Development of gum acacia based magnetic nanocomposite adsorbent for wastewater treatment

Prajwal Kulal1 · Preetha B. Krishnappa1 · Vishalakshi Badalamoole1

Received: 20 June 2021 / Revised: 18 September 2021 / Accepted: 27 September 2021 / Published online: 5 November 2021
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract
The present work reports development of a magnetic hydrogel adsorbent material based on the polysaccharide, gum acacia. This graft copolymer nanocomposite hydrogel of gum acacia and poly(3-chloro-2-hydroxypropylmethacrylate) has been made using microwave assisted technique. Magnetite nanoparticles have been generated by in-situ method and trapped in the network structure. The parent hydrogel and the hybrid nanocomposite were evaluated as adsorbents for sequestration of cationic dyes and metal ions from aqueous solution. The FTIR, XRD, SEM, TGA, VSM and BET studies have been performed to characterize the samples with respect to their physical and chemical structure, surface nature, thermal stability and magnetic property. The nanocomposite displayed super-paramagnetic nature owing to the presence of magnetite nanoparticles which also influenced the adsorption characteristics favourably as evident from the comparative studies performed with the non-magnetic parent gel. The nanocomposite exhibited larger surface area of 2.524 m²g⁻¹ compared to the parent hydrogel with surface area of 0.481 m²g⁻¹. The adsorption capability of the parent hydrogel towards methylene blue, rhodamine 6G, Cu(II) and Hg(II) are 224.4, 283.5, 282.4 and 275.3 mgg⁻¹, respectively, were enhanced to 265.2, 344.4, 307.5 and 292.8 mgg⁻¹, respectively, in the case of nanocomposite. The adsorption isotherm and kinetic studies indicated fit of Freundlich isotherm model and pseudo-second-order kinetic model, respectively. The adsorption has been shown to be a multistep process involving boundary layer diffusion and intra-particle diffusion playing major roles. The thermodynamic analysis manifested the adsorption as an exothermic and spontaneous process. The adsorption–desorption process studied in three cycles indicated excellent reusability characteristics of the nanocomposite making it a promising adsorbent material for wastewater treatment.
Keywords Gum acacia · Poly(3-chloro-2-hydroxypropylmethacrylate) · Magnetite nanoparticles · Nanocomposite · Cationic dyes · Heavy metal ions · Adsorption

Introduction

A wide variety of chemical contaminants enter the waterbodies through the effluents of cosmetic, textile, leather, pharmaceutical, paper, plating and mining industries. The existence of these contaminants beyond a certain level results in adverse environmental impacts, which have serious influence on human, plant and marine ecosystem [1–4]. For example, according to World Health Organization (WHO), the permissible concentration for Cu(II) and Hg(II) ions in portable and drinking water is 2.000 and 0.006 mg L\(^{-1}\), respectively [5]. It is imperative to minimize the ecological impact of these effluents by declining the environmental footprint at every stage of their use [6–8]. Therefore, several methods such as photo catalysis, ion-exchange, biological degradation, coagulation-flocculation, advanced oxidation processes, adsorption and membrane filtration have been adopted to reduce or minimize the pollution to a permitted level [9–11]. Among these methods, adsorption process is believed to be an effective method due to its handy operation, low-cost, easy and rapid extraction, etc. [12].

Nature affords an impressive range of polymers that have the potential to replace many synthetic polymers currently in use. Polysaccharides are naturally occurring organic macromolecules that are visualized as favourable alternatives of non-degradable synthetic polymers by virtue of their easy availability, low-cost, non-toxicity, biodegradability and biocompatibility [13–15]. Modification of polysaccharides by incorporation of functional groups with potential binding ability towards pollutants is a good approach to develop adsorbent materials. Graft copolymerization is an outstanding technique to improve the properties of the polysaccharides. Grafting of vinylic and acrylic monomers on natural plant exudate polysaccharides has delivered some exciting strategies in fabricating hydrogels with high adsorption capacities [16–20]. Great progress has been made in recent years with concern to the preparation of polysaccharide based hydrogel nanocomposites. Production of nanocomposites from natural polymers is aimed at increasing the properties of the hydrogels and developing newer techniques with the view of sustainability of the environment. The utilization of hydrogels of nanostructured hybrid materials has abundant advantages in wastewater treatment [21–26].

Gum acacia or Gum arabic (GA) is a highly branched arabinogalactan polysaccharide exuded by acacia trees [27]. This carbohydrate molecule is composed by D-galactose, ʟ-arabinose, ʟ-rhamnose, D-glucouronic acid and 4-o-methyl-D-glucouronic acid units [28]. The structure and properties of GA could be easily tailored by introducing extra functional groups in the molecule through the –COOH and –OH groups present in its monosaccharide units. GA modified with vinyl monomers have been used earlier as adsorbents for the treatment of contaminated water. Sharma et al. [29] fabricated a novel nanohydrogel of gum arabic and polyacrylamide using microwave assisted synthesis for adsorption of noxious crystal
violet dye from aqueous medium. The highest adsorption capacity of crystal violet onto nanogel was found to be 90.9 mg g\(^{-1}\). Abdel-Bary et al. [30] studied graft copolymerization of poly(acrylic acid) onto gum acacia as a prospective candidate for removing of the dye methylene blue from aqueous system. Elbedwehy et al. [31] reported development of a graft copolymer of polyacrylonitrile and gum acacia using KMnO\(_4\)/HNO\(_3\) redox pair as initiator. The adsorbent exhibited super adsorbent ability with adsorption capacity of 1017, 413 and 396 mg g\(^{-1}\) for Pb\(^{2+}\), Cd\(^{2+}\) and Cu\(^{2+}\), respectively.

The advent of nanotechnology has provided great opportunities for development of nanocomposite based adsorbents. Embedding magnetite nanoparticles (Fe\(_3\)O\(_4\)) in porous polymeric network of the hydrogel are attractive due to their recognized biocompatibility, sensitivity and rapid response to a remotely applied external magnetic field [32]. Imparting magnetic property to the materials facilitates easy separation of the adsorbent after use. They can further expand the sorption capacity of hydrogel attributable to their nanoscopic size and the surface characteristics [33].

There are no reports available on the modification of GA with the acrylic monomer, 3-chloro-2-hydroxypropylmethacrylate (CHPMA). This monomer molecule is known to form biocompatible and chemically stable hydrogels and finds specialized applications in water purification [34]. Grafting of CHPMA onto GA may lead to the development of an efficient adsorbent material fulfilling the requirements of ecofriendly adsorbents for water purification. Due to the presence of carbonyl and hydroxyl groups, it can greatly enhance the sorption capacity of GA. Hence, it is hypothesized that the modification of GA by functionalizing it with the poly(3-chloro-2-hydroxypropylmethacrylate) would yield an adsorbent with better adsorption ability. To make use of advantageous features of nanoparticles in adsorption, we intend to transform this material as a nanocomposite by embedding the magnetite nanoparticles in the gel structure. The presence of magnetite nanoparticles is expected to render it magnetic facilitating its separation after use by use of an external magnet.

In this paper, we report the preparation of a hybrid nanocomposite material based on GA and the monomer CHPMA via microwave assisted polymerization process. The hydrogel is further modified by incorporation of magnetite nanoparticles. The hydrogel and the nanocomposite samples have been studied as adsorbent materials for adsorptive removal of certain dyes and metal ions from their individual aqueous solutions. The adsorption characteristics have been evaluated in terms of isotherm, kinetic and thermodynamic studies. Finally, the materials were subjected to desorption studies to check their regenerative efficacy.

