

Supplementary Information

TEXTS

Text-S1

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), copper sulfate, ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), acetate buffer, ferric trichloride, 3-mercaptopropanoic acid ($\text{HSCH}_2\text{CH}_2\text{CO}_2\text{H}$), sodium hydroxide (NaOH), HCl , Na_2CO_3 , MgSO_4 , potassium ferricyanide and malachite green ($\text{C}_{23}\text{H}_{25}\text{ClN}_2$) (Aldrich, 99%), tripyridyltriazine (TPTZ, HPLC grade, Anaqua, 99.9%), gallic acid, ethanol ($\text{C}_2\text{H}_5\text{OH}$), (Merck, 99.9%) without any further purification. Distilled water (DI) was attained from Qingdao water purification agency to make all aqueous solution.

Text-S2

Elemental analyzer (EA, Vario EL cube, German), muffle furnace (HMX-1400, Shanghai HaoYue), centrifuge machine (model C-30BL), Atomic absorption spectrometry (Solaar M6, Thermo Elemental, USA), rotary shaker (THZ-92A, China), UV-vis spectrophotometer (T80, P.G. Instrument Ltd., UK), thermostatic water bath shaker (Max Q 7000, Thermo Scientific), magnetic stirrer (MS-M-S10, BiobaseBiodustry, Shandong Co., Ltd.), Erlenmeyer flasks (JOAN Lab Pyrex Glass Erlenmeyer Flask, Ningbo Yinzhou Joan Lab Equipments, china), pH meter (mV/ORP METTLER TOLEDO) and volumetric flasks were used. Further, transmission electron microscopy (TEM, JEM-2100HR, Japan), fourier transforms infrared spectroscopy (FTIR, Bruker Vertex 70), Brunauer-Emmet-Teller (BET) analyzer (Micromeritics'ASAP2020), X-ray diffractometer (XRD, Philips Electronic Instruments), Thermo-gravimetric analyzer (TGA, NETZSCH TG 209F3), 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) and Vibrating sample magnetometer (VSM, VSM600) were used for the characterization of fabricated material in the present research study.

Text-S3

The FRAP reagent was made by using 20 mM of FeCl_3 solution, 300 mM of acetate buffer and 10 mM of tripyridyltriazine (TPTZ) solution in HCl at a 1:1:10 ratio. The absorbance of samples containing 800 μL of FRAP reagent, 60 μL of H_2O , and 20 μL of extract was determined at $\lambda=593$ nm using UV-vis spectrophotometer. The FRAP reagent was kept at room temperature (25°C) throughout the experiments. The standard calibration curve for this test was also designed using six Fe^{+2} standards with concentration range between 100 and 1000 $\mu\text{mol/L}$ ($r > 0.999$). In addition, different color development tests were employed to investigate the presence of probable organic contents in the leaves extract which can reduce Fe^{+3} to Fe^{+2} . For this purpose, ferric trichloride-potassium ferricyanide, HCl-Mg reaction and alkaline copper sulfate tests were used.

Text-S4

A dilution sample was prepared containing plant leaves extract (20 μL) and 40 μL of pure DI water. Thereafter, Folin-Ciocalteu reagent (100 μL) was added and mixed. After mixing of 5 min, 300 mL of Na_2CO_3 solution was injected and permitted to stand for 15 min. Finally, the absorbance of the sample was determined at $\lambda=765$ nm by UV-vis spectrophotometer. The results of TPC were stated as milligrams of gallic acid equivalent (GAE) per gram of dry weight.

Text-S5

Pseudo-First-Order Kinetic

$$\log(q_e - q_t) = \log q_e - \frac{tk_1}{2.3.3} \dots \dots \dots (i)$$

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:

$$q_e = \frac{(C_o - C_e)}{m} V \text{-----(ii)}$$

$$q_t = \frac{(C_o - C_t)}{m} V \text{-----(iii)}$$

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

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \text{-----(iv)}$$

$$h = k_2(q_e)^2 \text{----- (v)}$$

Where, h ($\text{mgg}^{-1} \cdot \text{min}^{-1}$) 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

$$q_t = \frac{1}{\beta \ln \alpha \beta} + \frac{1}{\beta \ln t} \text{----- (vi)}$$

Where, α ($\text{mg g}^{-1} \cdot \text{min}^{-1}$) 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 $\ln t$ vs q_t . To check the diffusion mechanism between MG dye and 3-MPA@PMNPs, Weber and Morris kinetic equation was used as.

