Surface functionalization of graphene oxide using amino silane magnetic nanocomposite for Chromium (VI) removal and bacterial treatment

Jitendra Kumar Sahoo1,2, Sanjeev Kumar Paikra1, Archana Baliarsingh, Debasis Panda1, Sourav Rath1, Monalisa Mishra1 and Harekrushna Sahoo1,4

1 Department of Chemistry, National Institute of Technology, Rourkela-769008, Odisha, India
2 Department of Basic Science and Humanities, GIET University, Gunupur-765022, Odisha, India
3 Department of Life Science, National Institute of Technology, Rourkela-769008, Odisha, India
4 Author to whom any correspondence should be addressed.

E-mail: kumarjitu8093@gmail.com, sahoob@nitrkl.ac.in, archanabaliarsingh2016@gmail.com, debashispanda66@gmail.com, souravrath.21@gmail.com, sanjeevpaikra01@gmail.com and mishramo@nitrkl.ac.in

Keywords: graphene oxide, antibacterial activity, chromium removal, Fe3O4

Abstract
Amino silane magnetic nanocomposite decorated on graphene oxide (GO-Fe3O4−APTES) was successfully prepared by organic transformation reaction followed by co-precipitation method. The nanocomposite was characterised by using FT-IR, XRD, FE-SEM, TEM, EDS mapping, VSM, Raman spectroscopy, BET surface area analyzer, Zeta potential and UV-visible spectrophotometer. From TEM results we observed that 8 nm sized particles successfully modified on GO surface. The surface area of GO-Fe3O4−APTES was 57.9 m² g⁻¹. The magnetic Saturation value of GO-Fe3O4−APTES was 30.6 emu g⁻¹ and the S-like magnetization of all the samples shows super paramagnetic in nature. Due to magnetic nature adsorbent, it could be easily separated from aqueous solution. GO-Fe3O4−APTES material was highly selective for Chromium (VI) removal from aqueous solution. About 91% of Chromium (VI) was removed at pH 3, 160 rpm of shaking speed, 0.3 g l⁻¹ of adsorbent dose and 10 h of contact time. The adsorption process of Chromium (VI) on GO-Fe3O4−APTES follows Pseudo-second-order kinetic and Langmuir isotherm model because of high coefficient of determination value (R² = 0.99). The maximum adsorption capacity (q_m) of GO-Fe3O4−APTES was observed at 60.53 mg g⁻¹. The synthesized material was desorbed with 0.5 M NaOH and recycled up to five cycles. After five cycles, the removal efficiency of Chromium (VI) possesses high efficiency towards GO-Fe3O4−APTES. Mechanistically, adsorption of Chromium (VI) follows strong electrostatic attraction between adsorbate and adsorbent. GO-Fe3O4−APTES has potential adsorbent for the adsorption of Chromium (VI) in waste water treatment. Furthermore, the GO-Fe3O4−APTES were tested for antibacterial properties against gram negative (Escherichia coli) and gram positive (Bacillus subtilis) bacterial strain. The synthesized material responds positively towards antibacterial activity.

1. Introduction

The water contamination throughout the world occurs by toxic heavy metals (Cr, As, Pb, Hg, Ni, and Cd) above their permissible limit are a serious problem for living organism [1–3]. Among various toxic metal ions, Chromium (Cr) is one of the highly toxic heavy metal and often discharges to water from wood preservatives, electroplating, textile industries, metal refining and plant producing industrial inorganic chemicals and pigments [4–6]. A very low concentration of chromium creates serious health problem like stomach cancer, bronchial asthma, kidney damage, anaemia, liver damage and hepatotoxicity in human [7, 8]. Chromium exist in water both Chromium (III) and Chromium (VI) states, Chromium (VI) is highly contaminant because of

© 2020 The Author(s). Published by IOP Publishing Ltd
high solubility, smaller size and large mobility [9–14]. As compare to Chromium (VI), Chromium (III) is less toxic and also used as an essential micronutrient for sugar, protein and fat metabolism in mammals [15, 16]. Hence, Chromium (VI) can be converted to Chromium (III) as an alternative way to reduce the toxicity [17]. In current year, photo catalytic reduction is considered a prominent method to reduce the toxicity of Chromium (VI) to Chromium (II) but their initial and operational cost is very high [18]. There are several methods available to remove Chromium from contaminated water. Those methods are ion exchange [19, 20], ultrafiltration [21], reverse osmosis [22, 23], electro dialysis [24–26], bio sorption, adsorption and chemical precipitation [27]. Among all the removal methods, adsorption is one of the most commonly used method for Chromium (VI) removal because of its low cost, less energy, less chemical requirement, easy to operate, high regeneration capacity and removal efficiency [28]. A number of naturally occurring adsorbents such as almond shells, olive cake, wool, charcoal used tyres, cactus leaves, soot, coconut shell charcoal, banana peel, pine needles, sawdust, dead fungal biomass and green algae have been used for the removal of Chromium [29–32]. Among all the naturally available adsorbents, most of them are slow process kinetics and have low adsorption capacity. Hence, it is a necessary to prepare novel and innovative adsorbent useful for both the environment safety and industry.