**Experimental**

**Materials**

Gum acacia (GA), 3-chloro-2-hydroxypropylmethacrylate (CHPMA), iron(III) chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O), iron(II) chloride tetrahydrate (FeCl\(_2\)·4H\(_2\)O), potassium peroxy-disulfate (KPS), ammonium hydroxide (28%),...
$N,N$-methylenebisacrylamide (MBA) were received from Aldrich Chemical Company Inc., USA. Methanol was provided by Himedia Laboratories Pvt Ltd., Mumbai, India. Acetone and Hydrochloric acid (HCl) were purchased from S.D. Fine-Chem Ltd., Mumbai, India. Copper sulphate pentahydrate ($\text{CuSO}_4\cdot5\text{H}_2\text{O}$) was supplied by Qualigens Fine Chemicals, Mumbai, India. Mercuric chloride ($\text{HgCl}_2$) was provided by Reachem Laboratory Chemicals Pvt Ltd., Chennai, India. Methylene Blue (MB) was obtained from Rankem Chemicals, Delhi, India. Rhodamine 6G (R6G) was supplied by Loba Chemie Pvt Ltd., Mumbai, India. All chemicals were analytical grade reagents and used without further purification. Double distilled water was used in the preparation of solutions throughout the study.

**Methods**

**Microwave supported synthesis of Gum acacia-graft-poly(3-chloro-2-hydroxypropylmethacrylate) hydrogel (GA-$g$-PCHPMA)**

Microwave assisted synthesis of GA-$g$-PCHPMA hydrogel has been carried out using the free radical polymerization approach. To a solution of 0.2 g of GA in 10 mL distilled water, 2 mL of CHPMA (0.013 mol) was added slowly with uninterrupted stirring followed by 18 mg of KPS (0.066 mmol) and 14.9 mg of MBA (0.097 mmol). The resulting mixture was placed in the microwave oven (LG-Grill-Intellowave, India) and irradiated under a power of 80 W for 60 s. The unreacted components were removed from the gel by washing with acetone first followed by methanol and distilled water. The purified gel was dried at 50 °C in an oven for 24 h. It was designated as GA-$g$-PCHPMA.

**Preparation of Gum acacia-graft-poly(3-chloro-2-hydroxypropylmethacrylate)/magnetite nanocomposite (GA-$g$-PCHPMA/$\text{Fe}_3\text{O}_4$)**

The nanocomposite GA-$g$-PCHPMA/$\text{Fe}_3\text{O}_4$ was prepared using the procedure mentioned earlier [18, 35]. Briefly, a solution containing magnetite precursor was prepared by adding 2.1 g FeCl$_3\cdot6\text{H}_2\text{O}$ and 5.8 g of FeCl$_2\cdot4\text{H}_2\text{O}$ to a beaker containing 100 mL distilled water placed on a magnetic stirrer and subjected to vigorous stirring. After an hour, 0.5 g of GA-$g$-PCHPMA was added and allowed to stand at room temperature for 10 h to enable swelling along with diffusion of Fe$^{2+}$ and Fe$^{3+}$ ions into the gel structure. The resulting material was washed thoroughly with distilled water and then immersed in 0.5 M NH$_4$OH solution (100 mL) for 8 h. The gel gradually turns black owing to the formation of magnetite nanoparticles. It was separated from the solution by decantation of the supernatant, washed repeatedly with distilled water and dried in an oven at 50 °C for 24 h. The sample was designated as GA-$g$-PCHPMA/$\text{Fe}_3\text{O}_4$. 
Structural characterization

Grafting of CHPMA on GA and incorporation of Fe$_3$O$_4$ nanoparticles within the polymer matrix of GA-g-PCHPMA were confirmed by characterization of the gel and the nanocomposite as detailed below.

The FTIR spectra were recorded on Fourier transform infrared spectrometer, IR Prestige 21 (Shimadzu, Japan), in the spectral range of 500–4000 cm$^{-1}$. The surface morphology was studied using a scanning electron microscope, JEOL-JSM 5800LV (Japan) under the acceleration voltage of 5 kV with a magnification of 4 k. The X-ray diffraction patterns were recorded over a 2$\theta$ range of 0–80$^\circ$ using the bench top X-ray diffractometer, Rigaku MiniFlex 600 (Japan), the recording rate being 2$^\circ$/min. Thermal degradation was studied with Thermogravimetric analyser, SDT Q600 V20.9 (Japan). During the thermal analysis, the loss in weight of the samples was recorded as the samples were heated under nitrogen atmosphere from room temperature to 700 $^\circ$C at the rate of 10 $^\circ$C/min. The surface area and porosity measurements were made from nitrogen adsorption–desorption experiments using the Brunauer-Emmet-Teller BELSORP-max Microtrac BEL (Japan) surface area and porosity analyser. The magnetization value and hysteresis loop of the nanocomposite was measured at room temperature with the help of vibrating sample magnetometer, Model 7410S, Lakeshore Company, USA, having the range 15,000 to +15,000 Oe in an applied magnetic field of 1.5 T the sensitivity being $10^{-6}$ emu.

Adsorption studies

Determination of adsorption capacity and isotherm studies

The adsorption capacities of the hydrogel GA-g-PCHPMA and the nanocomposite GA-g-PCHPMA/Fe$_3$O$_4$ towards R6G, MB, Cu(II) and Hg(II) from their individual aqueous solutions were determined adopting the following procedure.

The aqueous solutions of the above adsorbates were prepared in the concentration range 20–1000 mg/L. A known quantity (≈ 0.1 g) of the dry adsorbent samples was placed in 50 mL of the above solutions maintained at 30 $^\circ$C. After 4 h, the residual concentration of the dye in the respective solutions was determined by recording the absorbance of the supernatant dye solutions at the maximum absorption wavelength of 663 nm for MB and 527 nm for R6G using the Ultraviolet–Visible spectrophotometer (Shimadzu UV-160A, Japan). The concentration of metal ions remaining in solution after adsorption was obtained from atomic absorption spectrophotometer (GBC 932 Plus, Australia) using the appropriate filters. From these data, the quantity of dyes and metal ions adsorbed by the adsorbents and the removal efficiencies were calculated using following Eqs.

\[
q_e = \left( C_o - C_e \right) \times \frac{V}{m} \tag{1}
\]
where $C_0$ and $C_e$ indicate the initial and equilibrium concentration of the dye or metal ion (mg/L) in solution respectively; ‘$q_e$’ denotes the equilibrium adsorption capacity of the adsorbent (mg/g). $V$ is the volume of aqueous solution (L) taken, $m$ is the mass (g) of the adsorbent considered for adsorption experiments and $R$ is the removal efficiency of the adsorbent (%).

**Kinetics of adsorption**

The kinetic studies were performed by collecting adsorption data as a function of time using 0.1 g of the samples in 50 mL of 500 mg/L adsorbate solutions. The measurements were done at 30 °C during 0–4 h period.

**Thermodynamics of adsorption**

The thermodynamic aspects were studied by carrying out the adoption studies following the same procedure as mentioned in "Determination of adsorption capacity and isotherm studies" section, at four temperatures in the range 30–50 °C.

**Desorption studies**

Regeneration ability of the hydrogel, GA-g-PCHPMA and the nanocomposite GA-g-PCHPMA/Fe$_3$O$_4$ essential for its repeated use, was studied by desorption experiments following adsorption. Initially, a known weight of the sample ($\approx$ 0.1 g) was suspended in 50 mL of adsorbate solution of concentration 500 mg/L and maintained under continuous stirring for 4 h. The adsorbate loaded sample was then taken out, washed, dried and suspended in HCl solution of pH 1.2 with constant stirring for 2 h. The quantity of adsorbate desorbed into the acid solution was analysed as per the method in "Determination of adsorption capacity and isotherm studies" section. The percentage desorption (%D) was obtained using Eq.

$$%D = \frac{\text{Amount of dye/metal ions desorbed}}{\text{Amount of dye/metal ions adsorbed}} \times 100$$

