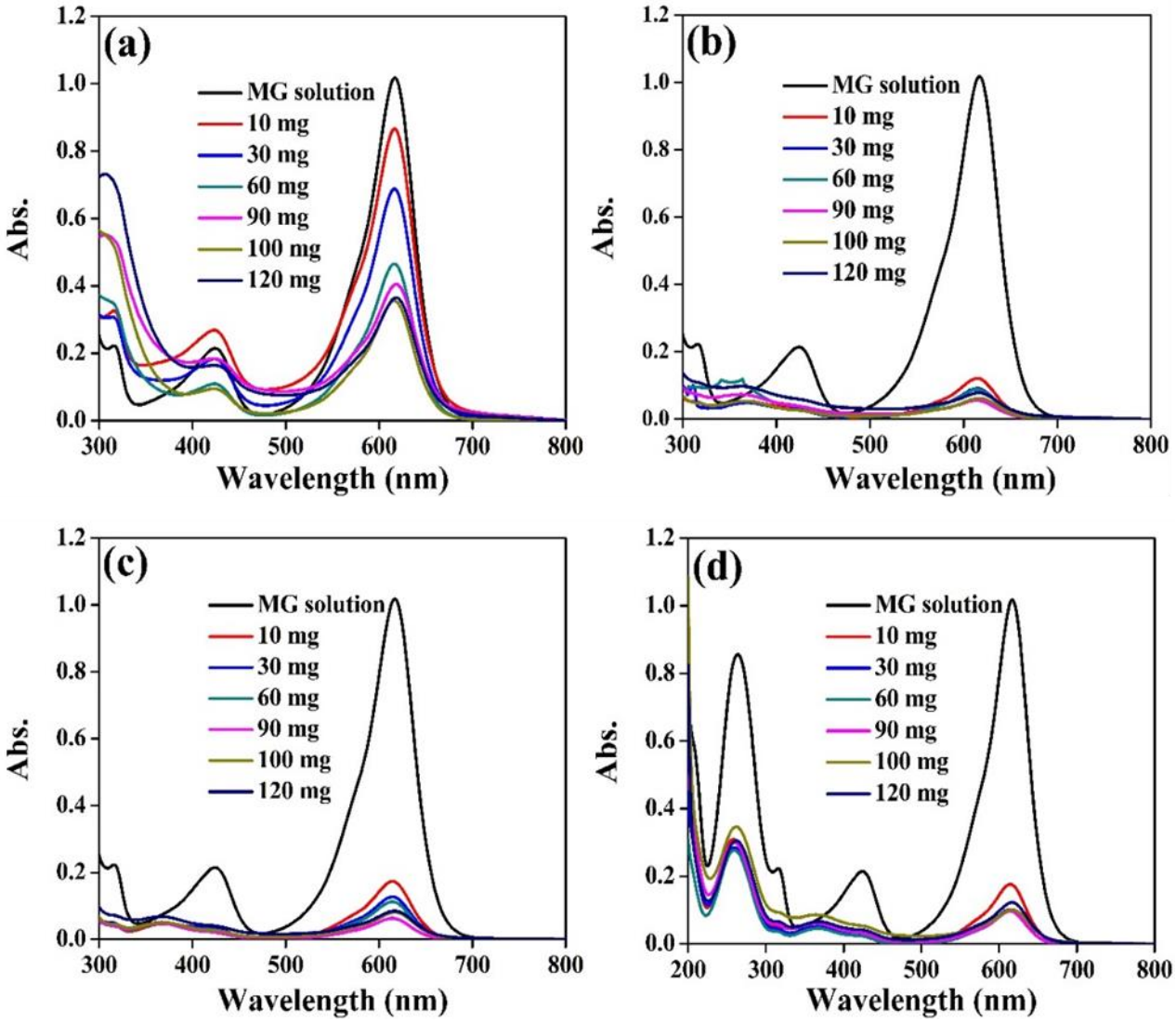


Fig. S12. UV-visible absorbance spectra of malachite green dye adsorbed by different dosage of (a) DE, (b) 1XDE, (c) 3XDE and (d) 5XDE (Dye concentration: 10 mgL^{-1}, pH: natural, working volume: 10 mL, working time: 1 h, temperature: 30 °C).