Due to high surface area–to-volume ratio, excellent magnetic character, surface property, great biocompatibility, reusability, easy separation by external magnetic field and comparatively low cost, iron oxide (Fe₃O₄) have already been investigated as excellent adsorbents for different heavy metal ions [33–35]. Iron oxide nanoparticle have several applications in various research areas such as catalytic oxidation of alcohol [36], magnetic carrier for protein separation [37], supercapacitor electrode materials [38–42], waste water treatment [43–45] and heavy metal adsorption [46]. In recent years, most of the researchers are interested to chemical modify Fe₃O₄ to enhance their adsorption capacity. Also aerosol based iron–carbon nanocomposites synthesized for Chromium (VI) adsorption [47]. Another pioneer work shows iron oxide decorated PEDOT: PSS used for cancer biosensor [48]. Keeping the above information in mind, we modified Fe₃O₄ on graphene oxide (GO) surface using (3-aminopropyl) triethoxysilane (APTES) as a cross linker.

GO is very commonly used adsorbent because of high surface area, aromatic sp³ domains and high functionality (containing hydroxyl, epoxy and carboxyl functional groups) and low manufacturing cost that make GO as a potential adsorbent for heavy metal adsorption. Many researchers have been focused on the preparations of metal oxide modified GO based nano adsorbent for heavy metal removal [49]. Wide ranges of metal oxide modified GO such as ZnO−ZnFe₂O₄ decorated on GO for adsorption of chromium, Go/MnFe₂O₄ magnetic nanohybrids for adsorption of As and Pb from water and nickel ferrite, iron and aluminium decorated GO surface for fluoride removal and RGO/Fe₂O₃ nanocomposite for Pb(II), Cr(IV) adsorption [50]. In order to further improve the adsorption percentage, current researchers has been interested to synthesize by grafting new functional group on GO surface [51]. Apart from this, GO have one limitation in terms of difficulty in like no easy separation from aqueous solution. However, separation of adsorbent after adsorption from contaminated water still challenging work. To overcome this limitation, iron oxide is the best modification on GO surface because of super paramagnetic nature, which can be easily separated because of its magnetic nature.

Metallic nanoparticle on GO matrix has a lot more biomedical importance [52]. The antibacterial property of graphene and GO is reported from various studies [53, 54]. Graphene sheet acts as a substrate for adhesion of cells or any other microorganism [55]. Graphene based nanomaterial have multifunctional application including photoluminescence, cellular imaging, as a vehicle for gene delivery and as a drug carrier for advanced drug delivery system [56–58]. Antibacterial activity of graphene nanomaterial is due to loss of membrane integrity. Sharp edges of graphene nanosheet damage the cell membrane of bacteria and lead to the leakage of cellular component i.e. RNA or protein contents of bacteria [59]. Various physical as well as a chemical factor of graphene is responsible for its antimicrobial property [60]. Graphene nanocomposite increases the cellular oxidative stress which disturbs the metabolic activity in bacteria resulting bacterial cell death [61]. Fabrication of silver nanoparticle with graphene oxide acts as a carrier for the efficient delivery of water insoluble drug into the cells [54, 57, 62–65]. Besides this it’s peculiar electrical conductivity and paramagnetic property allows to be used in various biomedical application [65, 66]. Chemical modification of graphene sheet can be easily dispersed with the polymeric matrix [67] or inorganic material matrix [68]. The smooth surface of GO enables the bacteria to adhere to the surface. The oxygen containing a functional group of GO provide a new dimension to trap the radioactive impurity from the water [69].