Weber and Morris kinetic equation

$$q_t = k_{ipd} t^{0.5} \text{----- (vii)}$$

Where, k_{ipd} ($\text{mgg}^{-1} \cdot \text{min}^{-0.5}$) is the intra particle diffusion rate constant and can be calculated from the slope of the straight line of $t^{0.5}$ vs q_t . The applicability of this model was estimated by plotting graph between $t^{0.5}$ vs q_t . Finally to confirm the film diffusion mechanism, liquid film diffusion kinetic model was employed to experimental data and applied equation is given below:

liquid film diffusion kinetic model

$$\ln(1 - F) = -k_{fd} t \text{----- (viii)}$$

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 $\ln(1-F)$.

Text-S6

Langmuir Model

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \text{----- (ix)}$$

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:

$$K_L = \frac{1}{1 + bC_e} \quad \text{-----(x)}$$

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 favourability of the sorption isotherm depends upon on the K_L value. If $K_L > 1$ sorption isotherm is unfavourable, 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 favourable.

Freundlich Model

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

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 $\log C_e$ vs $\log q_e$. 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 favourable at experimental conditions.

Temkin Model

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

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 (8.314 J/mol. K). T is the temperature in 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 .

Dubin-Radushkevich model

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad \text{-----(xiii)}$$

Where, q_e (mg/g) is the quantity of the MG 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 ε^2 vs $\ln q_e$. While, the values of ε were calculated by using this formula:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad \text{-----(xiv)}$$

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:

$$E = \frac{1}{\sqrt{(2\beta)}} \quad \text{-----(xv)}$$

$$\Delta G^\circ = -RT \ln K_D \text{-----(xvi)}$$

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

Where, ΔG° (kJ/mol) is the change in free energy, ΔH° (kJ/mol) is the enthalpy, ΔS° (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 $1/T$ vs $\ln K_D$.

TABLES

Table S1 Molecular structure and chemical properties of the Malachite Green (MG) dye

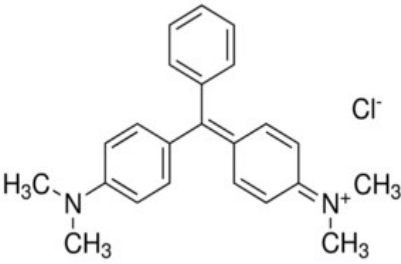
Dye name	Molecular structure	Chemical properties	
MG		Chemical name: Chemical formula Molar mass: Colour Index Number: Dye class: λ_{max} : Melting point: Boiling point:	4-{{4-(Dimethylamino)phenyl}}(phenyl)methylidene}-N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride $C_{23}H_{25}ClN_2$ 364.911 g/mol (chloride) 42000 Azo dyes 617 nm 112°C Not available, it decomposes. When there are a lot of branching in a compound the boiling point goes away

Table S2 Color development tests to investigate the presence of organic contents in the leaves extract of *Fraxinus chinensis Roxb*

Tests	Color development	Precipitation development	Suggestions
Ferric trichloride-potassium ferricyanide	Blue-green spots on the filter paper	No after adding gelatin	Existence of phenolic compounds and tannins
HCl-Mg reaction	Solution color changed to reddish brown	No	Existence of flavonoid
Alkaline copper sulfate	red	Red copper oxide precipitation appeared	Existence of reducing sugar