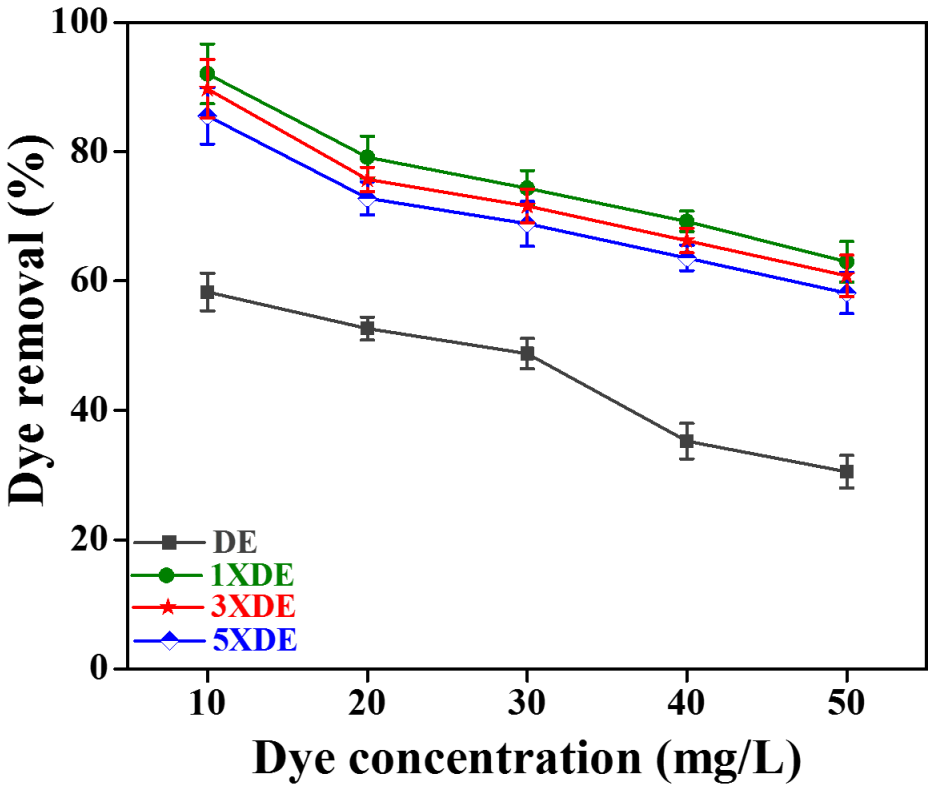


Fig. S13. Effect of initial concentration on dye removal efficiency by adsorbents. (Adsorbent dosage: 90 mg, volume: 10 mL, pH: natural, time: 1 h. and temperature: 30 °C).