Therefore, in this paper we reported the functionalization of Fe₃O₄–APTES on GO surface for Chromium (VI) removal from aqueous solution by varying the adsorbent dosage, initial Chromium (VI) concentration, immersion time and pH, which plays an important role for adsorption. To evaluate the experimental data statistical analysis done to make a predict model and to test its viability.
2. Materials and methods

2.1. Chemicals and reagents

Anhydrous Ferric Chloride (FeCl₃), Hydrogen chloride (HCl), Sulphuric acid (H₂SO₄), Sodium nitrate (NaNO₃), Hydrogen peroxide (H₂O₂, 30%), 1,5-diphenylcarbazide (DPC), Ethanol (C₂H₅OH), sodium sulphate (Na₂SO₄) and Acetone (CH₃COCH₃) were purchased from Merck life science (India). Thionyl chloride (SOCl₂, 97% purity), 2,7-dichlorofluorescin diacetate (DCFDA) and dimethyl formamide (DMF) were purchased from Sigma-Aldrich. Sodium chloride (NaCl) Sodium hydroxide pellet (NaOH), sodium fluoride (NaF) Ferrrous sulphate (FeSO₄) and (3-Aminopropyl) triethoxysilane (APTES), bacterial culture Luria bertani broth, Miller and Luria bertani agar, Miller were supplied by Hi-media, India. Ammonium hydroxide (NH₄OH), sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃) was purchased from Fisher scientific. Potassium dichromate (K₂Cr₂O₇) was supplied by Spectrochem, India. Potassium permanganate (KMnO₄) was supplied from Avra chemical, India. Graphene oxide [GO] was prepared according to reported work via modified hummers method [70].

2.2. Preparation of Iron oxide nanoparticles (Fe₃O₄)

Iron oxide (Fe₃O₄) was prepared using previously reported chemical co-precipitation method with some modification [70]. Briefly, 4 g of anhydrous FeCl₂ and 12 g of anhydrous FeCl₃ were dissolved in 50 ml of 0.1 M HCl solution. Further, the mixture was added slowly to 500 ml of 1.5 M NH₃ solution until reaches pH 11, after wards, stirred for 2 h at the temperature 40 °C. A black precipitate of Fe₃O₄ magnetic nanoparticle was formed after stirring for 2 h, which was collected by centrifugation and washed three times with distilled water and two times with ethanol, and then dried at 60°C.

2.3. Preparation of Fe₃O₄-APTES (FA)

The APTES modified Fe₃O₄ magnetic nanoparticles (FA) was synthesized based on our previously established method with small modification [71]. Firstly a solution mixture was prepared using 1 g of Fe₃O₄ and 100 ml of ethanol in a round bottom flask. In order to disperse the Fe₃O₄ nanoparticles the solution was ultrasonicated for 30 min. Then the resulting dispersion was bubbled with argon gas for 30 min, and then added 1 ml of APTES by a syringe under mechanical stirring. The reaction was then maintained at room temperature for 24 h. The reaction was incubated at room temperature for 24 h. Finally, the obtained solid product was collected with the help of a magnet and repeatedly washed with ethanol. The obtained FA nanocomposite was dried in a muffle furnace at 60 °C.

2.4. Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared according to reported work via modified hummers method [72]. In a typical synthesis, 1 g of graphite powder was suspended in 25 ml of H₂SO₄ (98%) and ultrasonicated for 20 min. After which, 100 mg of NaNO₃ was added to the above solution and stirred for 34 h at room temperature. The obtained mixture was kept in an ice bath to cool down 5 °C followed by the slow addition of 3 g of KMnO₄ with constant stirring, by keeping in mind the temperature should not rise above 20 °C. The stirring was continued for 4 h at same condition. Then the ice bath was removed and kept the reacting mixture at room temperature and 250 ml distilled water was added drop wise. The stirring was continued for another 45 min and 50 ml of warmed distilled water to terminate the reaction 5 ml of H₂O₂ (30%) was added drop wise to the contents and stirred for 12 h. A bright yellow colour indicates the complete oxidation of graphite to GO. The yellow suspension was centrifuged and washed three times with HCl (10%) to remove the metal ions and then several times with distilled water to maintain the pH7. Then the solution was dried at 60 °C and grind to get desire GO powder.

2.5. Preparation of GO-Fe₃O₄-APTES

Firstly 300 mg of GO powder was dispersed in 20 ml of DMF (as a catalyst) in 250 ml capacity of round bottom flask followed by the addition of 0.25 ml of SOCl₂ and the reaction was left to proceed for 24 h with constant stirring at 70 °C. SOCl₂ is a strong reducing agent, it can convert less reactive −COOH group of GO into much reactive −COCl group. Solvents like DMF are suitable catalyst to speed up the reaction. Then 600 mg of Fe₃O₄-APTES was added to the reacting mixture followed by addition of 10 ml of DMF and 0.38 ml of Et₃N. The temperature of the following mixture was kept upto 130 °C, then stirred and refluxed for next 72 h. In the following method, −COCl group react with −NH₂ group of Fe₃O₄-APTES to form amide bond. The solid residue
Scheme 1. Schematically detailed synthetic mechanism of GO-Fe₃O₄-APTES.
was separated by centrifugation followed by washing using distilled water. The residue was dried at 80 °C for 12 h to form desired product. The detailed synthetic mechanism was represented in scheme 1.