**Results and discussion**

**Formation of GA-g-PCHPMA/Fe$_3$O$_4$ nanocomposite**

The synthetic procedure adopted for the preparation of the gel and the nanocomposite samples is presented in Scheme 1. The sulphate anion radicals formed from KPS on microwave irradiation displace hydrogen atom from hydroxyl groups of gum acacia to generate GA macro-radicals (GA--O'). The GA--O' radicals attack
the monomer, CHPMA initiating the formation of graft polymer chain on the GA backbone. Inclusion of MBA, a tetrafunctional monomer in the graft polymer chain leads to the formation of a 3D structure. The loading of the Fe$^{2+}$ and Fe$^{3+}$ ions in the hydrogel could be monitored visually by the change in colour of the swollen hydrogel from colourless to yellow–orange. The intensity of colour in the hydrogel is indicative of the concentration of Fe ions in the gel. The colour is retained by the gel on repeated washing with water signifying that the Fe ions are strongly bound to the gel matrix. On suspending this sample in NH$_4$OH solution, a quick colour change was detected from yellow–orange to black, indicating spontaneous generation of magnetite nanoparticles in the hydrogel matrix. The reactions leading to the formation of Fe$_3$O$_4$ nanoparticles during in-situ generation are given as follows [36]:

$$\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3$$

$$\text{Fe(OH)}_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O}$$
Infrared spectral characterization

FTIR spectroscopy is helpful to confirm the modification of GA with CHPMA and Fe$_3$O$_4$ nanoparticles. The spectra of the grafted gel and the nanocomposite are displayed in Fig. 1b and c, respectively. The spectrum of GA is given in Fig. 1a for comparison. The broad band which appeared at 3381 cm$^{-1}$ in all three spectra is attributed to the O–H stretching of hydroxyl groups present in the GA. The band detected at 2942 cm$^{-1}$ indicated C–H stretching of GA. The symmetric stretching and asymmetric stretching vibrations of –COOH groups were observed at 1612 and 1409 cm$^{-1}$. The band corresponding to glycosidic linkage of GA appeared at 1026 cm$^{-1}$. In the IR spectra of GA-g-PCHPMA (Fig. 1b) a sharp and prominent band related to the C=O stretching vibration from ester linkage of CHPMA units can be seen at 1703 cm$^{-1}$. The band at 1444 cm$^{-1}$ is due to bending vibrations of methylene group, whereas bands at 1251 and 1151 cm$^{-1}$ are due to C–O stretching vibrational modes of the ester linkages and alcoholic groups on GA, respectively. Moderately low intensity band at 746 cm$^{-1}$ can be assigned to the C–Cl stretching vibration. The new band appearing in the spectrum of GA-g-PCHPMA/Fe$_3$O$_4$ (Fig. 1c) at 553 cm$^{-1}$ is attributed to Fe–O, indicative of the entrapment of magnetite within the gel matrix.

$$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2$$

$$2\text{FeOOH} + \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O}$$

**Fig. 1** FTIR spectra of a GA b GA-g-PCHPMA c GA-g-PCHPMA/Fe$_3$O$_4$
SEM analysis

FESEM image of GA-g-PCHPMA (Fig. 2a) shows a flake like smooth surface with tiny cavities in between. The morphology of the GA-g-PCHPMA/Fe₃O₄ as seen in Fig. 2b, appears to have a homogeneous distribution of spherical magnetite nanoparticles without noticeable agglomeration. The presence of voids in between the nanoparticles makes the surface more attractive for adsorption process. The roughly calculated average particle diameter of magnetite nanoparticles using the scale bar indicating resolution of the SEM image shown in Fig. 2b is found to be 10–19 nm.

XRD analysis

XRD is intensively employed as an efficient technique to examine the crystallinity of the material. The XRD patterns of GA-g-PCHPMA and GA-g-PCHPMA/Fe₃O₄ are displayed in Fig. 3a and b, respectively. As presented in Fig. 3a, GA-g-PCHPMA exhibits a diffraction peak centred on 2θ = 20.1°, which was typical impression of semicrystalline nature of the hydrogel. However, in the case of GA-g-PCHPMA/Fe₃O₄ (Fig. 3b), few sharp peaks are observed at 2θ = 19.5,
27.4, 35.5, 56.9, 62.6, 66.9, 71.3° which establish the uniform dispersion of a low amount of crystalline magnetite nanoparticles in the composite network. These characteristic peaks corresponding to the planes (111), (220), (311), (511), (440), (531), (620) are consistent with the JCPDS (19–0629) data indicating cubic inverse spinel structure of magnetite nanoparticles. The only notable change is the fall in peak intensities due to the incorporation of Fe₃O₄ nanoparticles. The result also reveals enhanced crystallinity of the gel on nanocomposite formation.

**TGA analysis**

The fabricated materials were subjected to thermogravimetric analysis to study their thermal stability and the results are depicted in Fig. 4. As shown in Fig. 4a, the exclusion of hydrogen bonded water leads to a weight loss of 15% as the GA is heated from 25 to 107 °C. The most significant weight loss of 52% occurred in the region 230–358 °C which is credited to the structural breakdown of the polysaccharide chain. When the temperature was increased to 610 °C, weight loss of 28% was observed due to complete loss of degraded sample. As seen from Fig. 4b, GA-g-PCHPMA experienced an initial weight loss of 8% followed by 83% loss in the second stage in the temperature range 253–437 °C. On heating beyond this temperature, an additional weight loss 9% was seen owing to degradation of grafted side chains and the decomposed polysaccharide components. As observed from Fig. 4c, the degradation of the nanocomposite sample appears to be very similar to the parent graft copolymer gel during the first two stages. Beyond 450 °C, no further weight loss is observed and a mass 12% remains undegraded owing to the presence of magnetite nanoparticles. The thermogravimetric analysis thus gives evidence for the incorporation of metal oxide particles into the hydrogel rendering it an inorganic–organic hybrid material.

Fig. 4  TGA curves of a GA b GA-g-PCHPMA c GA-g-PCHPMA/Fe₃O₄
Brunauer–Emmett–Teller (BET) surface area analysis

The interior variations in physical structure of the gel and the nanocomposite samples were observed by BET studies. The BET plots are displayed in supporting information (Fig S1). The surface area, pore diameter and pore volume obtained for hydrogel GA-g-PCHPMA were 0.481 m²g⁻¹, 3.0556 nm and 0.016 cm³g⁻¹, respectively. The nanocomposite GA-g-PCHPMA/Fe₃O₄ displayed a much larger surface area of 2.524 m²g⁻¹ but pore diameter remained almost similar (3.0578 nm). Moreover, the pore volume increases almost 3 times (0.043 cm³g⁻¹) on formation of the nanocomposite. The pore sizes of the hydrogel and the nanocomposite make them classified as mesoporous materials according to IUPAC standard [36]. The appreciable expansion in pore volume and surface area of the hybrid nanomaterial is due to the influence of Fe₃O₄ nanoparticles which provides channels for adsorption of adsorbate species and helps them to settle in the pores. A related observation has been reported in earlier studies [9, 37, 38].

Magnetic property measurement

The variation of the magnetization with applied magnetic field which provides evidence of the magnetic properties of the nanocomposite is displayed in Fig. 5. The magnetization curve reveals that the residual magnetization (remanence) and coercive force (coercivity) were found to be zero. The saturation magnetization ($M_s$) value observed was 0.15 emu g⁻¹ at room temperature. This value is much lower than the value observed for pure magnetite nanoparticles (66.1 emu g⁻¹) [35], which might be due to the low amount of magnetite nanoparticles in the nanocomposite. Further, it has been reported that $M_s$ value tends to reduce when

![Fig. 5](image_url) a) Magnetization curve of GA-g-PCHPMA/Fe₃O₄ at room temperature and, b) Photograph showing attraction of GA-g-PCHPMA/Fe₃O₄ towards a free standing magnet
magnetite nanoparticles are embedded in non-magnetic materials [39, 40]. The magnetization curve also recommended the superparamagnetic nature of GA-g-PCHPMA/Fe₃O₄. As seen in Fig. 5b, the material is attracted to an external magnet which facilitates easy separation of the adsorbent from contaminated water samples after use [41].

**Adsorption studies**

**Effect of initial dye/metal ion concentration**

The initial concentration of the adsorbate species has significant influence on the extent of adsorption. It provides essential driving force to conquer the resistance to mass transfer between the solid adsorbent and aqueous phase. The results shown in Fig. 6 indicate a linear increase of $q_e$ with increase in concentrations of the dyes and metal ions in solution from zero to 800 mg/L, while very little change was observed beyond 800 mg/L. Increase in $q_e$ can be attributed to the increasing concentration gradient of the adsorbate species around the vicinity of the adsorption spots and the bulk of the solution. However, no change in adsorption is witnessed when most of the binding sites are occupied by the adsorbate leading to equilibrium situation. The adsorbates were adsorbed to different extent on the gel and the nanocomposite, the amount on the nanocomposite being higher at any given time point. The order of adsorption has been R6G > Cu(II) > Hg(II) > MB in both cases.

**Effect of contact time**

Figure 7 presents the effect of time on the extent of adsorption on the hydrogel and the nanocomposite from a solution of 500 mg/L concentration. The impact of magnetite nanoparticles on adsorption process is significant from the enhanced adsorption capacity of GA-g-PCHPMA/Fe₃O₄ over GA-g-PCHPMA.

![Fig. 6](image_url) The effect of initial concentration of dyes and metal ions on adsorption for a GA-g-PCHPMA b GA-g-PCHPMA/Fe₃O₄ (contact time= 4 h, T = 30 °C)
Higher rate of initial uptake was observed for both the adsorbents due to the abundant availability of adsorption sites. Complete saturation of the adsorption sites occurred after a contact time of 120 min for MB, R6G and 45 min for Cu(II), Hg(II). No significant uptake of the dyes and metal ions was observed beyond this time indicating the attainment of equilibrium state. It was detected that the adsorption of metal ions was much rapid at the early stage when compared to dyes. It appears that the adsorption of metal ions is almost complete within few minutes of contact indicating faster diffusion of the metal ions from the bulk of the solution to the adsorption sites. This could be due to the smaller size of the metal ions and stronger binding. Also it is apparent from the figure that the adsorption of the dyes slowed down gradually following a faster initial adsorption process, the initial rate of adsorption being high for R6G compared to MB. Also, the saturation value was much higher for the former indicating higher affinity of the adsorbent samples towards R6G.

**Mechanism of adsorption**

The possible mechanism governing adsorption of cationic dyes (MB and R6G) on the adsorbent materials is presented in Fig. S2. Under neutral pH conditions, GA acts as an anionic polysaccharide, and the electrostatic interaction operating between the –COO\(^-\) groups on hydrogel and the cationic dye molecules has a crucial role in the adsorption process. Adsorption is also driven by the availability of polar functional groups on the hydrogel such as –CONH\(_2\), –OH and –CH\(_2\)Cl which are involved in dipole–dipole and H-bonding interactions with dye molecules [29]. The possible mechanism for adsorption of bivalent metal ions (Cu\(^{2+}\) and Hg\(^{2+}\)) on the materials is shown in Fig. S3. The foremost interactive sites for the adsorption of metal ions are the carboxyl, amide and hydroxyl groups of the hydrogel. The metal ions bind to the gel by forming ionic crosslinks involving two neighbouring carboxylic groups. Binding also occurs...
through coordinate bonds involving the lone pair of electrons on the nitrogen and oxygen atoms of the amide and carboxyl groups [31]. The adsorption of dyes and metal ions is also influenced by the presence of magnetite particles. Introduction of spherical magnetite nanoparticles into the gel matrix increases the surface area as the particles occupy the pore structures. The additional binding sites available on the surface of nanoparticles are responsible for the higher adsorption efficiency of the nanocomposite material [42].

**Adsorption isotherm models**

The adsorption isotherm explains the distribution of adsorbate species between the liquid and the solid phase, when the process involved is in equilibrium. To understand this, Langmuir [43] and Freundlich [44] isotherm models were used to fit the adsorption data obtained in the present study.

Langmuir isotherm can be represented as follows:

\[ \frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \]  \hspace{1cm} (4)

where \( C_e \) (mgL\(^{-1}\)) is the equilibrium concentration of adsorbates, \( q_e \) (mgg\(^{-1}\)) is the equilibrium adsorption capacity of adsorbent, \( q_m \) (mgg\(^{-1}\)) is the theoretical saturation adsorption capability for monolayer coverage and \( K_L \) is the Langmuir constant related to the nature of binding sites and is a measure of the adsorption energy. These constants can be obtained from the slope and intercept of the linear plot of \( C_e/q_e \) versus \( C_e \). In addition, the parameter \( R_L \) is obtained using Eq. (5) to identify feasibility of adsorption.

\[ R_L = \frac{1}{1 + K_L C_0} \]  \hspace{1cm} (5)

where, \( C_0 \) (mgL\(^{-1}\)) is the highest initial concentration of adsorbate conforming to maximum adsorption. If \( R_L = 1 \), the adsorption is linear; if \( R_L > 1 \), the adsorption is unfavourable; if \( R_L = 0 \), the adsorption is irreversible and if \( 0 < R_L < 1 \), the adsorption is considered as favourable.

Freundlich adsorption isotherm is appropriate for adsorbents with heterogeneous surface structure and for adsorption taking place when adsorbate concentrations are low. Mathematical form of Freundlich model is represented as:

\[ \log q_e = \frac{1}{n} \log C_e + \log K_F \]  \hspace{1cm} (6)

where, \( q_e \) and \( C_e \) have their importance as stated before. The Freundlich isotherm constants, \( n \) and \( K_F \) are associated to the adsorption intensity and the adsorption capability of the material, respectively. Their values are obtained from the slope and intercept of the linear plot between \( \log q_e \) and \( \log C_e \), respectively. The values of ‘\( n \)’ varying from 1 to 10 support the promising situation for adsorption.
Fig. S4 and Fig. 8 represent Langmuir and Freundlich isotherm fit of adsorption data for the four adsorbate species used in the present study, respectively. The values of various parameters of Langmuir and Freundlich isotherm model are given in Table 1. It is evident from Fig. 8 that the Freundlich isotherm model shows a better fit in comparison with the Langmuir model which is confirmed by the higher $R^2$ values for the Freundlich model fit. The heterogeneity factor ‘$n$’ in Freundlich isotherm is greater than unity, suggesting the adsorption to be a favourable process in the studied systems. The Freundlich isotherm model fit also implies the surface to be heterogeneous and adsorption leading to multilayer formation.

Kinetics of adsorption

The rate of dye and metal ion uptake is governed by the nature of adsorbent and the adsorbate pair, the concentration of the adsorbate solution, and the contact time of the solid adsorbent with the adsorbate solution. As the adsorption process begins, the adsorbate species relocate from solution to the external surface of the adsorbent, forespread in the frontier layer and eventually migrate from the surface into the interior sites by way of pore diffusion [45]. Thus, to explore the adsorption kinetics and to understand the mechanism of adsorption, adsorption data were fitted into pseudo-first-order and pseudo-second-order kinetic models [46, 47].

Integrated mathematical forms of pseudo-first order and pseudo-second-order rate expressions are denoted by Eqs. (7) and (8), respectively.

\[
\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{7}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}
\]

Fig. 8 Freundlich isotherm model fit for adsorption of dyes and metal ions on a GA–g–PCHPMA and b GA–g–PCHPMA/Fe$_3$O$_4$
| Isotherm model | Adsorbate species | MB | R6G | Cu(II) | Hg(II) |
|---------------|-------------------|----|-----|--------|--------|
| Freundlich    | GA-g-PCHPMA       | 1.17 | 1.56 | 2.02  | 5.48  | 2.28 | 10.02 | 1.03 | 2.72 |
|               | GA-g-PCHPMA/Fe3O4 | 1.21 | 1.24 | 1.17  | 1.41  | 1.28 | 1.36  | 1.02 | 1.14 |
|               | PCHPMA            | 0.96 | 1.04 | 0.95  | 0.97  | 0.91 | 0.92  | 0.97 | 0.91 |
|               | PCHPMA/Fe3O4      | 0.96 | 1.04 | 0.95  | 0.97  | 0.91 | 0.92  | 0.97 | 0.91 |
| Langmuir      | GA-g-PCHPMA       | 1.21 | 1.24 | 1.17  | 1.41  | 1.28 | 1.36  | 1.02 | 1.14 |
|               | GA-g-PCHPMA/Fe3O4 | 1.21 | 1.24 | 1.17  | 1.41  | 1.28 | 1.36  | 1.02 | 1.14 |
|               | PCHPMA            | 0.96 | 1.04 | 0.95  | 0.97  | 0.91 | 0.92  | 0.97 | 0.91 |
|               | PCHPMA/Fe3O4      | 0.96 | 1.04 | 0.95  | 0.97  | 0.91 | 0.92  | 0.97 | 0.91 |