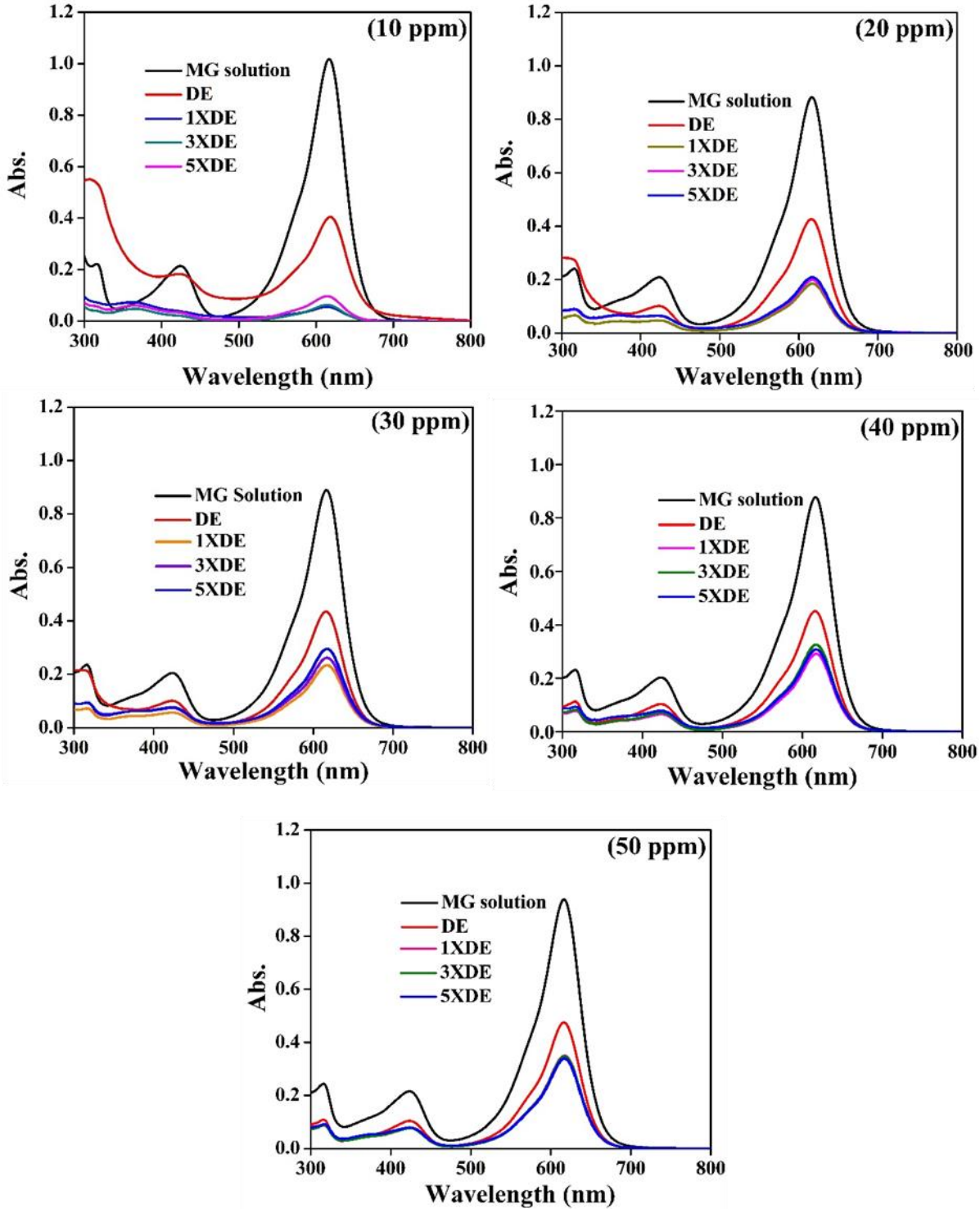


Fig. S14. UV-visible absorbance spectra of different concentration of MG dye adsorbed by DE, 1XDE, 3XDE and 5XDE. (Adsorbent dosage: 90 mg, dye concentration: 10-50 mgL^{-1}, working volume: 10 mL, pH: natural, contact time: 1 h, temperature: 30 °C).

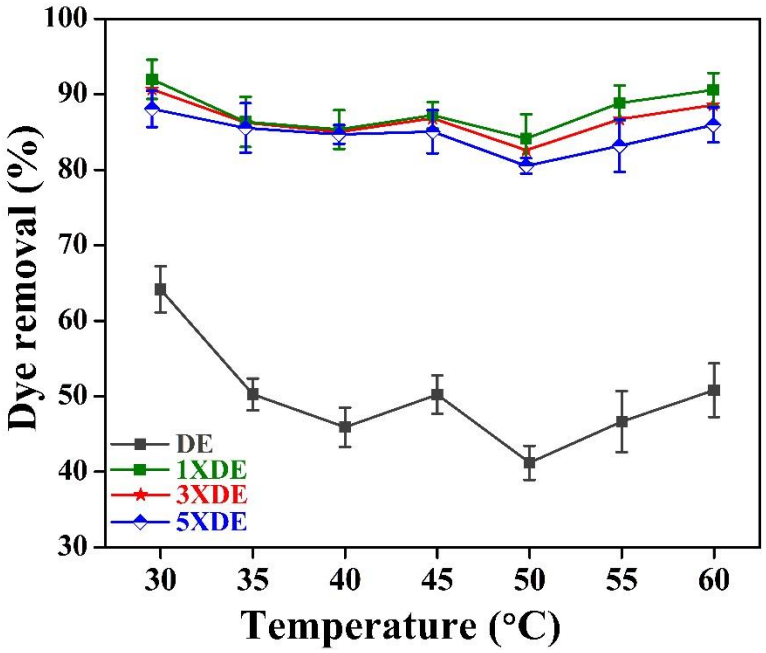


Fig. S15. Effect of temperature on dye removal efficiency by adsorbents. (Adsorbent dosage: 90 mg, dye concentration: 10 mgL^{-1}, pH: natural, volume: 10 mL and time: 1 h).

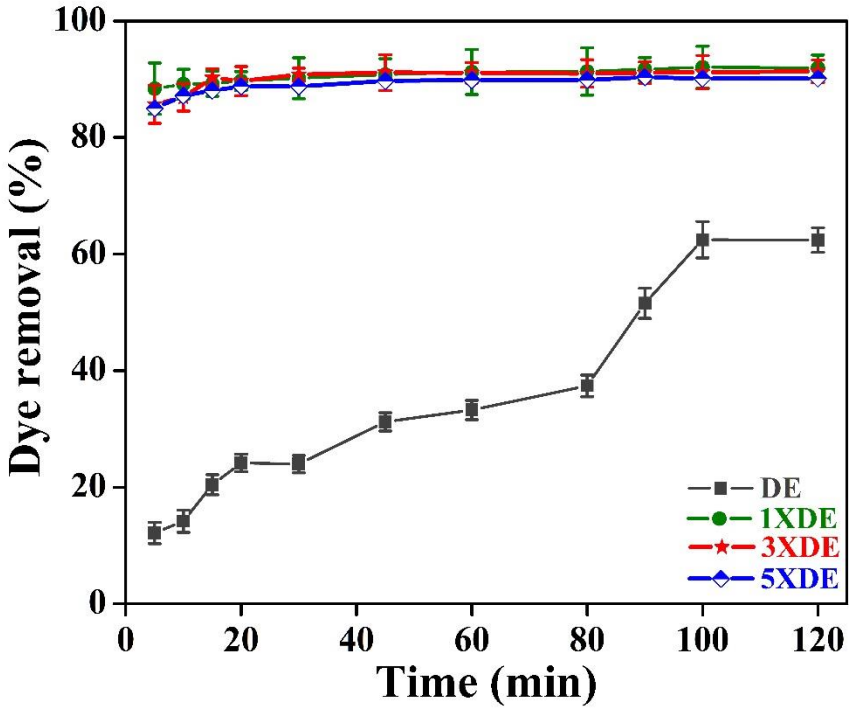


Fig. S16. Effect of contact time on dye removal efficiency by adsorbents. (Adsorbent dosage: 90 mg, pH: natural, dye concentration: 10 mgL^{-1}, working volume: 10 mL and temperature: 30 °C).