2.6. Adsorption experiment
All the batch adsorption experiments were carried out in 200 ml capacity of polypropylene bottles by considering various concentration of Chromium solution. For the adsorption studies, 0.3 g of GO-Fe₂O₃-APTES was added in 20 mg l⁻¹ of Chromium solution at pH 3. The reaction bottles were shaken using an incubator shaker (RC 5100) at shaking rate 200 rpm at room temperature. After 10 h, the adsorbent was separated out by Whatman-42 filter paper. The remaining concentration of Chromium was analysed by UV-Visible spectrophotometer using 1,5-diphenyl carbazide (DPC) method at the wave length of 540 nm [73]. The impact of various parameters like pH (2–12), adsorbent dosage (0.15–0.35 g), time (2–10 h) and room temperature (25 °C) influencing the removal of Chromium ion were examined separately by keeping the others constant, so as to optimize the adsorption process. The adsorbed amount of chromium ion and the removal efficiency (%) was determined using the subsequent equations.

\[ q_e = \frac{C_0 - C_e}{W} \times V \]  
\[ \% \text{ of adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \]  

From the above equation, \( q_e \) shows the adsorbed amount of Chromium (VI). \( C_0 \) is the initial concentration of chromium (VI) (mg l⁻¹), \( C_e \) is the final concentration of chromium ion (mg l⁻¹), \( V \) is the volume of Chromium (VI) solution and \( W \) is the mass of adsorbent. All experiments were repeated for 3 times.

2.7. Instrumentation and characterization
Fourier Transformation Infrared Spectrophotometer (FTIR, PERKINELMER-1000) was used to detect the structural changes in wave number ranging from 400–4000 cm⁻¹ by utilizing KBr pellet. Powder x-ray Diffractometer (XRD, RIGAKU ULTIMA-IV, Japan) was used detect the crystalline phase of the nanocomposite via Cu Kα radiation of wavelength \( \lambda = 154 \) nm. The morphology of the nanocomposite was scanned by Field Emission Scanning Electron Microscopy (FESEM, NOVA NANO SEM 450) and was run at 15–20 kV. For the determination of particle size a JEOL high resolution TEM (HRTEM, JEM-2100, and Japan) was used and was operated at 200 kV. The elemental mapping and composition were studied by EDX analyzer (Oxford INCA) fitted with TEM. Raman Spectrometer (LABRAM-010) having the range of wave number 500–2500 cm⁻¹ was used to get the structural information. The Vibrating Sample Magnetometer (VSM- PPM5) was used for the measurement of magnetic properties of the sample. The surface area was analysed by N₂ adsorption-desorption isotherm with a measured at 77 K on a Quantachrome Autosorb 3-B apparatus. The zeta potential value with different pH of the solution was analyzed by ZETACAD CD, France. The UV-visible Spectrophotometer (UV-SHIMADZU 2450, Malaysia) was used to determine the concentration of Chromium (VI) present in solution by using the method 1, 5-diphenylcarbazide (DPC). To maintain different pH of the solution using a digital pH meter (Sartorious Mechatronics India Pvt. Ltd).

2.8. Bacterial culture
E. coli and B. subtilis were grown in Luria-Bertini (LB) broth. For colony counting purpose LB agar was taken and plates were prepared in Petridishes.

2.9. Antibacterial activity of GO-Fe₂O₃-APTES
Assessment of antibacterial activity of GO-Fe₂O₃-APTES was checked against gramnegative bacteria, E. coli and gram positive bacteria B. subtilis. For the evaluation of antibacterial activity both the bacteria were grown in LB broth and an appropriate concentration of bacteria was taken for the antimicrobial assay. The bacteria were inoculated on the LB agar plate and the antimicrobial activity of GO-Fe₂O₃-APTES was checked by using the disc diffusion method [74]. To check the concentration dependent activity of GO-Fe₂O₃-APTES, the bacteria (E. coli and B. subtilis) were grown in LB media with different concentration of GOFE (10, 20, 40, 80, 160 μg ml⁻¹) and then it is incubated for 8 to 12 h at 37 °C at 120 rpm. Bacterial growth was examined by measuring the optical density at 595 nm using the ELISA plate reader (Biobase-EL10A Elisa reader) obtained from Biobase Bioindustry (Shandong) Co. Ltd. Bacterial growth kinetics was studied by varying interval of time with and without GO-Fe₂O₃-APTES treatment.