FIGURES

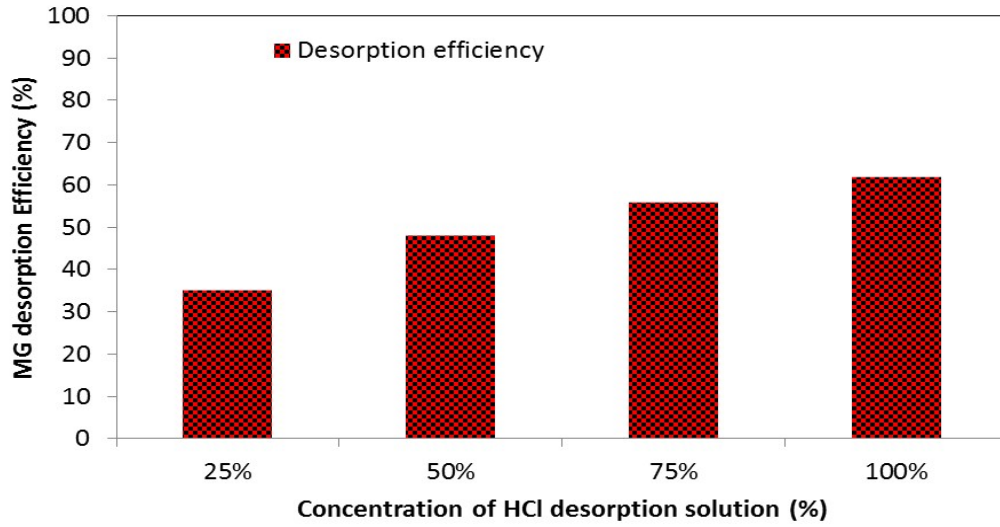


Fig. S1 Effect of different concentration of HCl desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.5 g/L, MG initial concentration (C_0) = 25 mg/L)

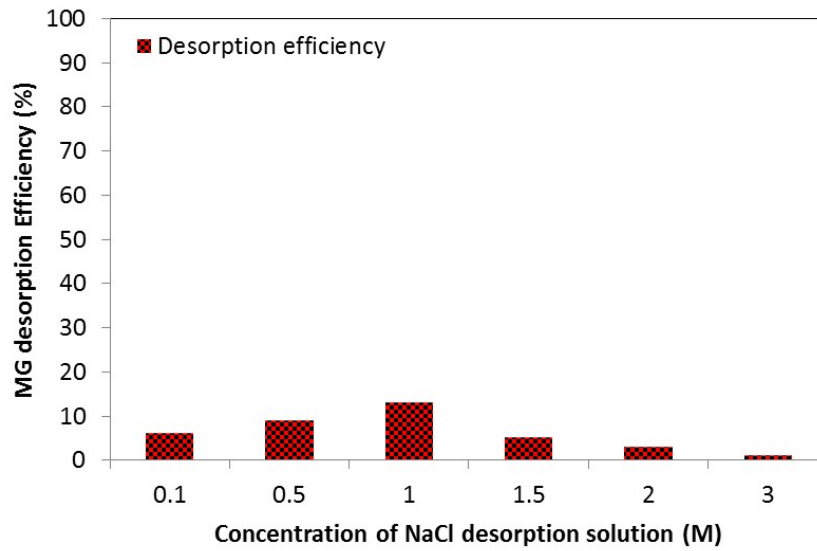


Fig. S2 Effect of different concentration of NaCl desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.5 g/L, MG initial concentration (C_0) = 25 mg/L)

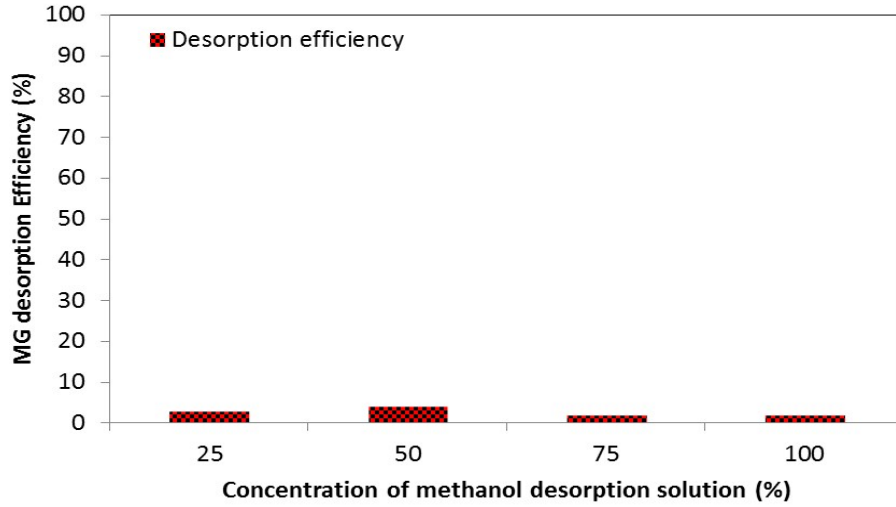


Fig. S3 Effect of different concentration of methanol desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.5 g/L, MG initial concentration (C_0) = 25 mg/L)

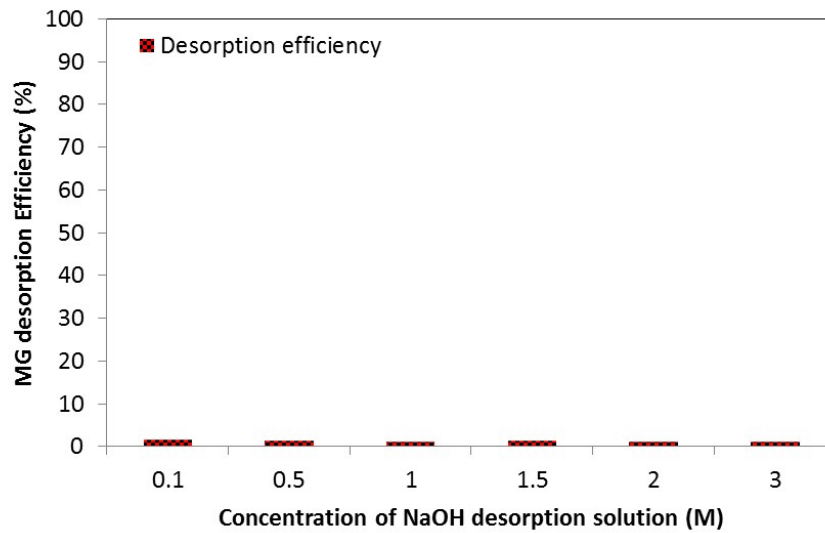


Fig. S4 Effect of different concentration of NaOH desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.5 g/L, MG initial concentration (C_0) = 25 mg/L)

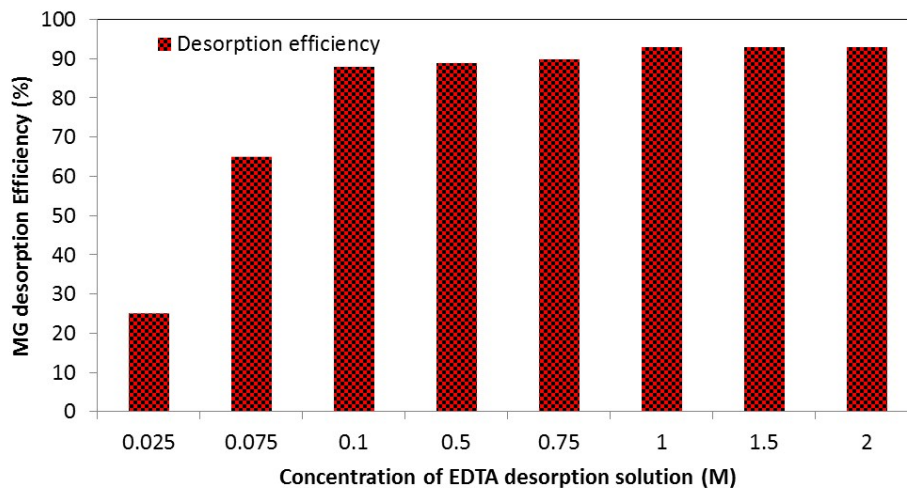


Fig. S5 Effect of different concentration of EDTA desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.5 g/L, MG initial concentration (C_0) = 25 mg/L)

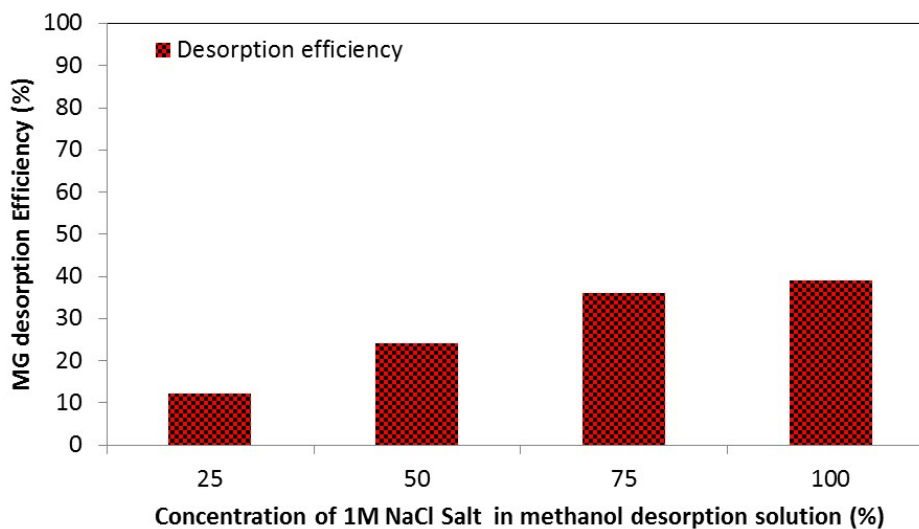


Fig. S6 Effect of different concentration of 1M NaCl salt in methanol desorption solutions on the desorption efficiency of MG dye (adsorbents dosage = 0.5 g/L, MG initial concentration (C_0) = 25 mg/L)

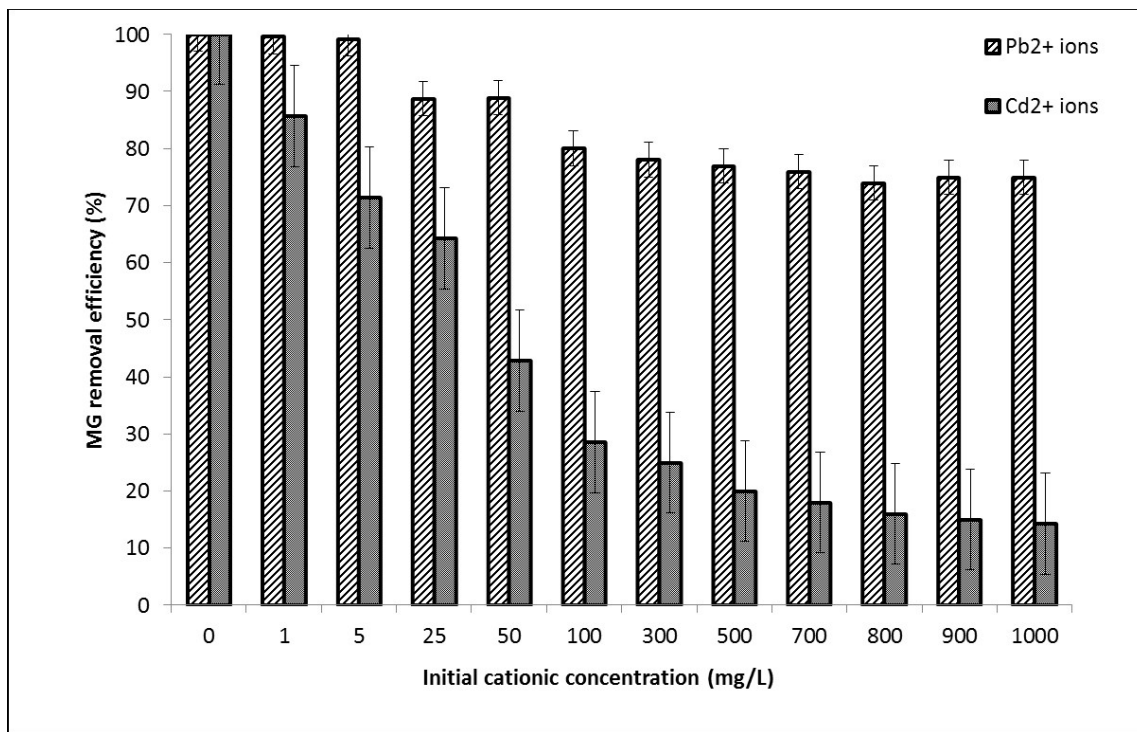


Fig. S7 Study of the influence of co-present cationic ions on MG removal by PMNPs@3-MPA (adsorbents dosage = 0.3 g/L; MG initial concentration (C_0) = 10 mg/L; contact time: 1 h)