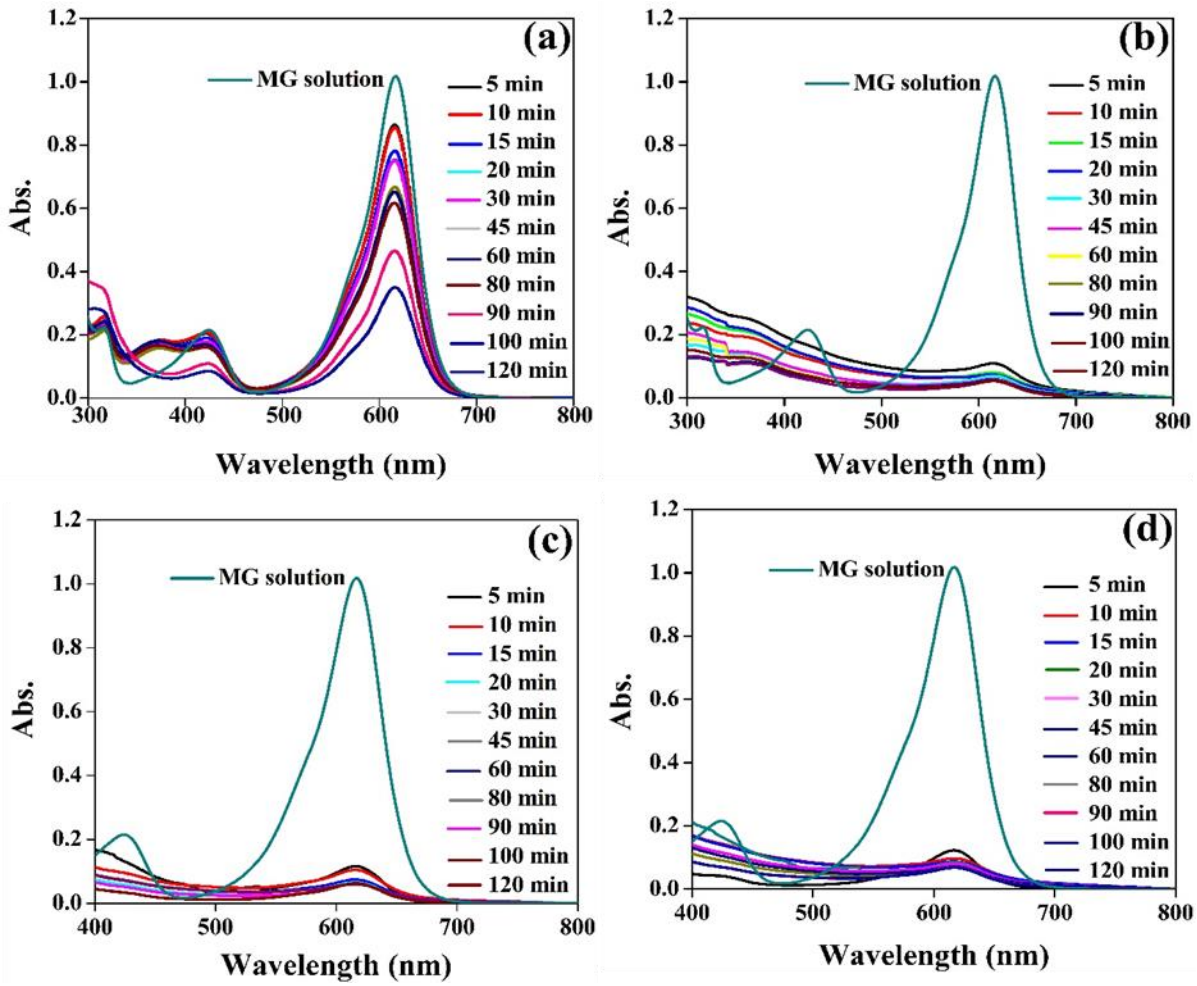


Fig. S17. UV-visible absorbance spectra of contact time of malachite green dye adsorption onto (a) DE, (b) 1XDE, (c) 3XDE and (d) 5XDE (Adsorbent dosage: 90 mg, dye concentration: 10 mgL^{-1}, pH: natural, working volume: 10 mL and temperature: 30 °C).