2.10. Analysis of bacterial damage under field emission scanning electron microscopy (FE-SEM)
Bacterial damage was analyzed by field emission scanning electron microscopy (FESEM). This experiment helps us to visualize the fine structure of bacterial cells before and after GO-Fe₂O₃-APTES treatment. Treated and
untreated cells were washed properly with 0.9% sodium chloride and then fixed with 4% Paraformaldehyde. After fixation, it was washed with phosphate buffered saline (PBS) and then dehydrated by using graded series (30, 50, 70, 90 and 100%) of alcohol. Afterwards it was fixed on a clean glass slide and gold sputtering was done before taking the images. For detection of different elements deposited in the bacterial cells EDX analysis was done.

2.11. Detection of ROS production
Assessment of ROS generation by bacteria was check by using the 2,7-Dichlorofluorescin diacetate (DCFDA) dye. It is a peroxynitrile indicator which confirms the generation of different reactive oxygen species (nitric oxide or hydrogen peroxide) [75]. Bacterial cells treated with and without GO-Fe3O4-APTES were exposed to DCFDA dye (1 μM) and then its fluorescence intensity was measured at emission wavelength 529 nm with an excitation of 495 nm by using the fluorescence spectrophotometer.

3. Result and discussion

3.1. Characterisation
In order to study the presence of functional groups in GO-Fe3O4-APTES, FTIR measurement was carried out. Figure 1 shows the comparison FT-IR data of GO, Fe3O4, Fe3O4-APTES and GO-Fe3O4-APTES. In the spectrum of GO, the presence of peaks at 1051 cm−1 (C–O–C stretching vibration of epoxide group), 1224 cm−1 (C–OH), 1384 cm−1 (C–O asymmetric stretching vibration of carboxylic group), 1615 cm−1 (C= in the carbon skeletal network), 1723 cm−1 (C=O stretching vibration of carboxylic group), 2337 cm−1 (CO2), 2849 cm−1 (CH bending vibration), 2920 cm−1 (CH stretching vibration) and the strong peak around 3434 cm−1 can ascribe to the O–H stretching mode of water molecules [76–78]. In the spectrum of Fe3O4, the existence of peaks at 441 cm−1 ascribed to the shifting of the υ2 band of the Fe–O bond of bulk magnetite, two strong peaks at 583 cm−1 and 628 cm−1 are ascribed to the presence of Fe–O and two peaks at 1622 cm−1 and 3431 cm−1 are ascribed to the O–H bending and stretching frequency of water molecules [79, 80]. The existence of silica network on Fe3O4 was confirmed by Fe–O–Si bonds, this peak cannot show in the FT-IR spectrum because it appears at 584 cm−1 and therefore 583 cm−1 peak of Fe3O4 overlaps [81, 82]. So, the presence of silane polymer on Fe3O4 was confirmed by the peak at 993 cm−1 assign to Si–O–Si groups. The two broad peaks at 1627 cm−1 and 3413 cm−1 can be ascribed to NH2 bending mode of free NH2 and N–H stretching vibration [83, 84].

Comparing to the FT-IR data of GO and Fe3O4-APTES with GO-Fe3O4-APTES, the peaks of GO-Fe3O4-APTES are similar with GO and Fe3O4-APTES but two new peak at 1570 cm−1 and 1650 cm−1 were observed, this peak corresponds to N–H bending and amide bond (–NHCO–) formation in between free NH2 group of Fe3O4-APTES and –COOH group of GO. These observed data was also comparing with other published data [75, 85–87].
Figure 2 represents the XRD patterns of GO, Fe₃O₄, Fe₃O₄-APTES and GO-Fe₃O₄-APTES. In the XRD peak of GO, a strongest peak at 2θ = 11.4° was observed which corresponds to (001) crystal plane. This 011 plane can confirm the formation of GO [88]. The XRD patterns of Fe₃O₄, Fe₃O₄-APTES and GO-Fe₃O₄-APTES were found to be similar. The crystalline peaks at 2θ = 30.3° (220), 35.7° (311), 43.5° (400), 53.9° (422), 57.5° (511) and 63.0° (440) corresponds to the structure of Fe₃O₄ according to the JCPDS no- 019-0629 [89]. The XRD patterns of Fe₃O₄-APTES on GO surface, GO peaks might be absence because of overlapping Fe₃O₄ peaks. It can conclude by XRD pattern of the GO-Fe₃O₄-APTES material that there is no change in the characteristic peaks of Fe₃O₄ after modification of APTES and GO [90, 91].