Table 1: Isotherm parameters for the adsorption of dyes and metal ions on GA-g-PCHPMA and GA-g-PCHPMA/Fe3O4.
where $q_e$ (mg g$^{-1}$) and $q_t$ (mg g$^{-1}$) are amount of adsorbate species adsorbed per unit mass of adsorbent at equilibrium and at time $t$, respectively, $k_1$ (min$^{-1}$) is pseudo-first-order adsorption rate constant and $k_2$ (g mg$^{-1}$ min$^{-1}$) is pseudo-second-order adsorption rate constant. The slope of plots between ‘log ($q_e$-$q_t$) vs $t$’ and ‘$t$/$q_t$ vs $t$’, give the values of $k_1$ and $k_2$, respectively.

Figure S5 and Fig. 9 represent kinetic adsorption plots of GA-g-PCHPMA and GA-g-PCHPMA/Fe$_3$O$_4$ for four different adsorbate species. Values of various constants obtained using these two models along with $R^2$ values are given in Table 2. Values of $q_e$ calculated using pseudo-second-order rate equation was found to match well with the experimental values which suggests the suitability of pseudo-second-order kinetic model to describe the adsorption of dyes and metal ions onto GA-g-PCHPMA and GA-g-PCHPMA/Fe$_3$O$_4$. The best fit of pseudo-second-order model is further confirmed by the $R^2$ values close to unity obtained for this model fit. This points out the involvement of both, adsorbate and binding sites, in the rate limiting step of adsorption. [45].

To understand the diffusion mechanism of studied adsorbate species on GA–g–PCHPMA and GA–g–PCHPMA/Fe$_3$O$_4$, intra-particle diffusion model proposed by Weber and Morris [48] was considered. The equation representing this model is given by

$$q_t = k_i t^{\frac{1}{2}} + C_i \tag{9}$$

where $C_i$ is the intercept (mg g$^{-1}$) which characterizes the boundary layer thickness and $k_i$ (mg g$^{-1}$ min$^{-\frac{1}{2}}$) is the intra-particle diffusion rate constant which can be obtained from the slope of the plot of $q_t$ vs $t^{\frac{1}{2}}$ (Fig. 10). The obtained $k_i$ and $C_i$ values along with $R^2$ values are shown in Table 3.

The existence of three steps in the adsorption process is evident from three sections with diverse slopes for adsorption of dyes as shown in Fig. 10. The first segment is owing to the transport of adsorbate species from the bulk solution to the outer surface of the adsorbent via boundary layer diffusion (or film diffusion). The second portion corresponds to the intra-particle diffusion process when
Table 2  Kinetic parameters for the adsorption of dyes and metal ions on GA–g–PCHPMA and GA–g–PCHPMA/Fe₃O₄

| Adsorbate species | MB          | R6G          | Cu(II)        | Hg(II)        |
|-------------------|-------------|--------------|---------------|---------------|
|                   | GA–g–PCHPMA | GA–g–PCHPMA/Fe₃O₄ | GA–g–PCHPMA | GA–g–PCHPMA/Fe₃O₄ | GA–g–PCHPMA | GA–g–PCHPMA/Fe₃O₄ |
| qₑ(exp) (mg g⁻¹)  | 224.4       | 265.2        | 283.5         | 344.4         | 282.4       | 307.5         | 275.3         | 292.8         |
| Removal efficiency (%) | 57.6        | 73.9         | 74.8          | 87.9          | 90.4        | 98.4          | 88.2          | 93.7          |
| Kinetic model     | Pseudo first order |          |              |               |             |               |             |               |
| qₑ (mg g⁻¹)       | 243.9       | 285.3        | 285.7         | 344.8         | 285.5       | 312.5         | 240.0         | 294.1         |
| kₑ (×10⁵)         | 6.7         | 5.5          | 19.4          | 15.2          | 298.8       | 249.8         | 277.7         | 152.1         |
| (gmg⁻¹ min⁻¹)     | 0.97        | 0.95         | 0.99          | 0.99          | 1.00        | 1.00          | 0.99          | 0.99          |
| R²                |             |              |               |               |            |               |             |               |

C₀ = 500 mgL⁻¹, T = 30 °C
adsorbate species diffuses from the external surface into the pores of the adsorbent. In this step, as the resistance to diffusion increases, diffusion slows down as reflected by the lower slope of the second portion of the curve. The third segment represents the equilibrium stage of adsorption where the intra-particle diffusion starts to retard due to the saturation of most of the active adsorption spots. Furthermore, the middle straight line representing the intra-particle diffusion makes an intercept on the ordinate axis inferring that the intra-particle diffusion is not the rate determining step of adsorption. The slopes of the three segments indicate the order of magnitude of rate constants as $k_{i1} > k_{i2} > k_{i3}$. The importance of the boundary layer effect is evidently observed as the value of the intercept follows the order $C_{i1} < C_{i2} < C_{i3}$. This signifies that surface adsorption is the prominent stage in adsorption process. It is also found that the thickness of boundary layer is enlarged in case of nanocomposite compared to the non-magnetite hydrogel. Very similar results have been reported in earlier studies [49, 50]. The three regions clearly recognized for the adsorption of dyes are not observed in the case of metal ions. Variation in slopes of second and the third region is not much indicating quick attainment of equilibrium following surface adsorption. This could be due to the faster diffusion of metal ions to the surface followed by quick diffusion through the pores leading to saturation of binding sites.

The GA–g–PCHPMA/Fe$_3$O$_4$ exhibited higher adsorption capacity for all the studied adsorbate species in comparison to GA–g–PCHPMA. The maximum adsorption capacity of the GA–g–PCHPMA towards MB, R6G, Cu(II) and Hg(II) were found to be 224.4, 283.5, 282.4 and 275.3 mg g$^{-1}$, respectively, and the corresponding values for GA–g–PCHPMA/Fe$_3$O$_4$ are 265.2, 344.4, 307.5 and 292.8 mg g$^{-1}$. This is also reflected in the higher removal efficiency of GA–g–PCHPMA/Fe$_3$O$_4$ compared to GA–g–PCHPMA as shown in Table 2. The enhanced adsorption ability or in other words, removal efficiency of the GA–g–PCHPMA/Fe$_3$O$_4$ could be ascribed to increased surface area and porosity of the nanocomposite owing to the embedded Fe$_3$O$_4$ nanoparticles. The adsorption was higher in the case of R6G compared

Fig. 10 Plots of the intra-particle diffusion model for a GA–g–PCHPMA and b GA–g–PCHPMA /Fe$_3$O$_4$
Table 3 Intra-particle diffusion constants as per the Weber-Morris model

| Step | Parameters | MB | R6G | Cu(II) | Hg(II) |
|------|------------|----|-----|--------|--------|
|      |            | GA–g–PCHPMA | GA–g–PCHPMA/Fe₃O₄ | GA–g–PCHPMA | GA–g–PCHPMA/Fe₃O₄ | GA–g–PCHPMA | GA–g–PCHPMA/Fe₃O₄ |
| 1    | $k_i$ (mg g⁻¹ min⁻¹) | 15.7 | 22.1 | 57.6 | 62.5 | 115.5 | 123.9 | 112.7 | 115.3 |
|      | $C_i$      | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
|      | $R^2$      | 0.99 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 2    | $k_i$ (mg g⁻¹ min⁻¹) | 14.5 | 12.4 | 15.6 | 21.5 | 3.3 | 4.1 | 2.8 | 2.4 |
|      | $C_i$      | 10.5 | 24.8 | 94.6 | 99.4 | 252.9 | 269.9 | 249.9 | 251.8 |
|      | $R^2$      | 0.93 | 0.98 | 0.98 | 0.98 | 0.98 | 0.98 | 0.98 | 0.98 |
| 3    | $k_i$ (mg g⁻¹ min⁻¹) | 7.2 | 8.9 | 5.5 | 6.9 | 2.7 | 3.9 | 2.6 | 2.1 |
|      | $C_i$      | 63.1 | 74.5 | 208.7 | 234.6 | 271.5 | 297.2 | 269.4 | 275.4 |
|      | $R^2$      | 0.99 | 0.98 | 0.99 | 0.98 | 0.98 | 0.98 | 0.98 | 0.98 |
to MB. Despite their larger size, R6G molecules are adsorbed to higher extent than MB which could be due to the greater binding possibilities for the former compared to the latter. This phenomenon could also be related with the higher solubility of MB (43.6 gL⁻¹) compared to R6G (20.0 gL⁻¹) as it has been established that substances more soluble in water are temperately less easily adsorbed than substances with reduced solubility [51]. Regarding adsorption of metal ions, the results indicated lower extent of adsorption for Hg²⁺ compared to Cu²⁺. The larger ionic radius and a smaller charge density of Hg²⁺ ion (102 pm and 49 C/mm³) compared to Cu²⁺ ion (73 pm and 116 C/mm³) reduced the adsorption of Hg(II) on both adsorbents. This evidently specifies that the formation of more stable complexes occurs due to interaction of lone pair of electrons on the nitrogen and oxygen atoms of the gel with Cu²⁺ ions compared with Hg²⁺ ions [52].

### Thermodynamics of adsorption

To understand the thermodynamic feasibility of adsorption, the adsorption data were analysed based on van’t Hoff equation:

\[
\ln K_C = -\frac{\Delta H^0}{R} \frac{1}{T} + \frac{\Delta S^0}{R}
\]

In Eq. 10, the ratio of \(q_e\) and \(C_e\) gives the value of the equilibrium constant of adsorption, \(K_C\), \(T\) is temperature (K) and \(R\) is gas constant (8.314 Jmol⁻¹ K⁻¹). Figure 11 shows the linear plot of \(\ln K_C\) vs \(1/T\). The standard entropy change (\(\Delta S^0\)) and standard enthalpy change of adsorption (\(\Delta H^0\)) are obtained from the intercept and slope of the linear plots, respectively. The standard free energy change, \(\Delta G^0\) was obtained using Eq.\

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

The obtained values of the thermodynamic parameters are displayed in Table 4.
The negative values of $\Delta G^\circ$ revealed the spontaneous nature of adsorption of dyes and metal ions on both the adsorbents. Also, the decrease in the magnitude of $\Delta G^\circ$ with temperature suggested that the adsorption is favourable at low temperatures. The negative values of $\Delta H^\circ$ for all the studied adsorbates indicated the exothermic nature of the process [53]. In addition, the negative value of $\Delta S^\circ$ corresponded to decrease in the degree of freedom of the adsorbed dyes and metal ions on the adsorbents [54]. The magnitude of all three thermodynamic parameters was higher for the nanocomposite compared to the parent gel indicating stronger binding in the former.

### Desorption study

For efficient use of the designed adsorbents, it is necessary that the adsorbent should be able to desorb the adsorbed species leading to regeneration of the adsorbent. The possibility of repeated use in different cycles makes the adsorption process economical in industrial applications. The desorption efficiency and regeneration power of GA–g–PCHPMA and GA–g–PCHPMA/Fe₃O₄ were studied in acidic solution of pH 1.2. The availability of H⁺ ions in solution, ensures an increased driving force for ion-exchange, facilitating the desorption process [55]. Figure 12 shows the desorption capacities of both the adsorbents for studied adsorbates did not change significantly over three successive adsorption–desorption cycles. In the third cycle, dye and metal ion adsorption capacity was decreased by approximately 12% and 9%, respectively, for hydrogel, whereas the corresponding values for nanocomposite were reduced by 9% and 7%. The results also indicate that the desorption capacities of GA–g–PCHPMA for MB, R6G, Cu(II) and Hg(II) are 85.3, 74.8, 77.9 and 67.4%, respectively, for the third cycle. For the third cycle, the nanocomposite GA–g–PCHPMA/Fe₃O₄ exhibited higher desorption percentage, the corresponding values being 86.7, 79.3, 79.1 and 70.7%. It was also found that cationic dyes are desorbed to a greater extent than that of metal ions confirming the stronger binding of metal ions in comparison to dyes. The desorption

| Adsorbent | Adsorbate | $-\Delta H^\circ$ (kJ mol⁻¹) | $-\Delta S^\circ$ (kJ mol⁻¹ K⁻¹) | $-\Delta G^\circ$ (kJ mol⁻¹) |
|-----------|-----------|-----------------------------|---------------------------------|-----------------------------|
| GA–g–PCHPMA | MB        | 19.39                       | 0.05                            | 1.24                        |
| | R6G       | 25.84                       | 0.07                            | 2.64                        |
| | Cu(II)    | 16.51                       | 0.04                            | 4.28                        |
| | Hg(II)    | 13.32                       | 0.03                            | 3.59                        |
| GA–g–PCHPMA/Fe₃O₄ | MB | 29.82                       | 0.09                            | 2.54                        |
| | R6G       | 45.66                       | 0.13                            | 4.83                        |
| | Cu(II)    | 35.84                       | 0.09                            | 8.31                        |
| | Hg(II)    | 17.82                       | 0.04                            | 5.31                        |
study confirms the possibility of recovery of adsorbate species and reuse of the adsorbent effectively.

**Comparison study**

The adsorption capability of the GA–g–PCHPMA/Fe₃O₄ is matched with other developed gum acacia or gum arabic adsorbent materials reported in literature. The isotherm and kinetic models applicable for adsorption on these materials have also been provided. The comparison data are presented in Table 5 show good efficacy of GA–g–PCHPMA/Fe₃O₄ to remove the studied adsorbates compared to many other reported materials.
Table 5  Comparison of the adsorption capacity, isotherm and kinetic model fit of present system with other reported systems

| Adsorbent                                  | Dye/Metal        | $q_e$ (mg/g) | Isotherm model | Kinetic model         | Reference |
|--------------------------------------------|------------------|--------------|----------------|-----------------------|-----------|
| Gum arabic-g-polyacrylamide/ZnO            | Malachite green  | 766.5        | Langmuir       | Pseudo second order   | [56]      |
| Gum arabic-g-polyacrylamide                | Crystal violet   | 90.9         | Langmuir       | Pseudo first order    | [29]      |
| Gum arabic-Magnetic nanoparticle           | Cu(II)           | 38.5         | Langmuir       | –                     | [57]      |
| Gum arabic-g-polyacrylonitrile             | Pb(II)           | 1017.0       | Langmuir       | Pseudo second order   | [31]      |
|                                            | Cd(II)           | 413.0        |                |                       |           |
|                                            | Cu(II)           | 396.0        |                |                       |           |
| Gum arabic-g-polyacrylamide/SiO$_2$        | Eu(III)          | 5.7          | Langmuir       | Pseudo first order    | [58]      |
|                                            | La(III)          | 5.6          |                |                       |           |
|                                            | Nd(III)          | 7.3          |                |                       |           |
|                                            | Sc(III)          | 5.1          |                |                       |           |
| Gum acacia-g-poly(3-chloro-2-hydroxypropylmethacrylate) | MB               | 224.4        | Freundlich     | Pseudo second order   | Present study |
|                                            | R6G              | 283.5        |                |                       |           |
|                                            | Cu(II)           | 282.4        |                |                       |           |
|                                            | Hg(II)           | 275.3        |                |                       |           |
| Gum acacia-g-poly(3-chloro-2-hydroxypropylmethacrylate)/Fe$_3$O$_4$ | MB               | 265.2        | Freundlich     | Pseudo second order   | Present study |
|                                            | R6G              | 344.4        |                |                       |           |
|                                            | Cu(II)           | 307.5        |                |                       |           |
|                                            | Hg(II)           | 292.8        |                |                       |           |
Conclusion

The biopolymer GA could be modified by grafting with PCHPMA by microwave irradiation. The presence of MBA units resulted in the formation of 3D network structure making the material a hydrogel. Incorporation of nano-sized magnetite particles transformed the hydrogel to a hybrid nanocomposite material. The FTIR, SEM, XRD, TGA, BET and VSM studies evidenced the formation of the graft copolymer network, its surface structure, thermal stability and magnetic nature. The hydrogel and the nanocomposite exhibited promising ability to absorb cationic dyes and bivalent metal ions as inferred from the study carried out with MB, R6G, Cu(II) and Hg(II). As compared to the parent gel, the magnetic nanocomposite exhibited higher adsorption efficiency towards these adsorbates, the enhancement being attributed to the increased surface area arising due to presence of magnetite nanoparticles. The observed order of adsorption is R6G > MB and Cu(II) > Hg(II). The adsorption followed Freundlich isotherm model and was well explained by pseudo-second-order kinetic model. The thermodynamic analysis manifested the fact that adsorption is exothermic and spontaneous. Meanwhile, excellent regeneration of the adsorbents and recovery of the adsorbed species studied in three cycles indicated its promising reuse in wastewater treatment. The super-paramagnetic nature of the nanocomposite adsorbent facilitates its easy separation using an external magnet from water after use. With all its unique characteristics, the GA–g–PCHPMA/Fe₃O₄ nanocomposite appears to be a good candidate as adsorbent material in wastewater treatment.

Supplementary Information  The online version contains supplementary material available at https://doi.org/10.1007/s00289-021-03909-1.

References

1. Arun Krishna K, Vishalakshi B (2017) Gellan gum-based novel composite hydrogel: evaluation as adsorbent for cationic dyes. J Appl 134:45527
2. Rajabi M, Mahanpoor K, Moradi O (2017) Removal of dye molecules from aqueous solution by carbon nanotubes and carbon nanotube functional groups: critical review. RSC Adv 7:47083–47090
3. Shah HUR, Ahmad K, Naseem HA, Parveen S, Ashfaq M, Rauf A, Aziz T (2021) Water stable graphene oxide-metal-organic frameworks composite (ZIF-67@GO) for efficient removal of malachite green from water. Food Chem Toxicol 154:112312
4. Ahmad K, Shah HR, Ashfaq M, Shoaib S, Shah A, Hussain E, Naseem HA, Parveen S, Ayub A (2021) Effect of metal atom in zeolitic imidazolate frameworks (ZIF-8 & 67) for removal of Pb₂⁺ & Hg₂⁺ from water. Food Chem Toxicol 149:112008
5. Mohod CV, Dhote J (2013) Review of heavy metals in drinking water and their effect on human health. Int J Innov Res Sci Eng Technol 2:2992–2996
6. Han X, Yuan J, Ma X (2014) Adsorption of malachite green from aqueous solutions onto lotus leaf: equilibrium, kinetic, and thermodynamic studies. Desalin Water Treat 52:5563–5574
7. Dragan ES, Loghin DFA (2018) Fabrication and characterization of composite cryobeads based on chitosan and starches-g-PAN as efficient and reusable biosorbents for removal of Cu²⁺, Ni²⁺ and Co³⁺ ions. Int J Biol Macromol 120:1872–1883
8. Ahmad K, Shah HR, Parveen S, Hafiza TA, Muhammad AN, Rauf AA (2021) Metal organic framework (KIUB-MOF-1) as efficient adsorbent for cationic and anionic dyes from brackish water. J Mol Struct 1242:130898
9. Sun S, Zhu L, Liu X, Wu L, Dai K, Liu C, Shen C, Guo X, Zheng G, Guo Z (2018) Superhydrophobic shish-kebab membrane with self-cleaning and oil/water separation properties. ACS Sustain Chem Eng 6:9866–9875
10. Gong K, Hu Q, Yao L, Li M, Sun D, Shao Q, Qiu B, Guo Z (2018) Ultrasonic pretreated sludge derived stable magnetic active carbon for Cr(VI) removal from wastewater. ACS Sustain Chem Eng 6:7283–7291
11. Ahmad K, Shah HR, Nasim HA, Ayub A, Ashfaq M, Rauf A, Shah SSA, Ahmad MM, Nawaz H, Hussain E (2021) Synthesis and characterization of water stable polymeric metal organic composite (PMOC) for the removal of arsenic and lead from brackish water. Toxin Rev 1–11:1919902
12. Chen J, Wang X, Huang Y, Lv S, Cao X, Yun J, Cao D (2018) Adsorption removal of pollutant dyes in wastewater by nitrogen-doped porous carbons derived from natural leaves. Eng Sci 5:30–38
13. Qi X, Liu R, Chen M, Li Z, Qin T, Qian Y, Zhao S, Liu M, Zeng Q, Shen J (2019) Removal of copper ions from water using polysaccharide-constructed hydrogels. Carbohydr Polym 209:101–110
14. Su T, Wu L, Pan X, Zhang C, Shi M, Gao R, Qi X, Dong W (2019) Pullulan-derived nanocomposite hydrogels for wastewater remediation: synthesis and characterization. J Colloid Interf Sci 542:253–262
15. Hamza MF, Wei Y, Mira HI, Abdel-Rahman AAH, Guibal E (2019) Synthesis and adsorption characteristics of grafted hydrazyl amine magnetite-chitosan for Ni(II) and Pb(II) recovery. Chem Eng J 362:310–324
16. Sirajo AZ, Vishalakshi B (2018) Absorptive removal of Cu^{2+} and Pb^{2+} from aqueous solutions using xanthan gum-g-poly[N, N′-dimethylacrylamide]-co-(2-acrylamido-2-methylpropanesulfonic acid]-ZnO nanocomposite gel. Sep Sci Technol 54:2164–2179
17. Mittal H, Parashar V, Mishra S, Mishra A (2014) Fe_{3}O_{4} MNPs and gum xanthan based hydrogels nanocomposites for the efficient capture of malachite green from aqueous solution. Chem Eng J 255:471–482
18. Prajwal K, Vishalakshi B (2020) Efficient removal of dyes and heavy metal ions from waste water using Gum ghatti–graft–poly(4-acryloylmorpholine) hydrogel incorporated with magnetite nanoparticles. J Environ 8:104207
19. Preetha BK, Vishalakshi B (2019) Karaya gum-graft-poly(2-(dimethylamino)ethyl methacrylate) gel: an efficient adsorbent for removal of ionic dyes from water. Int J Biol Macromol 122:997–1007
20. Mahto A, Mishra S (2021) Guar gum grafted itaconic acid: a solution for different waste water treatment. J Polym Environ 29:3525–3538
21. Gangadhar B, Vishalakshi B (2019) Silver nanoparticles embedded pectin-based hydrogel: a novel adsorbent material for separation of cationic dyes. Polym Bull 76:4215–4236
22. Radi S, El Abiad C, Carvalho AP, Santos SM, Faustino MAF, Neves PMS, Moura NMM (2018) An efficient hybrid adsorbent based on silica-supported amino penta-carboxylic acid for water purification. J Mater Chem A 27:13096–13109
23. Lazar MM, Dinu IA, Silion M, Dragan ES, Dinu MV (2019) Could the porous chitosan-based composite materials have a chance to a “NEW LIFE” after Cu(II) ion binding? Int J Biol Macromol 136:870–890
24. Anush SM, Vishalakshi B (2019) Modified chitosan gel incorporated with magnetic nanoparticle for removal of Cu(II) and Cr(VI) from aqueous solution. Int J Biol Macromol 133:1051–1062
25. Anush SM, Chandan HR, Vishalakshi B (2019) Synthesis and metal ion adsorption characteristics of graphene oxide incorporated chitosan Schiff base. Int J Biol Macromol 126:908–916
26. Anush SM, Chandan HR, Gayathri BH, Asma MN, Kalluraya B, Vishalakshi B (2020) Graphene oxide functionalized chitosan-magnetite nanocomposite for removal of cu(II) and Cr(VI) from waste water. Int J Biol Macromol 164:4391–4402
27. Ahmad S, Ahmad M, Manzoor K, Purwar R, Ikram S (2019) A review on latest innovations in natural gums based hydrogels: preparations & applications. Int J Biol Macromol 136:870–890
28. Singh B, Abhishek D (2017) Evaluation of gentamicin and lidocaine release profile from gum acacia-crosslinked-poly(2-hydroxyethylmethacrylate)-carbopol based hydrogels. Curr Drug Deliv 14:981–991
29. Sharma G, Kumar A, Naushad M, Garcia-Penas A, Al-Muhtaseb AH, Ghfar AA, Sharma V, Ahamad T, Stadler FJ (2018) Fabrication and characterization of gum arabic-cl-poly(acrylamide) nanohydrogel for effective adsorption of crystal violet dye. Carbohydr Polym 202:444–453
30. Abdel-Bary EM, Elbedwehy AM (2018) Graft copolymerization of polyacrylic acid onto acacia gum using erythrosine–thiourea as a visible light photoinitiator: application for dye removal. Polym Bull 75:3325–3340
31. Elbedwady AM, Abou-Elanwar AM, Ezzat AO, Atta AM (2019) Super effective removal of toxic metals water pollutants using multi functionalized polyacrylonitrile and arabic gum grafts. Polymers 11:1938
32. Sun P, Hui C, Khan AR, Du J, Zhang Q, Zhaoa YH (2015) Efficient removal of crystal violet using Fe$_3$O$_4$-coated biochar: the role of the Fe$_3$O$_4$ nanoparticles and modeling study their adsorption behavior. Sci Rep 5:12638–12649
33. Pourjavadi A, Hosseini SH, Seidi F, Soleymann R (2013) Magnetic removal of crystal violet from aqueous solutions using polysaccharide-based magnetic nanocomposite hydrogels. Polym Int 62:1038–1044
34. Hossan MS, Ochiai B (2018) Preparation of TiO$_2$-poly(3-chloro-2-hydroxypropyl methacrylate) nanocomposite for selective adsorption and degradation of dyes. Technologies 6:92
35. Reddy NN, Mohan YM, Varaprasad K, Ravindra S, Joy PA, Raju KM (2011) Magnetic and electric responsive hydrogel–magnetic nanocomposites for drug-delivery application. J Appl Polym Sci 122:1364–1375
36. Mahdavi M, Ahmad MB, Haron MJ, Namvar F, Nadi B, Rahman MZA, Amin J (2013) Synthesis, surface modification and characterization of biocompatible magnetic iron oxide nanoparticles for biomedical applications. Molecules 18:7533–7548
37. Sing KSW, Everett DH, Haul RAW, Moscou L, Pierroti RA, Rouquerol J, Siemieniewska T (2008) Reporting physisorption data for gas/solid systems. Pure Appl Chem 57:603–661
38. Prajwal K, Vishalakshi B (2020) Hybrid nanocomposite of kappa-carrageenan and magnetite as adsorbent material for water purification. Int J Biol Macromol 165:542–553
39. Mittal H, Kumar V, Ray SS, Saruchi, (2016) Adsorption of methyl violet from aqueous solution using gum xanthan/Fe$_3$O$_4$ based nanocomposite hydrogel. Int J Biol Macromol 89:1–11
40. Akbarzadeh A, Samiei M, Davaran S (2012) Magnetic nanoparticles: preparation, physical properties, and applications in biomedicine. Nanoscale Res Lett 7:144
41. Prajwal K, Vishalakshi B (2020) Magnétique nanoparticle embedded pectin-graft-poly(N-hydroxyethylacrylamide) hydrogel: evaluation as adsorbent for dyes and heavy metal ions from waste water. Int J Biol Macromol 156:1408–1417
42. Zeng Q, Qi X, Zang M, Tong X, Jiang N, Pan W, Xiong W, Li Y, Xu J, Shen J, Xu L (2020) Efficient decontamination of heavy metals from aqueous solution using pullulan/polydopamine hydrogels. Int J Biol Macromol 145:1049–1058
43. Ayawei N, Ebelegi AN, Wankasi D (2017) Modelling and interpretation of adsorption isotherms. J Chem 2017:1–11
44. Freundlich H (1926) Colloid and capillary chemistry. J Soc Chem Ind 45:797–798
45. Khan NA, Najam T, Shah SSA, Hussain E, Ali H, Hussain S, Shaheen A, Ahmad K, Ashfaq M (2020) Development of Mn-PBA on GO sheets for adsorptive removal of ciprofloxacin from water: kinetics, isothermal, thermodynamic and mechanistic studies. Mater Chem Phy 245:122737
46. Lagergren S (1898) About the theory of so called adsorption of soluble substances. Handlingar 24:1–39
47. Ho YS, McKay G (1999) Pseudo-second order model for sorption processes. Process Biochem 34:451–465
48. Ahmad K, Nazira MA, Qureshi AK, Hussain E, Najam T, Javed MS, Shah SSA, Tufail MK, Hussain S, Khan NA, Shah HR, Ashfaq M (2020) Engineering of Zirconium based metal-organic frameworks (Zr-MOFs) as efficient adsorbents. Mater Sci Eng B 262:114766
49. Pholosi A, Naadoo EB, Ofomaja AE (2020) Intraparticle diffusion of Cr(VI) through biomass and magnetite coated biomass: a comparative kinetic and diffusion study. S Afr J Chem 32:39–55
50. Campos NF, Barbosa CM, Rodriguez-Diaz JM, Duarte MM (2018) Removal of naphthenic acids using activated charcoal: kinetic and equilibrium studies. Adsorp Sci Technol 36:1–17
51. Ilgin P, Ozay H, Ozay O (2019) Selective adsorption of cationic dyes from colored noxious effluent using a novel N-tert-butylmaleic acid based hydrogels. React Funct Polym 142:189–198
52. Pour ZS, Ghaemy M (2015) Removal of dyes and heavy metal ions from water by magnetic hydrogel beads based on poly(vinyl alcohol)/carboxymethylstarch-g-poly(vinyl imidazole). RSC Adv 5:64106–64118
53. Mahdavinia GR, Etemadi H (2019) Surface modification of iron oxide nanoparticles with κ-carrageenan/carboxymethyl chitosan for effective adsorption of bovine serum albumin. Arab J Chem 12:3692–3703
54. Abramian L, El-Rassy H (2009) Removal of disperse blue 56 from synthetic textile effluent using ionic flocculation. Chem Eng J 150:403–410
55. Gupta VK, Rastogi A, Nayak A (2010) Biosorption of nickel onto treated alga (Oedogonium hatei): application of isotherm and kinetic models. J Colloid Interface Sci 342:533–539
56. Mittal H, Morakkar PP, Alhassan SM (2020) In-situ synthesis of ZnO nanoparticles using gum arabic based hydrogels as a self-template for effective malachite green dye adsorption. J Polym Environ 28:1637–1653
57. Banerjee SS, Chen DH (2007) Fast removal of copper ions by gum arabic modified magnetic nanoadsorbent. J Hazard Mater 147:792–799
58. Iftekhar S, Srivastava V, Casas A, Sillanpa M (2018) Synthesis of novel GA-g-PAM/SiO₂ nanocomposite for the recovery of rare earth elements (REE) ions from aqueous solution. J Clean Prod 170:251–259

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Authors and Affiliations

Prajwal Kulal¹ · Preetha B. Krishnappa¹ · Vishalakshi Badalamoole¹

Vishalakshi Badalamoole
vishalakshi2009@yahoo.com

Prajwal Kulal
prajwal92kulal@gmail.com

Preetha B. Krishnappa
preethakrishnappa@gmail.com

¹ Department of Post-Graduate Studies and Research in Chemistry, Mangalore University, Mangalagangothri, DK, Karnataka 574199, India