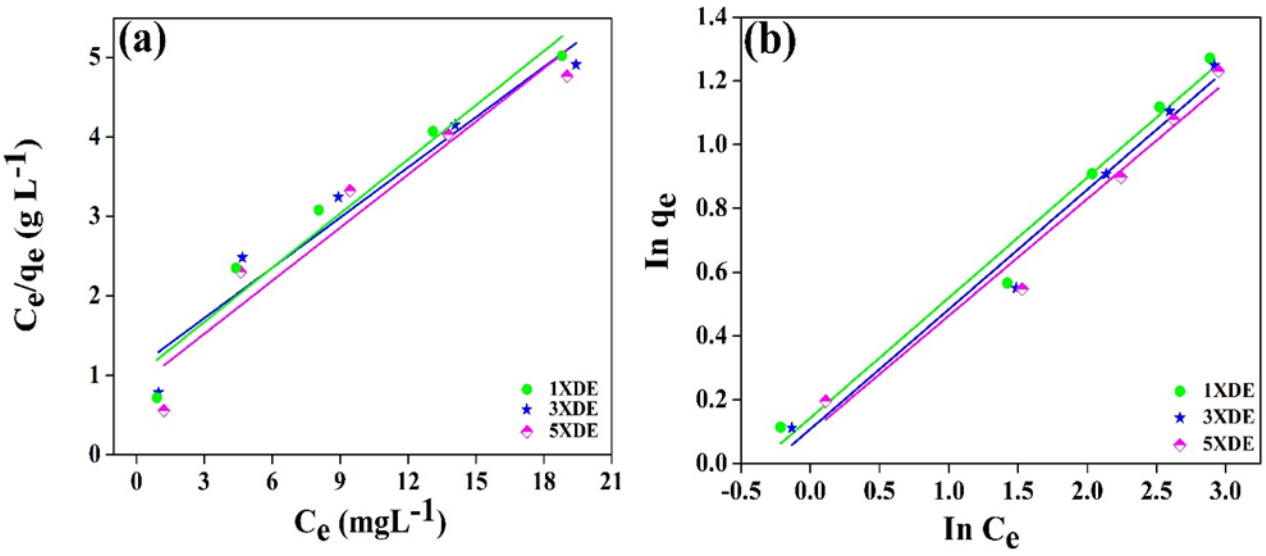


Fig. S18. Adsorption isotherm of MG adsorbed onto 1XDE, 3XDE and 5XDE: (a) Langmuir isotherm, (b) Freundlich isotherm (Adsorbent dosage: 90 mg, dye initial concentration: 10-50 mgL^{-1}, pH: natural, working volume: 10 mL, contact time: 1 h, temperature: 30 °C).