Techniques such as FE-SEM and TEM were used to explore the surface morphology of the synthesized material. Figure 3(a) shows the FE-SEM image of the Fe₃O₄-APTES. It is observed that the shape of Fe₃O₄-APTES was nano sized spherical shape and homogeneously distributed [92–94]. The FE-SEM image of GO (figure 3(b)) shows the layer type structure [95–97]. Figure 3(c) illustrates the FE-SEM image of GO-Fe₃O₄-APTES, which indicates the formation of nanospheres on GO layer. The structure and morphology of Fe₃O₄-APTES and GO-Fe₃O₄-APTES was further examined by TEM analysis. Figure 3(d) shows the TEM image of Fe₃O₄-APTES and figure 4(b) shows the particle size distribution of Fe₃O₄-APTES. From TEM image, it is clearly seen that the Fe₃O₄-APTES having fine spherical particles and the histogram of Fe₃O₄-APTES shows the average particle size 8 nm. The average particle size was calculated by measuring the diameters of 53 nanoparticles by ImageJ software. Figures 4(c) and (d) represents the TEM image of GO-Fe₃O₄-APTES with various resolutions (200 and 100 nm resolution). These images clearly shown that the 8 nm sized spherical particles are successfully modified on GO layer. The HRTEM image of GO-Fe₃O₄-APTES was given in figures 4(e)–(g), respectively. Figure 4(e) shows two different lattice fringes, which ascribe the crystalline nature of GO and Fe₃O₄-APTES. From figure 4(g), we confirm the d-spacing 0.344 nm attribute to the (111) lattice plane of Fe₃O₄. The above results were also similar with XRD data in JCPDC files for Fe₃O₄. The SAED pattern GO-Fe₃O₄-APTES is shown in figure 5(a). The ring like shape of SAED pattern shows the crystalline nature of the material. The elemental mapping (EDS) of GO-Fe₃O₄-APTES (figures 5(b)–(h)) represents the presence of elements like Fe, C, O, N and Si with different colour. Again EDX spectrum confirms the synthesized material contains iron (Fe), carbon (C), oxygen (O), nitrogen (N) and silicon (Si) elements with 16.4, 65.8, 9.0, 5.4 and 3.4 atomic percentages, respectively. The elemental mapping and EDX result shows there is no impurity peak found in GO-Fe₃O₄-APTES material.

The Raman spectroscopy was carried out to study the structural configuration of GO and GO-Fe₃O₄-APTES during the process of adsorption and the data was shown in figure 6. The Raman spectrum of GO shows two strong peaks one is D band at 1353 cm⁻¹ due to the disorder of GO arising from imperfection linked with vacancies, amorphous carbon species and grain boundaries and other is G band at 1607 cm⁻¹ which specifies the E₂g Phenomenon of Sp² hybridised carbon in a 2-dimensional hexagonal lattice [98]. After the modification of Fe₃O₄-APTES on the surface of GO, the intensity of D and G band became higher than pristine GO. In case of GO-Fe₃O₄-APTES, it is observed that two strong bands at 1350 cm⁻¹ and 1588 cm⁻¹ are found. The D and G band of GO-Fe₃O₄-APTES was slightly shifted by 3 cm⁻¹ and 19 cm⁻¹ as compared to pristine GO. This Raman
The shift of D and G band for GO-Fe₃O₄-APTES sheet demonstrates that the charge transfer occurs between the sheets of GO and Fe₃O₄-APTES. It exhibits a strong interaction between GO and Fe₃O₄-APTES nanocomposite. The intensity ratio I_D/I_G of GO and GO-Fe₃O₄-APTES was calculated to be 1.00 and 1.12, respectively. However, the intensity ratio I_D/I_G of GO-Fe₃O₄-APTES was higher than pure GO, which was due to the defects arises by the interaction between Fe₃O₄-APTES and GO [99, 100].

Vibrating sample magnetometer (VSM) analysis was carried out to know the magnetic properties of prepared Fe₃O₄, Fe₃O₄-APTES and GO-Fe₃O₄-APTES. Magnetization curve of Fe₃O₄, Fe₃O₄-APTES and GO-Fe₃O₄-APTES are shown in figure 7. The magnetic saturation (M_s) value of Fe₃O₄, Fe₃O₄-APTES and GO-Fe₃O₄-APTES are 52.8 emu g⁻¹, 47.4 emu g⁻¹ and 30.6 emu g⁻¹. The magnetic saturation value decreases, after modifying APTES and GO on Fe₃O₄ [88]. These modifications on the surface of Fe₃O₄ nanoparticles are non-magnetic and their shielding effect resulted in the decrease of magnetic property of Fe₃O₄ nanoparticles. The S-like magnetization of all the samples shows superparamagnetic in nature at room temperature because of negligible coercivity and remanence. The right inset of figure 7 shows that GO-Fe₃O₄-APTES is attracted by an external magnet and the clear solution can be easily removed pipette.

The N₂ adsorption-desorption isotherm is carried out to calculate the specific surface area of synthesized material. Figure 8 shows BET isotherm plot curve of GO, Fe₃O₄ and GO-Fe₃O₄-APTES. The surface area of GO, Fe₃O₄ and GO-Fe₃O₄-APTES were found to be 35.3, 48.2, and 57.9 m² g⁻¹ respectively. The isotherm curve of GO-Fe₃O₄-APTES exhibit typical type IV with comparatively high surface area. Similar observations were also reported by other researcher groups [99, 101]. Surface area of GO-Fe₃O₄-APTES increases after modification of Fe₃O₄-APTES on GO. The higher surface area is further improving the adsorption capacity toward the removal of Chromium (VI).
Figure 4. (a) TEM image of Fe$_3$O$_4$-APTES (b) the particle size distribution of Fe$_3$O$_4$-APTES (c), (d) TEM image of GO-Fe$_3$O$_4$-APTES (200 and 100 nm resolution), (e)-(g) HRTEM micrograph with interplanar spacing of GO-Fe$_3$O$_4$-APTES.
3.2. Impact of different parameter on adsorption

3.2.1. Effect of chromium (VI) concentration on adsorption

Initial concentration of Chromium (VI) is one of the most efficient factors on adsorption field. Figure 9(a) shows the variation of initial Chromium (VI) concentration from 5 to 70 mg l$^{-1}$ at constant parameters such as adsorbent dosage (0.3 g), pH 3, room temperature (25 °C), contact time (10 h) and shaking speed (160 rpm). From this plot we observe the Chromium (VI) removal efficiency nearly same from 5 mg l$^{-1}$ to 20 mg l$^{-1}$. After 20 mg l$^{-1}$ the removal efficiency starts to decrease. This occurs due to that at lower concentrations of Chromium (VI), the ratio of the initial number of Chromium (IV) ions to the obtainable surface area of the adsorbent is high. Although at higher concentrations of Chromium (VI), the remaining sites of adsorption become lower and then the percentage of removal efficiency of Chromium (VI) decreases which depends on the initial concentration of Chromium (VI). Thus 20 mg l$^{-1}$ of Chromium (VI) concentration was taken as the optimum concentration for further experiment.

3.2.2. Effect of adsorbent dosage on chromium (VI) adsorption

Figure 9(b) demonstrates the effect of adsorbent dosage on the removal of Chromium (VI) from the aqueous solution. We changes the adsorbent dosage from 0.15 to 0.35 g l$^{-1}$ by keeping other parameters constant such as pH 3, room temperature (25 °C), contact time (10 h) and 160 rpm of shaking speed. In this plot we observed that the removal efficiency of Chromium (VI) increases by increasing the adsorbent dosage because the number of active binding sites increases by increasing adsorbent dosage [10, 102]. The adsorbent dosage from 0.3 g l$^{-1}$ to
0.35 g l\(^{-1}\) shows the percentage of the removal efficiency remains same. From the above plot it was noticed that the percentage of removal efficiency of Cr(\text{VI}) is found to be maximum at 0.3 g of adsorbent dose. 0.3 g of adsorbent dose was selected as optimum dose for further experiments.

3.2.3. Effect of contact time on Chromium (VI) adsorption

Among all the parameters contact time is one of the most important factor which affect the adsorption capacity of the adsorbent. This is shown in figure 9(c). We varied the contact time from 1 to 25 h by keeping other parameters constant (pH 3, 20 mg l\(^{-1}\) Chromium (VI) concentration, adsorbent dose 0.3 g, room temperature (25 °C) and shaking speed 160 rpm). In this plot we observed that 1 to 10 h of contact time the removal efficiency of Chromium (VI) gradually increases. The maximum adsorption of Chromium (VI) occurred at in 10 h to 25 h of contact time indicating 91% of removal efficiency. It occurs due to the availability of maximum numbers of unoccupied surface sites for adsorption process [103]. Thus 10 h was selected as optimum contact time for further experiments.
3.2.4. Effect of pH on Chromium (VI) adsorption

The effect of pH on the adsorption process is an important parameter and shown in figure 9(d). We varied the pH 3 to 10 by keeping other parameters constant such as room adsorbent dose (0.3 g), Initial Chromium (VI) concentration 20 mg l\(^{-1}\), temperature (25°C), contact time (10 h) and shaking speed (160 rpm). It was observed...
that at pH 3 the removal efficiency was found to be 91%. After that it significantly decreases up to 34% at pH 10. In acidic medium Chromium (VI) exist as HCrO\textsubscript{4}\textsuperscript{−}, Cr\textsubscript{2}O\textsubscript{7}2− and it is found in the form of CrO\textsubscript{4}\textsuperscript{2−} above pH 6. Now it is important to find the surface charge of GO-Fe\textsubscript{3}O\textsubscript{4}-APTES at different pH. Zeta-potential is the best technique to confirm the surface charge of the material. From Zeta-potential (figure S1 is available online at stacks.iop.org/NANOX/1/010062/mmedia) measurement we found that 8.2 is isoelectric point. The GO-Fe\textsubscript{3}O\textsubscript{4}-APTES has positive charge at pH < 8.2, so it favours electrostatic attraction [104]. Furthermore, at pH 3 maximum positive charge was observed corresponding to strong electrostatic attraction between highly positive charged material and negatively charged chromium ion. Above pH 3, the positive charge decreases so the removal efficiency decreases. Similarly, pH > 8.2 the adsorbent surface becomes negatively charge and hence the material repels negative chromium ion ref. At pH < 3, the removal efficiency decreases because more H\textsuperscript{+} ions react with Cr\textsubscript{2}O\textsubscript{7}2− and HCrO\textsubscript{4}− forming H\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} and H\textsubscript{2}CrO\textsubscript{4} which are neutral and could not adsorb [105].

3.2.5. Effect of shaking speed on Chromium (VI) adsorption

Shaking speed is one of the most important factors which affect the adsorption capacity of the adsorbent. To determine the effect of agitation speed, 80 to 160 rpm of agitation speed were set to check the adsorption efficiency. Figure S2 shows that increasing the speed of agitation from 80 to 160 rpm, the percentage of Chromium (VI) removal efficiency also increases. At 160 rpm of agitation speed maximum adsorption of Chromium (VI) occurs. This is caused due to increase in the intra-particle diffusion and film diffusivity [106].

3.2.6. Adsorption kinetics

To understand the mechanism of adsorption process well on contact time, we investigate adsorption kinetics. Three models were introduce to simulate the predictable data such as Pseudo first order kinetic theory, Pseudo second order kinetic theory and Intra-particle diffusion model.

The Pseudo first order kinetic equation is expressed as follows [93, 94, 107].

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

(3)

Here $q_e$ = Adsorbed amount of Chromium (VI) at equilibrium concentration (mg g\textsuperscript{-1}), $q_t$ = Adsorbed amount of Chromium (VI) at equilibrium time, $K_1$ = Pseudo first order rate constant. The values of $K_1$, $q_e$ and $R^2$ were calculated from the slope & intercept of the plot log($q_e - q_t$) vs t and the values are listed in table 1.

The Pseudo second order kinetic equation is expressed as follows [92, 108, 109].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

(4)

Here $K_2$ = Pseudo second order rate constant. The values of $q_e$, $K_2$ and $R^2$ were calculated from the slope and intercept of the plot $t/q$ vs t and the values are listed in table 1.

The intra particle diffusion model is expressed by using the following equation.

$$q_t = k_p \times t^{0.5} + C$$

(5)

Here $k_p$ is the intra-particle diffusion constant (mg g\textsuperscript{-1} min\textsuperscript{0.5}) and C is the boundary layer thickness constant (mg g\textsuperscript{-1}). The values of $k_p$, C and $R^2$ were calculated from the plot $q_t$ versus $t^{0.5}$ and the values are listed in table 1.

Figure 10 shows the linear form of Pseudo-first-order, Pseudo-second-order and intra-particle diffusion model for Chromium (VI) adsorption. The computed result which obtained from three models is listed in table 1 comparing to the $R^2$ value, pseudo-second-order kinetics is well fitted with the Chromium (VI) adsorption [110]. Therefore, this result shows chemisorption in between adsorbent and adsorbate [111]. