

Keggin-type heteropoly acid $H_3PW_{12}O_{40}$ supported on magnetic amine-grafted Graphene oxide: A new magnetically separable adsorbent for rapid and selective removal of cationic organic pollutants in aqueous solutions

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Abstract

In the present study, phosphotungstic acid decorated on magnetic amine-grafted graphene oxide (GO-Amine/ $Fe_3O_4/H_3PW_{12}O_{40}$; GOA/ Fe_3O_4/HPW) was prepared and evaluated as a new adsorbent for removal and separation of organic dyes from water. The obtained nanocomposite was fully characterized by means of XRD, FT-IR, Raman, VSM, SEM, EDX, AFM and BET surface area analysis. The results demonstrated the successful loading of HPW (~34 wt.%) on the surface of magnetic aminosilanized graphene oxide. The adsorption ability of the nanocomposite was tested towards cationic methylene blue (MB) and anionic methyl orange (MO) dyes. The nanocomposite exhibited very good adsorption performance for cationic organic pollutants; it could absorb approximately 100% of methylene blue (MB) from an aqueous solution within only 5 min. The removal rate of GOA/ Fe_3O_4/HPW nanocomposite was greater than that of pure GOA, Fe_3O_4 and HPW. Further study revealed that the GOA/ Fe_3O_4/HPW exhibited a fast adsorption rate and selective adsorption ability towards the cationic dyes from dyes mixtures. The effect of adsorbent dosage, initial concentration of dye and pH were studied in detail. Due to the existence of the Fe_3O_4 , the GOA/ Fe_3O_4/HPW nanocomposite could be magnetically separated from the reaction mixture and reused without any change in structure. This research could provide a new easy platform for wastewater purification.

Keywords: Aminated Graphene Oxide; Keggin-Type $H_3PW_{12}O_{40}$; Magnetic Adsorbent; Nanocomposite; Organic Dyes; Polyoxometalate.

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INTRODUCTION

At present, organic dyes are widely used in textiles, papers, food, plastic, leather, pharmaceutical and etc [1–4]. The extensive use of dyes often brings more pollution problems in the form of colored wastewater. The release of colored wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation [5–7]. Different treatment processes such as chemical coagulation, photo or sonodegradation, adsorption

with different materials and membrane filtration have been utilized for dye removal over the years [8–10]. Among them, adsorption is getting special interest from the researchers worldwide due to its high efficiency, simple operation process and low energy consumption [11–13]. Until now, a huge amount of adsorbents have been investigated such as nanotubes of carbon [14], zeolites [15], polyoxometalates [16], graphene [17] and so on. However, there is still a tendency of the researchers to find new adsorbent materials with high adsorption capacity, even high selectivity and

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short contact time toward specific dyes.

Graphene, a monolayer or few layers of sp^2 -bonded carbon atoms, is a novel nanomaterial which has been intensively studied since its discovery by Novoselov and co-workers in 2004 [18]. Graphene oxide (GO) is a highly oxidative form of graphene. The large surface area and high water solubility make GO a material of great interest in adsorption-based technologies such as removal of dye contaminants from wastewater [19]. For further improving the performance of GO, anchoring second components such as polyoxometalates (POMs) is highly desirable [20].

POMs are an outstanding family of metal oxide clusters with controllable shape and size [21]. They are versatile and easily accessible, and they possess strong acidity, favorable redox properties, oxo enriched surfaces and high electronegativity which facilitate their use in various applications, such as catalysis [22], optics, magnetism, medicine [23] as well as dye adsorption [24]. However, the application range of these active species is limited due to their low surface area (less than $10\text{ m}^2\text{g}^{-1}$) and problematic separation and recycling processes. The coupling of POM anion with GO could improve the surface area and avoid the dissolution of POM which greatly improve their adsorption ability for target dyes [20]. However, in spite of improved adsorption capacity of GO/POMs, separating and recycling of this composite from a mixed suspension limits the expansion of applications. One effective pathway to solve the above problem is the coupling with magnetic materials [25-27]. Magnetic separation provides a convenient technique for removing and recycling magnetized composites under an external magnetic field. Magnetic ferrite (MFe_2O_4) nanoparticles have been of great interest, because they have proven to be useful in many applications. Ferrite-based nanocomposites provide a potential advantage for repeated magnetic separation purposes [28,29].

Based on the above considerations, in the present study, amino-functionalized magnetic graphene oxide ($\text{GO-NH}_2/\text{Fe}_3\text{O}_4$; $\text{GOA}/\text{Fe}_3\text{O}_4$) was synthesized and used as a novel support for immobilizing Keggin heteropoly acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$; HPW). This magnetically recoverable ternary nanocomposite material ($\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$) was prepared by a simple acid-base electrostatic interaction between HPW and amino groups of $\text{GOA}/\text{Fe}_3\text{O}_4$. For one thing, $\text{PW}_{12}\text{O}_{40}^{3-}$ anion with highly electronegative and hydrophilic properties

and structural stability could be utilized as a potential adsorbent for removal of the cationic dyes in dye-wastewater. For another, magnetic GO possesses outstanding porosity and extremely large surface area, and it is insoluble in water, which is an appropriate solid matrix to anchor Keggin-type HPW. The combination of polyoxoanions and $\text{GOA}/\text{Fe}_3\text{O}_4$ could improve the surface area and avoid the dissolution of POM. This nanocomposite was characterized and used as a new adsorbent for removing organic dyes from aqueous solutions. The effects of some key parameters such as adsorbent dosage, initial dye concentration and initial pH on dye adsorption were investigated in detail. The selective adsorption ability of this nanocomposite towards cationic dyes was also studied.

EXPERIMENTAL

Materials and methods

The applied materials in current research, their purities, and suppliers are as follows: Graphite powder (99.9%, Timcal), potassium permanganate and sodium nitrate (99.5%, Merck), sulfuric acid (98%, Sigma-Aldrich), hydrogen peroxide (30% in H_2O , Merck) 3-aminopropyltriethoxysilane (APTES, 99%), phosphotungstic acid (98%, Sigma-Aldrich), and ethanol (99.5%, Sigma-Aldrich). Methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, 98%) and methyl orange (MO, $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, 98%) were provided from Merck Chemical Co.

Preparation of the $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite

Graphene oxide (GO) was synthesized using the modified Hummers method [30] according to our previous work [31]. The GO suspension (30 mL, 0.3 g) was added to 150 mL of ethanol containing APTES (3 mL), and the reaction mixture was refluxed. After 24 h, the solvent was removed by filtration to obtain the amine-grafted graphene oxide (GOA), which was extensively washed with water and then ethanol. To prepare magnetic amine graphene oxide, 0.25 g of the resulting GOA was dispersed in 90 mL of water by sonication for 1 hour. Then, 0.84 g of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ and 2.08 g of $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ were added to the GOA dispersion and its pH was adjusted at 12 by adding NaOH. The mixture was stirred at $50\text{ }^\circ\text{C}$ for 2 h. Then it was filtered and washed with water and ethanol three times. For immobilizing the phosphotungstic acid, $\text{GOA}/\text{Fe}_3\text{O}_4$ (0.2 g) was stirred with 150 mL of

a methanolic solution of 0.4 g of phosphotungstic acid (HPW) at 25°C. After 48 h, the solvent was removed by filtration, and the resulting solid was washed in pure water to remove unreacted acid and then dried under vacuum, which afforded the magnetic acid/base bifunctional material amine-grafted graphene oxide (GOA/Fe₃O₄/HPW). The ICP-AES results indicated that the loading amount of HPW in the as-prepared nanocomposite was ca.34 wt%.

Adsorption ability

The adsorption experiments of the dyes were carried out into an Erlenmeyer flask and the adsorption reaction temperature was maintained at 25 °C. Various quantities (20, 35, 50 and 65 mg) of the nanocomposite were transferred into 50 mL of aqueous solution of methylene blue (MB) or methyl orange (MO) with initial concentration of 25 mg/L. In order to prevent photodegradation of dyes by the nanocomposite, the dye solution was covered with a dark paper during the adsorption tests. The mixture was stirred gently and during the reaction, small portions (2 mL) of the solution were pipetted out and then the magnetic adsorbent was separated by a magnet. The upper clear solutions were then used for examination of MB and MO concentrations by measuring the absorbance of the solution at fixed wavelengths of 664 nm for MB solution and 467 nm for MO using a UV-visible spectrophotometer. A similar experiment was also done with 50 mL of MB solutions (5, 25, 40, 55 and 70 mg/L). To study the effects of initial solution pH on the adsorption process, several experiments were performed. The initial pH of MB solution was adjusted to values in the range of 2–10 by drop wise addition of NaOH or HCl solutions (0.1 M). Also, the nanocomposite was transferred into mixtures of MB-MO (v:v 1/1, 50 mL, 25 mg/L). The UV-Vis spectroscopy was performed to determine the selective adsorption ability of nanocomposite at given time intervals. The adsorption percentage of the nanocomposite is defined as $C_t/C_0 \times 100\%$, where C_0 and C_t are the dye concentrations before and after irradiation.

Reuse/Cycling experiments

To evaluate recycling potential and material reuse, after each reaction cycle, the GOA/Fe₃O₄/HPW with adsorbed MB was separated from the dye solution by a magnet and washed several times with water and ethanol at room

temperature. The reusability of the regenerated GOA/Fe₃O₄/HPW was tested by four consecutive adsorptions/desorption experiments under the same adsorption conditions.

Characterization

Infrared spectra were recorded on a Shimadzu system FT-IR 160 spectrophotometer using KBr pellets. The XRD pattern were done on a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Ka radiation ($\lambda=1.5406 \text{ \AA}$) to determine the phases present in the as-prepared nanocomposite. The shape and morphology of samples were observed by a MIRA3 TESCAN scanning electron microscope (SEM) equipped with a link energy-dispersive X-ray (EDX) analyzer. Raman spectroscopy was performed using a SENTERRA (2009) dispersive Raman microscope from BRUKER (Germany) with a laser wavenumber of 785 nm. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM, Magnetic Daneshpajoh Kashan Co., Iran) with a maximum magnetic field of 10 kOe. The Brunauer Emmette Teller (BET) surface area was measured by N₂ adsorption measurements at 77.3 K using Nova 2000 instrument. AFM images were recorded on a multi-mode atomic force microscopy (ARA-AFM, model Full Plus, ARA Research Co., Iran). UV-Vis spectra of the aqueous solutions during the reaction were recorded using a Cary 100 double beam spectrophotometer operated at a resolution of 2 nm using quartz cells with path length of 1 cm.

RESULTS AND DISCUSSION

FT-IR analysis

FT-IR spectroscopy is a sensitive technique to detect the vibrations of different bonds, and therefore it can provide important information for structural integrity of the as-prepared nanocomposite. Figs. 1(a-e), show the FT-IR of pure HPW, GO, Fe₃O₄, GOA/Fe₃O₄ and GOA/Fe₃O₄/HPW nanocomposite. For pure HPW in Fig. 1(a), the characteristic vibrational frequencies related to the keggin unit appear at 1080, 981, 891 and 802 cm⁻¹ which are assigned to the vibrations of the P-O, W=O and two W-O-W bonds [32]. The spectrum of the GO in Fig. 1(b) shows the C=O and graphitic C=C stretching bands at about 1735 and 1626 cm⁻¹ respectively, and a strong band of C-OH at 1030 cm⁻¹ [33]. In the case of pure Fe₃O₄ (Fig. 1(c)), the band appearing at about 576 cm⁻¹ is assigned to Fe-O bond [6]. In Fig. 1(d), the

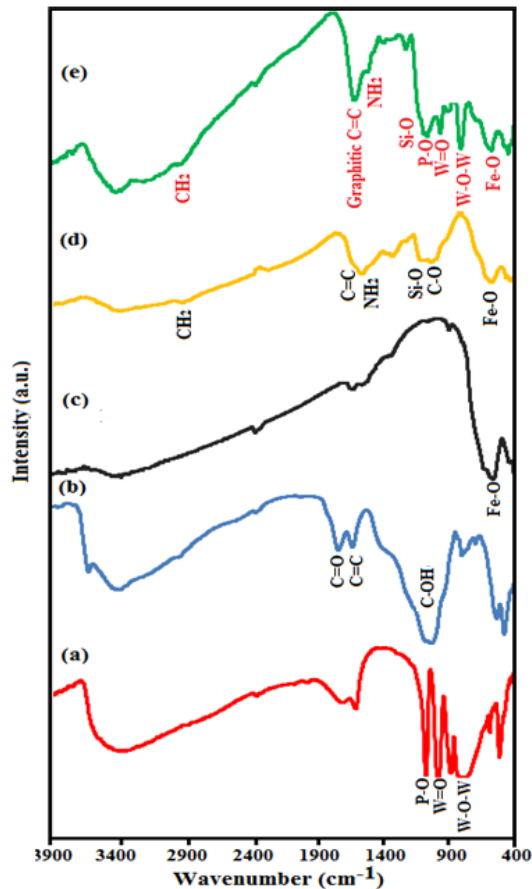


Fig. 1. FT-IR spectra of (a) HPW, (b) GO, (c) Fe_3O_4 , (d) $\text{GOA}/\text{Fe}_3\text{O}_4$ and (e) $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$.

presence of the anchored APTES chain to the GO sheets was confirmed by stretching vibrations of C–H bond (2950 cm^{-1}), $-\text{NH}_2$ bonds (1614 cm^{-1}) and C–N stretching vibration (1060 cm^{-1}). For as-prepared nanocomposite (Fig. 1(e)), All vibrational bands corresponding to the HPW structures can be seen clearly in the nanocomposite, suggesting the remaining of the Keggin structure. In general, appearance the peaks of precursors confirms the successful synthesis of the $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite.