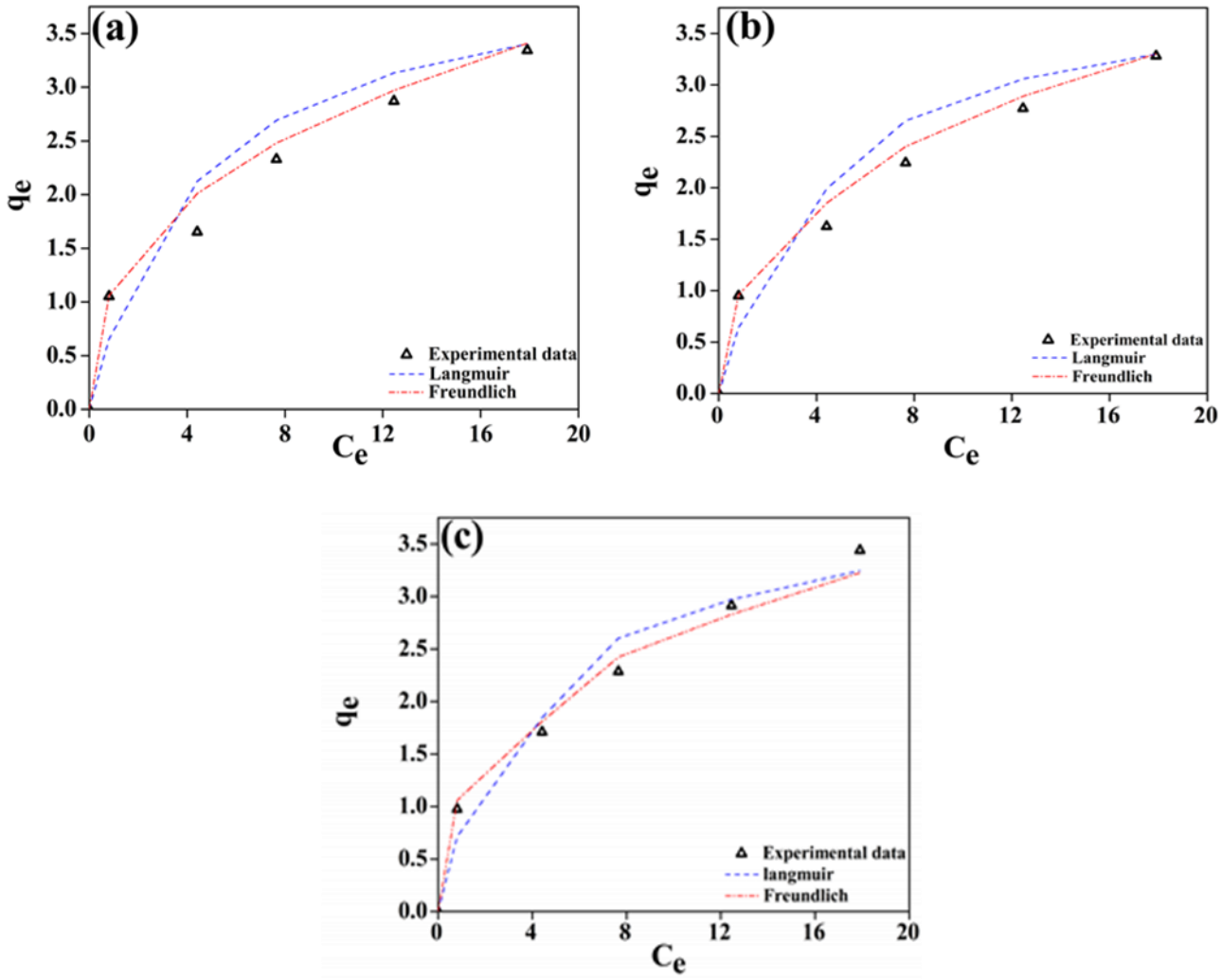


Fig. S19. Investigation of adsorption isotherm models fitting with experimental data for (a) 1XDE, (b) 3XDE and (c) 5XDE.

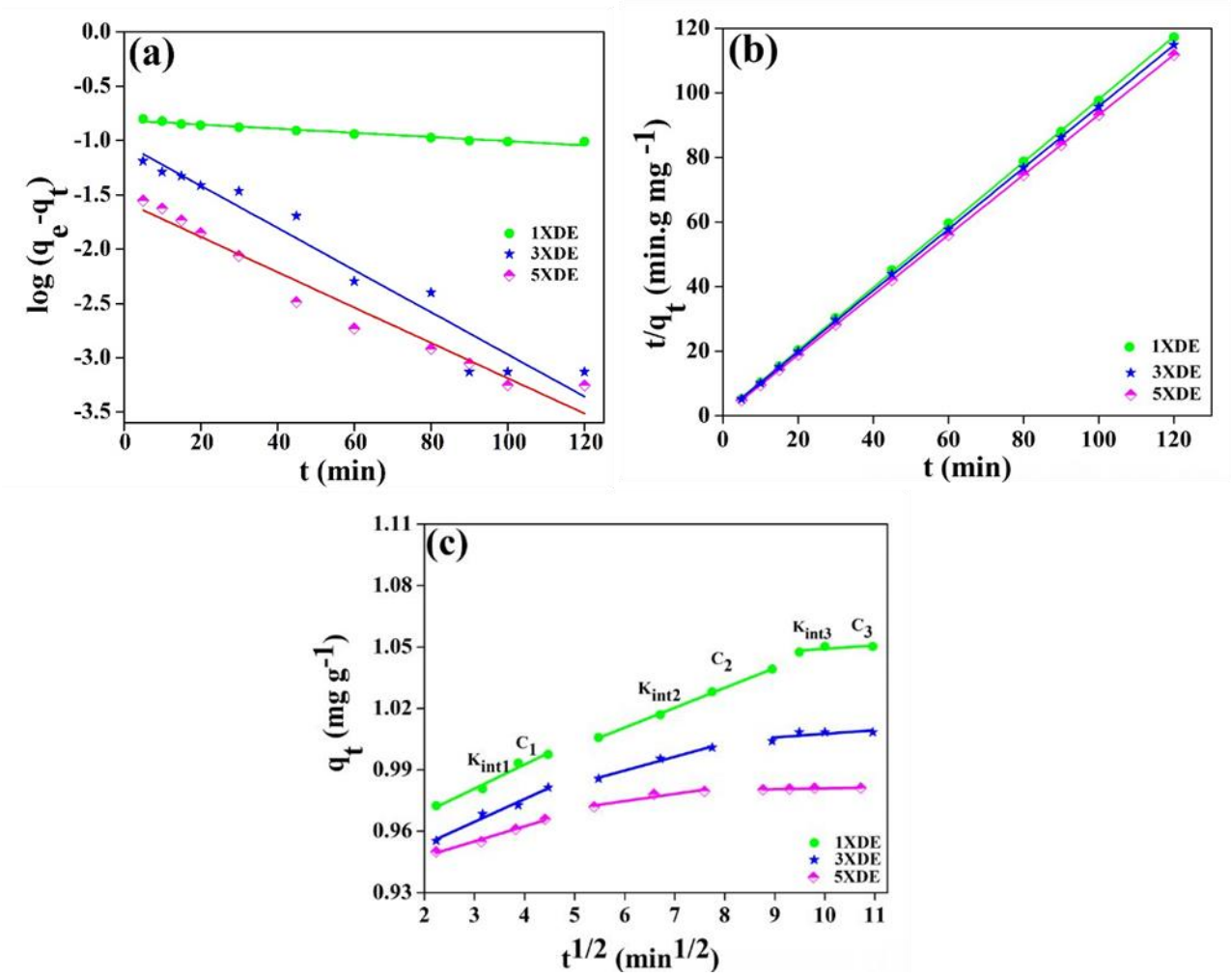


Fig. S20. Adsorption kinetics of malachite green onto 1XDE, 3XDE and 5XDE: (a) Pseudo-first-order kinetics, (b) Pseudo-second-order kinetics and (c) Intraparticle diffusion models (Adsorbent dosage: 90 mg, pH: natural, dye concentration: 10 mgL^{-1}, working volume: 10 mL, contact time: 1 h, temperature: 30 °C).

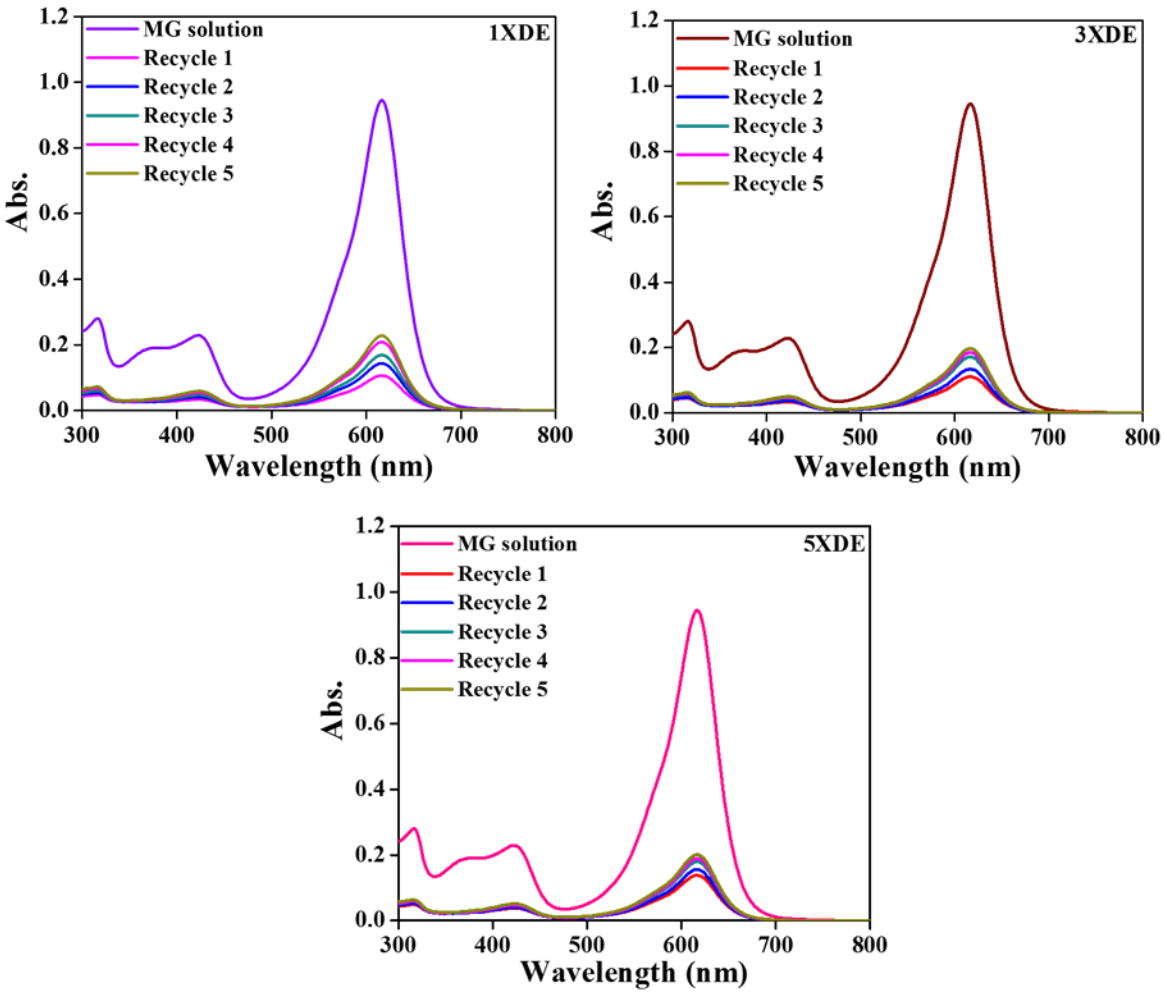


Fig. S21. UV-visible absorbance spectra of recycle test for removal MG by using 1XDE, 3XDE and 5XDE from aqueous solutions (Desorbent dosage: 90 mg, dye concentration: 10 mgL^{-1}, pH: natural, working volume: 10 mL, contact time: 1 h, temperature: 30 °C, regeneration agent: Methanol).

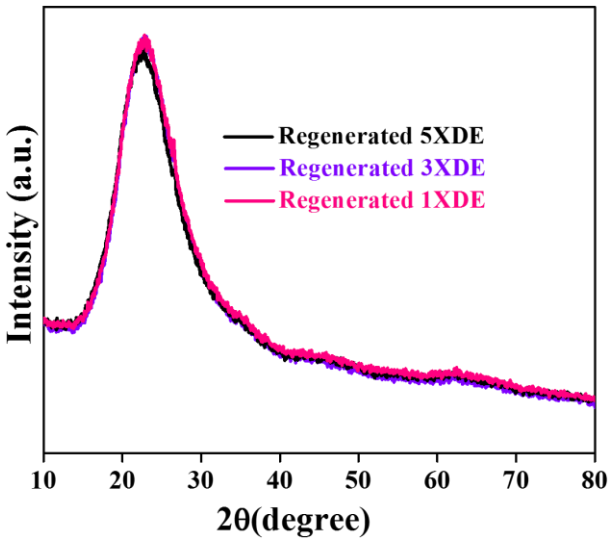


Fig. S22. XRD pattern for 1XDE, 3XDE and 5XDE adsorbents regenerated by 5th cycle.

Table S1

Summary of N_2 Adsorption-Desorption Isotherm Parameters of Adsorbents for Before and after MG Adsorption.

	Before adsorption				After adsorption			
Adsorbents	$a_{s,BET}$ (m^2g^{-1})	d_p (nm)	V_p (cm^3g^{-1})	Isotherm type	$a_{s,BET}$ (m^2g^{-1})	d_p (nm)	V_p (cm^3g^{-1})	Isotherm type
DE	30.2	5.0	0.0443	Type II	30.0	8.3	0.0512	Type IV
1XDE	94.7	4.4	0.1243	Type II	109.6	4.4	0.1478	Type IV
3XDE	129.3	4.4	0.1745	Type II	157.2	4.4	0.2298	Type IV
5XDE	159.5	4.4	0.1744	Type II	168.4	4.4	0.1975	Type IV

Table S2

XPS Elemental Analysis Data of DE and XDE Before and after MG Adsorption.

	Before MG adsorption			After MG adsorption		
Adsorbents	Elements	Binding energy (eV)	Atomic Wt. (%)	Elements	Binding energy (eV)	Atomic Wt. (%)
DE	Si2p	102.64	23.98	Si2p	102.78	34.05
	C1s	284.60	5.41	C1s	284.60	5.69
	O1s	531.90	70.61	O1s	532.25	60.26
1XDE	Si2p	102.57	31.79	Si2p	103.50	33.62
	C1s	284.60	03.82	C1s	284.60	2.16
	O1s	532.01	64.31	O1s	533.04	63.47
				N1s	400.48	0.75
3XDE	Si2p	102.93	37.11	Si2p	103.30	36.17
	C1s	284.60	02.82	C1s	284.60	2.18
	O1s	532.58	60.07	O1s	532.93	61.58
				N1s	397.97	0.07
5XDE	Si2p	102.47	36.25	Si2p	103.21	36.00
	C1s	284.60	02.25	C1s	284.60	2.06
	O1s	532.08	61.50	O1s	532.69	61.33
				N1s	400.09	0.610

Table S3

Intraparticle Diffusion Constants of Malachite Green Dye Adsorption onto XDE.

Adsorbents	K_{int1}	K_{int2}	K_{int3}	C_1	C_2	C_3	R_1^2	R_2^2	R_3^2
1XDE	0.0091	0.0075	0.0012	0.9420	0.9473	1.0097	0.964	0.998	0.178
3XDE	0.0111	0.0067	0.0017	0.9312	0.9494	0.9898	0.969	0.973	0.241
5XDE	0.0058	0.0038	0.0003	0.9343	0.9457	0.9720	0.961	0.926	0.660

Table S4

Thermodynamic Parameters of MG Adsorbed on Different Adsorbents at Various Temperatures.

Adsorbents	ΔH° ($KJmol^{-1}$)	ΔS° ($KJmol^{-1}K^{-1}$)	ΔG° ($KJmol^{-1}$)						
			303 K	308 K	313 K	318 K	323 K	328 K	333 K
DE	-4.734	-0.033	4.740	5.786	6.133	5.699	7.099	6.009	5.721
1XDE	-2.122	-0.007	-0.592	0.677	0.801	0.459	1.005	0.602	-0.371
3XDE	-7.246	-0.025	-0.337	0.855	1.098	0.556	1.650	1.067	0.404
5XDE	-8.663	-0.031	0.556	0.819	1.241	1.116	2.019	1.694	1.104

References

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