XRD analysis

X-ray diffraction patterns of pure GO, Fe_3O_4 , $\text{GOA}/\text{Fe}_3\text{O}_4$ and $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposites are presented in Figs. 2(a)-(d). The diffraction pattern of GO shows a strong peak at around $2\theta = 10.51$, originates from its (001) reflection (Fig. 2(a)) [34]. After surface decoration, as shown in Fig. 2(d), the diffraction peak of GO disappears and a broad peak at about $2\theta = 25$ is observed,

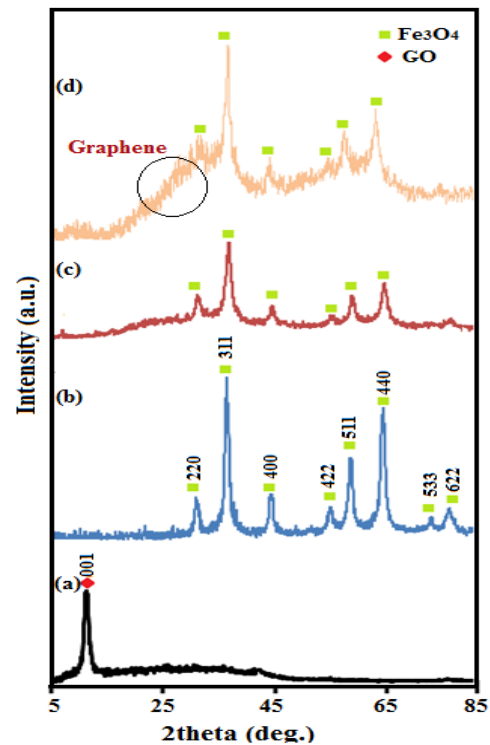


Fig. 2. XRD patterns of (a) GO, (b) Fe_3O_4 , (c) $\text{GOA}/\text{Fe}_3\text{O}_4$ and (d) $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$.

which can be assigned to graphene (002) planes, due to reduction of GO. The diffraction peaks at $2\theta = 30.7, 35.7, 43.9, 57.2,$ and 62.9 can be easily assigned to respectively (220), (311), (400), (422), (511), (440), (533) and (622) reflections of Fe_3O_4 (JCPDS no. 19-0629) [35]. However, no characteristic peaks of HPW are found, which suggests they tend to be highly dispersed into the graphene nanosheets and mesopores of Fe_3O_4 . This will be benefit to enhance the adsorption activity of the nanocomposite.

SEM analysis

Fig. 3 shows the scanning electron microscopy (SEM) images of pure GO, Fe_3O_4 and $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite. As shown in Fig. 3(a), the SEM image of GO consists of layered structure, which is slightly agglomerated. The surface of GO is relatively flat compared with that of the nanocomposite. The SEM image of Fe_3O_4 consists of small and near spherical particles which is highly agglomerated (Fig. 3(b)). For the $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite, (Figs. 3(c-d)), Fe_3O_4 and HPW nanoparticles, are completely distributed on the surface of GO.

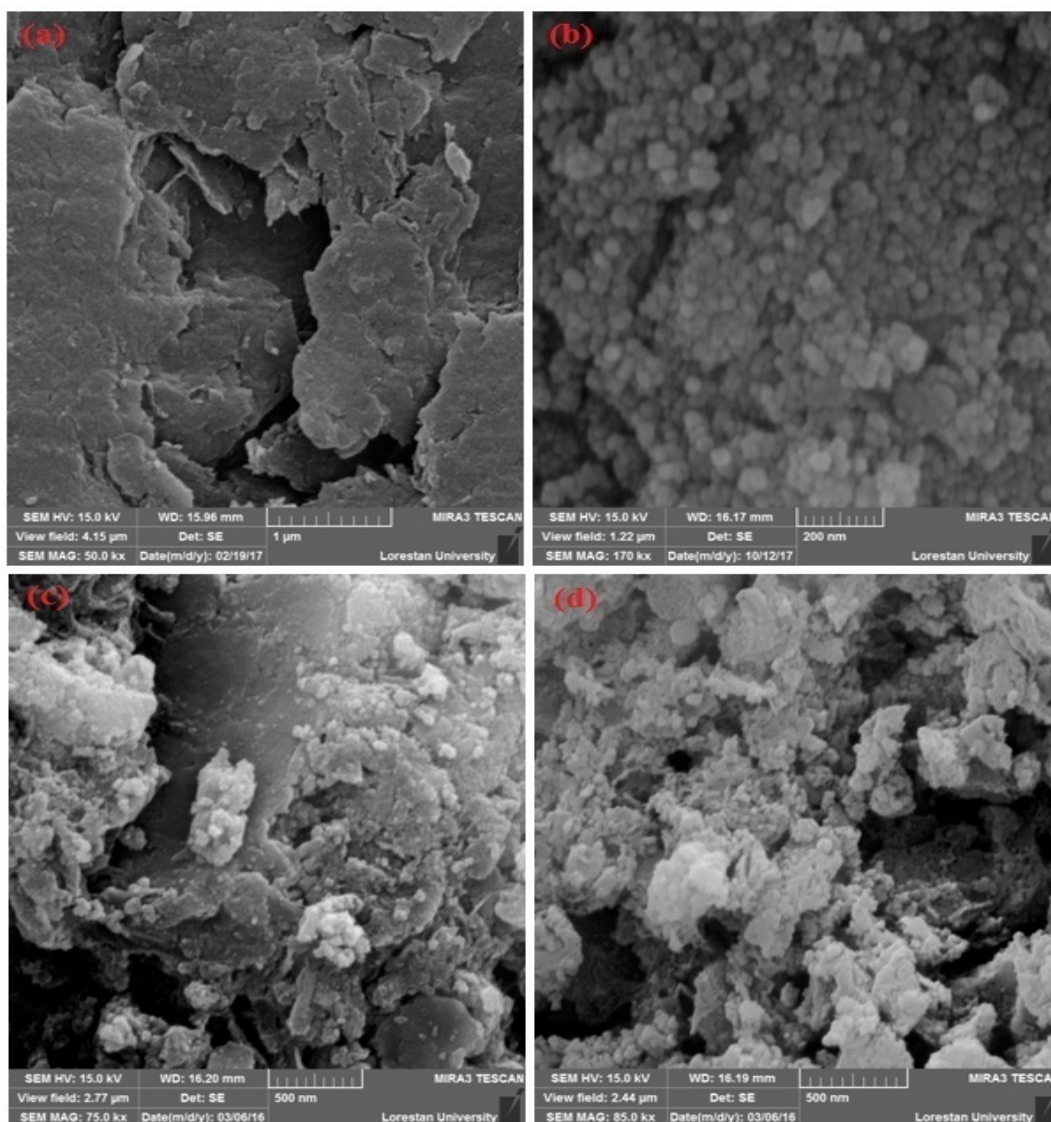


Fig. 3. SEM images of (a) GO, (b) Fe_3O_4 , (c) and (d) $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$.

EDX analysis

The existence of elements in the $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite is detected by EDX spectroscopy and the results are shown in Fig. 4. It can be clearly seen that C, N, O, Si, P, Fe and W elements are truly existed in the product. Moreover, the element distribution analysis demonstrates that the elements C, N, O, Si, P, Fe and W are homogeneously distributed on the entire surface of the as-prepared nanocomposite, indicating the uniform attachment of silanes with terminal amine and phosphotungstic acid groups on magnetic GO.

Raman analysis

Raman spectroscopy is a good and non-destructive spectroscopic tool used to acquire valuable evidence for carbonaceous materials such as graphene. The Raman spectra of the GO and $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite are depicted in Fig. 5. For pure GO (Fig. 5 (a)), there are two intense peaks at 1318 cm^{-1} (D band, sp^3 carbon atoms of disorders and defects) and 1586 cm^{-1} (G band, sp^2 carbon atoms in graphitic sheets). In the case of $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite, as shown in Fig. 5(b), these peaks appear at 1311 and 1593 cm^{-1} respectively. The Raman spectra of them

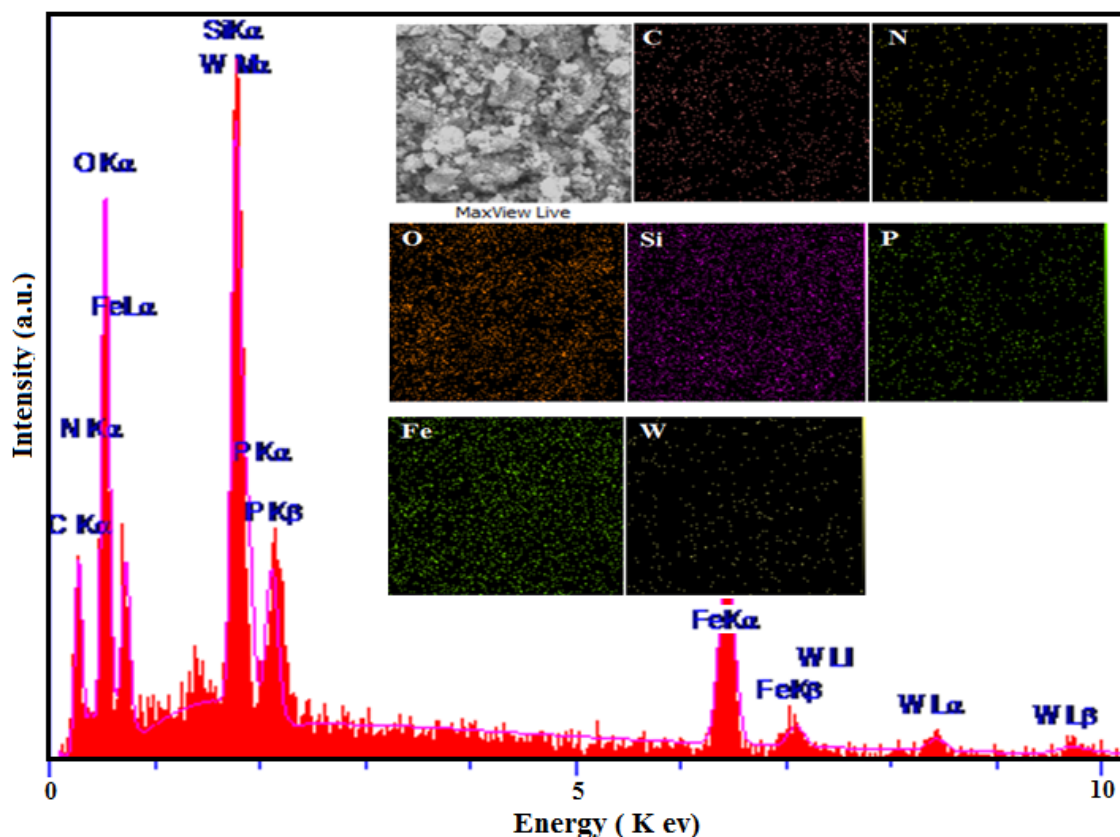


Fig. 4 EDX spectrum and a representative SEM image of the GOA/Fe₃O₄/HPW nanocomposite with corresponding EDX elemental mappings.

are similar, indicating HPW and Fe₃O₄ nanoparticles do not disrupt the graphitic structure of the support. The ratio of D and G band intensities (I_D/I_G) for these samples remains virtually unchanged (from 1.17 (flat GO) to 1.16 (GOA/Fe₃O₄/HPW)), representing a good balance of synthesis conditions while maintaining hydrophilicity via surface oxidation [36].

BET analysis

Fig. 6 shows the nitrogen adsorption-desorption isotherms and corresponding pore size distributions curves (the insets) of GO and GOA/Fe₃O₄/HPW samples. These isotherms in Figs. 6 (a) and (b) can be classified to type-IV for two samples with H3 hysteresis loop for GO and H4 hysteresis loop for the GOA/Fe₃O₄/HPW nanocomposite, which indicate the presence of mesopores [37]. The BET surface area and pore volume of the as-prepared nanocomposite ($S_{BET} = 82.8 \text{ m}^2/\text{g}$, pore volume = $0.384 \text{ cm}^3/\text{g}$) are higher than the values of GO ($S_{BET} = 79.15 \text{ m}^2/\text{g}$, pore volume = 0.126

cm^3/g). It can be concluded that the addition of HPW and Fe₃O₄ nanoparticles has a great effect on the structure of GO and increases the surface area and pore volume, which are all favorable factors for improving the adsorption performance.

VSM analysis

The magnetic properties of the pure Fe₃O₄ and GOA/Fe₃O₄/HPW samples were investigated using vibrating sample magnetometry (VSM) at room temperature, and the magnetic hysteresis loops are depicted in Fig. 7. As seen, the saturation magnetizations (M_s) of the Fe₃O₄ and GOA/Fe₃O₄/HPW are 72 and 9 emu/g, respectively. The slope defined as S-like shape of the magnetic hysteresis loops as well as the fact that both materials exhibit zero coercivity (H_c) and very low remanence (M_r) at room temperature allows ranking them as superparamagnetic materials [38]. The M_s of the magnetic nanocomposite decreased substantially compared with that of pure Fe₃O₄, which could be attributed to the less magnetic component

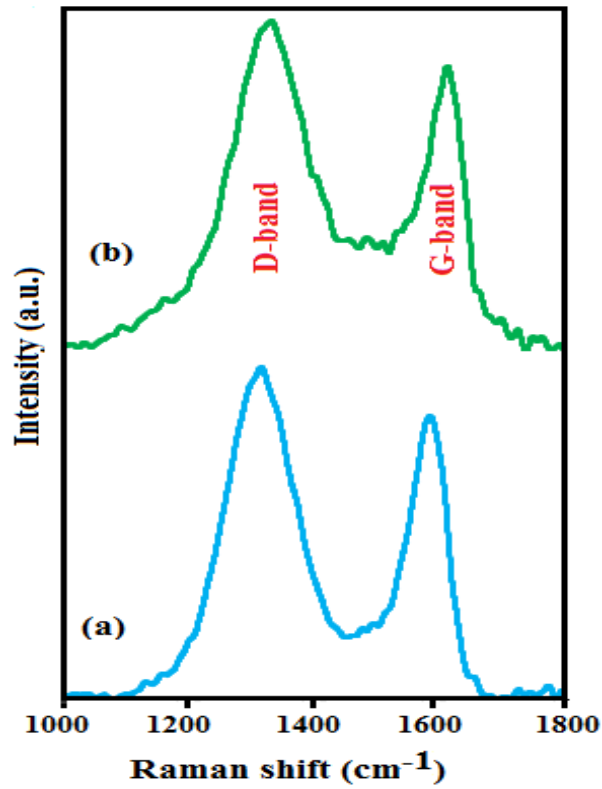


Fig. 5. Raman spectra of (a) GO and (b) GOA/Fe₃O₄/HPW nanocomposite.

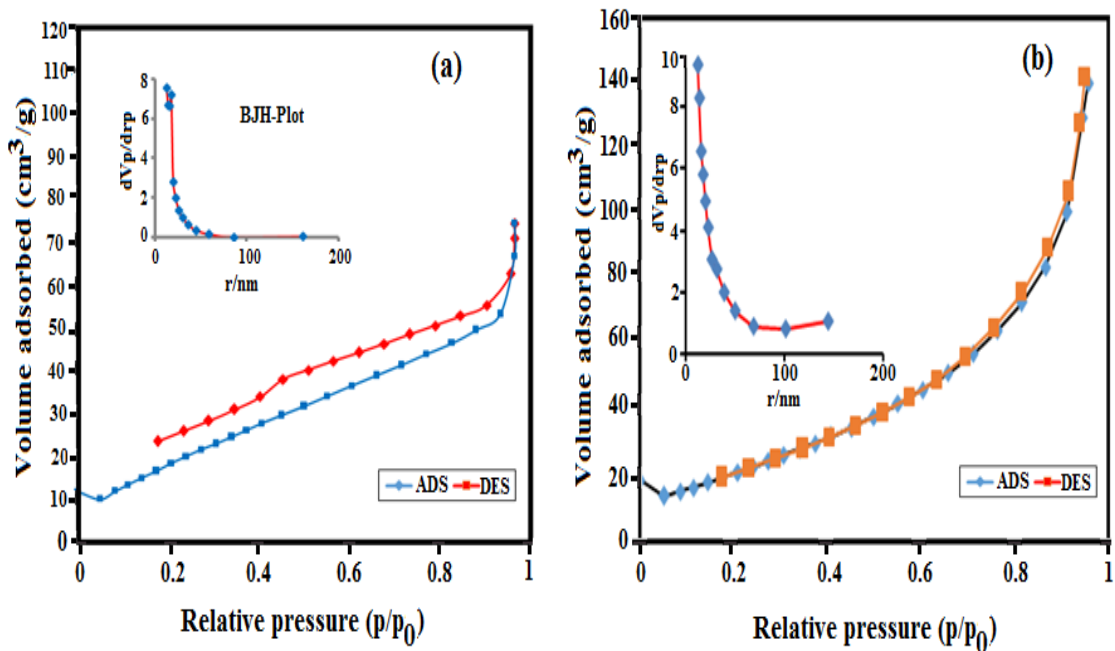


Fig. 6. Nitrogen adsorption–desorption isotherms of (a) pure GO and (b) GOA/Fe₃O₄/HPW nanocomposite, and pore-size distributions of them (inset of Figures).

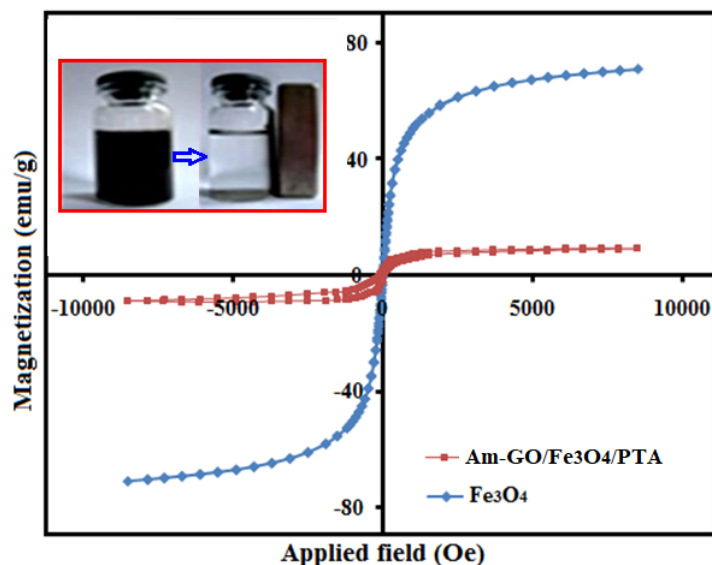


Fig. 7. Magnetic hysteresis loop of (a) Fe_3O_4 , (b) $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ at room temperature. The inset shows the behavior of the nanocomposite under an external magnetic field.

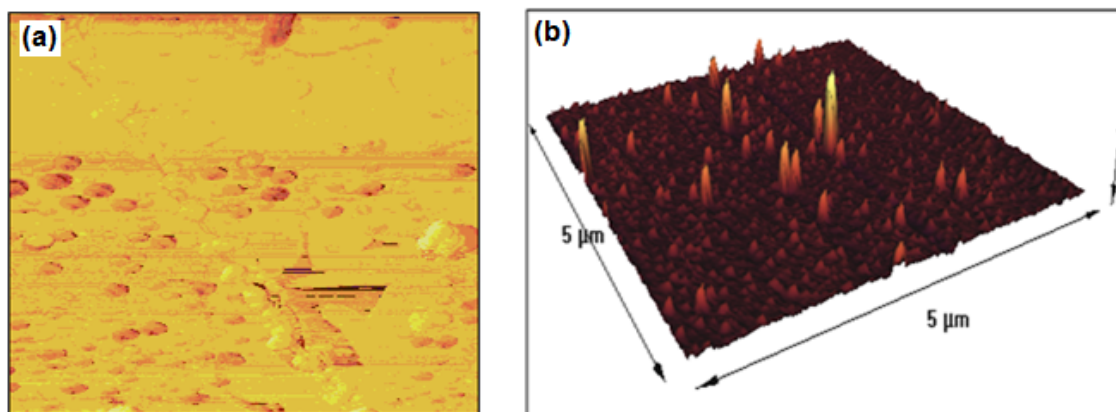


Fig. 8. (a) and (b) AFM images of the $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite.

(Fe_3O_4) per gram in the nanocomposite sample. However, M_s value of the nanocomposite made it easy to separate from the aqueous solution by an external magnetic field. The magnetic separability of this nanocomposite was also tested by placing a magnet near the glass bottle and instantly was attracted toward the magnet, as shown in the inset of this figure.

AFM analysis

The AFM image and corresponding height profile of the as-prepared $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite are shown in Figs. 8(a) and (b). This analysis shows that HPW and Fe_3O_4 nanoparticles are coupled to the individual GO sheets which are

in good agreement with other analyses.

Adsorption capability of nanocomposite toward organic dyes

To evaluate the adsorption capability of the $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite for the removal of organic dyes from contaminated water, two organic pollutants including cationic MB (molecule size: $1.38 \text{ nm} \times 0.64 \text{ nm} \times 0.21 \text{ nm}$) and anionic MO (molecule size: $1.54 \text{ nm} \times 0.48 \text{ nm} \times 0.28 \text{ nm}$) [39] were selected for the experimental runs. The time dependent UV-Vis absorption spectra of MB and MO under the adsorption condition in the presence of the $\text{GOA}/\text{Fe}_3\text{O}_4/\text{HPW}$ nanocomposite are presented in Figs. 9(a) and (b). The adsorption

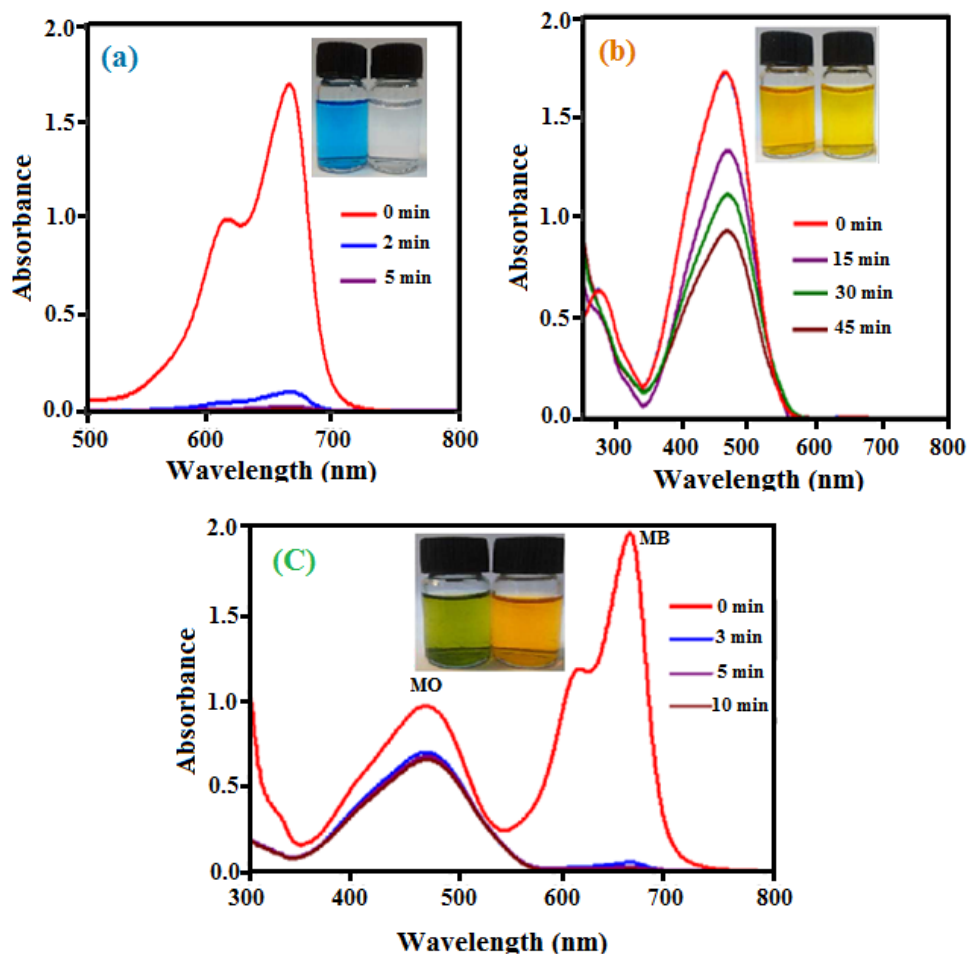


Fig. 9. UV-Vis spectral changes of dyes aqueous solutions with GOA/Fe₃O₄/HPW nanocomposite at different time intervals: (a) MB dye, (b) MO and (c) mixed dyes MB and MO. Conditions: [dye]= 25 mg/L; adsorbent amount= 50 mg and at room temperature.

of MB was manifested by evident fading of the blue color after 5 min with the removal efficiency of 100%. The adsorption ability towards MO dye was also investigated. As seen in Fig. 9(b), the absorbance of MO at 463 nm decreased slightly after 45 min under adsorption conditions, and the removal efficiency of MO dye by sample was about 55%. Although the size of MO molecules is similar with MB molecules, a little uptake capacity of MO was observed. There are like charges that repel each other between the nanocomposite and MO, leading to decreased adsorption of MO molecules on the surface of as-prepared nanocomposite. In fact, a large number of negative charges of POMs and GO may have a stronger force with the positive charges of dyes. So the nanocomposite has demonstrated a good adsorption property towards the cationic dye molecules. A mixed MB + MO dye

solution was selected to determine the selective adsorption capacity of the nanocomposite. From the UV/Vis spectra in Fig. 9(c), the peaks of MB disappeared quickly, just leaving the characteristic absorption peak of MO, indicating that GOA/Fe₃O₄/HPW nanocomposite could selectively capture the cationic MB dye when exposed to the corresponding binary mixture. This finding confirms that GOA/Fe₃O₄/HPW nanocomposite also has possesses selective adsorption ability towards cationic dyes in wastewater.

Effect of contact time and adsorbent amount

For practical applications, the contact time on equilibrium adsorption is an important parameter for an adsorbent. The contact time was varied in a range from 5-20 min (Fig. 10 (a)). The percentage of removal of the MB dye was increased with time.

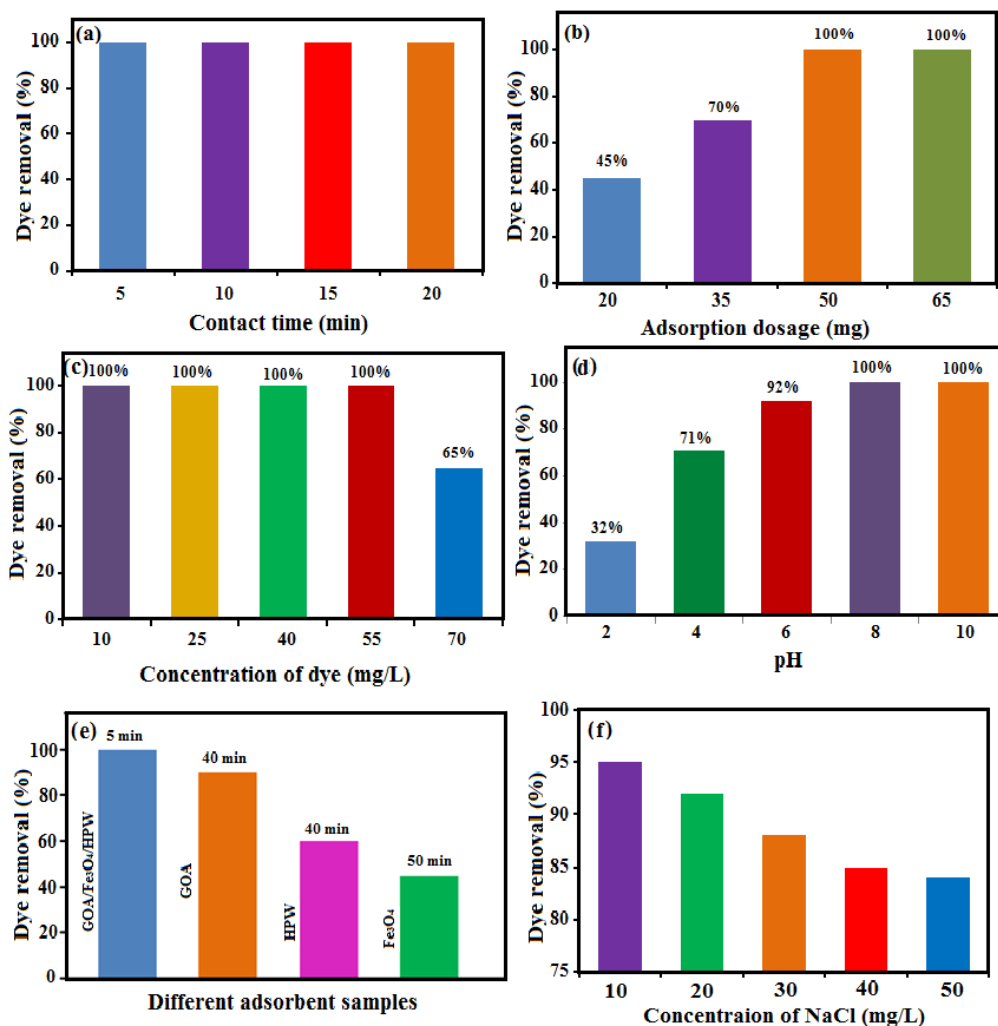


Fig. 10. Effect of various parameter on adsorption process: (a) effect of the adsorbent amount, Conditions: [dye]= 25 mg/L, pH= 8, (b) effect of dye concentration, Conditions: adsorbent amount =50 mg, pH= 8, (c) effect of pH, Conditions: [dye]= 25 mg/L, adsorbent amount =50 mg, and (d) effect of different adsorbents, Conditions: [dye]= 25 mg/L, adsorbent amount= 50 mg at room temperature.

After 5 min, the removal efficiency was achieved to 100 % and it remains constant with further increase in time. Hence the contact time was optimized as 5 min.

In order to wastewater purification, determining a suitable adsorbent dosage is also very important. The influence of adsorbent dosage on the removal of MB dye was investigated as shown in Fig. 10 (b). The adsorbent dosages were varied from 20, 35, 50 and 65 mg. With increasing adsorbent dosage, the removal of MB dye increased which could be related to the more adsorption sites. Therefore, 50 mg was selected for further studies.

Effect of concentration of MB

The effects of the initial concentration of MB

solution (10, 25, 40, 55 and 70 mg/L) on removal efficiency of the nanocomposite were examined as shown in Fig. 10(c). The adsorption percentage of the adsorbent towards MB could reach up to 100% at lower initial concentrations. When the initial concentration of MB increased from 55 to 70 mg/L, the adsorption percentage decreased, indicating that the adsorption capacity was saturated.

Effect of initial pH

The initial solution pH can influence the adsorption ability of adsorbent, by affecting the surface binding-sites or charges of the adsorbent [40]. Therefore, the adsorption investigations toward MB dye were performed at pH 2–10 to

Table 1. The comparative removal efficiency of dyes with different adsorbents.

Adsorbent	Adsorbate	Concentration of dye (mg/L)	Removal efficiency	Time (min)	Ref.
GO/Co ₃ O ₄	MB	25	98	12	10
GO-Ag	MB	10	78	10	41
H ₃ PW ₁₂ O ₄₀ /MIL-101(Fe)	MB	20	97.5	30	42
Fe ₃ O ₄ /rGO	RhB	5	91	120	43
Fe ₃ O ₄ /MIL-101(Cr)	MO	25	25	150	44
H ₃ PW ₁₂ O ₄₀ /ZIF-8	MB	60	100	30	45
GO/Bi ₂ O ₃	MO	5	72	45	46
GOA/Fe ₃ O ₄ /HPW	MB	25	100	5	This work

determine the adsorption capacity. As shown in Fig. 10(d), the nanocomposite had a different adsorption rate for the MB in the solutions with various pH amounts. The adsorption percentages were 32, 71, 92, 100 and 100% at pH values of 2, 4, 6, 8 and 10 respectively, after 5 min. In fact, the basic solutions enhanced MB adsorption. This phenomenon could be described by the fact that at higher pH values, the surface of the GOA/Fe₃O₄/HPW nanocomposite may become negatively charged, which can attract positively charged MB cations through electrostatic forces.

Removal of MB dye with bare materials

To demonstrate the role of the components of the GOA/Fe₃O₄/HPW nanocomposite for removal of MB dye, a series of control experiments were designed on pure GOA, HPW and Fe₃O₄ samples as adsorbents for removing the MB dye. As shown in Fig. 10 (e), the removal efficiency of these materials towards MB was 90, 59 and 48% within 40, 40 and 50 min respectively. Apparently, the removal efficiency of bare materials for cationic MB dye is much smaller than that of the nanocomposite and with respect to removal percentages and times, the GOA/Fe₃O₄/HPW nanocomposite is more suitable and superior for cationic dyes removal.

Interference studies

The effect of co-existing ions was studied by evaluating the interference effects of NaCl at different concentrations (Fig. 10 (f)). This species was chosen because it might reasonably be expected to have feasible interaction with the functional groups of GOA/Fe₃O₄/HPW and also existing in real samples. In the presence of NaCl with variable concentrations ranging from 10 to 50 mg/L, the adsorption capacity of MB was decreased about 5, 8, 12, 15 and 16 % respectively. However, this decrease in adsorption capacity is not very high, which indicates GOA/Fe₃O₄/HPW

can effectively remove MB from aqueous solution even in the presence of high salt concentrations.

Comparison with some adsorbent materials

To show the advantage of the present method, the obtained results in the adsorption capability of MB dye over the GOA/Fe₃O₄/HPW nanocomposite were compared with those of some reported adsorbents in the literature [10,41–46]. As shown in Table 1, the comparison was performed based on the consumed adsorbent amount, adsorption time, initial dye concentration, and removal efficiency. It was clear that with respect to the conditions and time, the present adsorbent was more suitable and superior. The most reported adsorbents required long reaction times and high amounts for adsorption of dyes.

Stability and recyclability

Consecutive application of the adsorbent by maintaining its activity is critical for its usage. To evaluate the reusability and stability of the GOA/Fe₃O₄/HPW nanocomposite, recycling experiments for the removal of MB were conducted. After each cycle, the adsorbent was completely separated and the release process of the adsorbed MB was achieved by thoroughly washing the adsorbent with a dilute solution of NaCl and ethanol three times for 30 min. Then, the recovered adsorbent was added to 30 mL of 25 mg/L MB solution under stirring. The results showed a negligible drop in adsorption capacity after four repeated cycles and the adsorption efficiency of 100, 97, 93 and 90 % were obtained (Fig. 11). At the same time, the concentrations of W and Fe in the filtrate were determined to be less than 0.1 % by ICP-AES. The hot filtration test was performed by taking the adsorbent out of the reaction solution one minute after reaction. The removal rates of MB dye over the four minutes are almost constant, which indicates that the adsorbent is truly heterogeneous. The

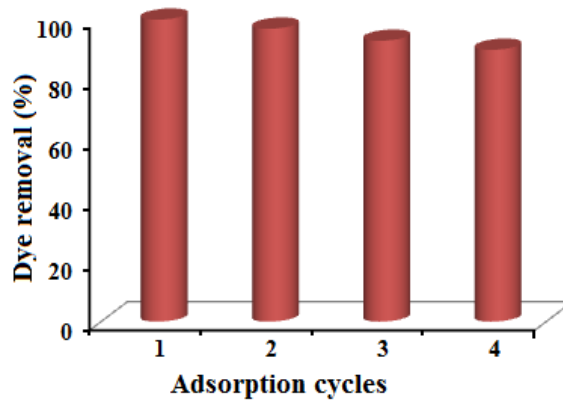


Fig. 11. Recyclability of the GOA/Fe₃O₄/HPW nanocomposite in the removal of MB dye.

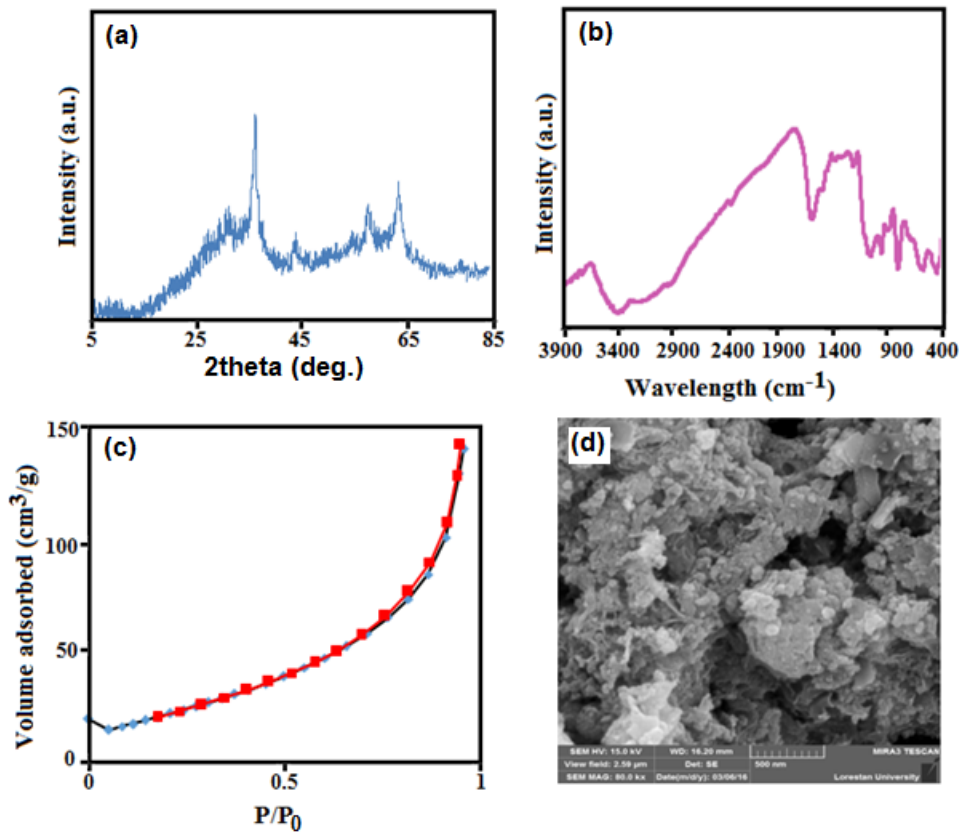


Fig. 12. (a) XRD pattern, (b) FT-IR, (c) BET and (d) SEM images of the fresh and recovered nanocomposite after four runs.

hot filtration test also indicates that none of HPW molecules are released from the nanocomposite during the adsorption process. Furthermore, the structural stability of the recovered adsorbent was confirmed by XRD, FT-IR, BET and SEM analyses (Figs. 12(a)-(d)). As shown in Fig. 12(a-c), XRD pattern, FT-IR and BET of the recovered composite

did not show significant change after four runs in comparison with those of the fresh composite. The morphology of the recycled composite after four runs of adsorption was also analyzed (Fig. 12(d)). It could be observed that the recovered adsorbent almost kept initial size and morphology. These results confirm that the adsorbent is

durable and effective for the treatment of colored wastewaters.

CONCLUSION

In summary, a magnetically separable GOA/ Fe_3O_4 /HPW adsorbent was successfully prepared using a hydrothermal method and its adsorptive property of cationic dye MB was investigated. As compared with pure HPW, GO and Fe_3O_4 , the nanocomposite exhibited higher adsorption capability toward MB dye. Effective parameters involving pH, primary dye concentration, and the adsorbent dosage were studied and the outcomes show that the maximum removal of dyes occurred at 25 mg/L of primary dye concentration with 50 mg of the adsorbent. The adsorption performance of mixed dyes further proved the selective properties toward cationic dyes. Furthermore, the GOA/ Fe_3O_4 /HPW adsorbent could be easily separated from wastewater for reusing by simply applying an external magnetic field. Therefore, the GOA/ Fe_3O_4 /HPW composite can be applied as a hopeful adsorbent for the treatment of dye effluents.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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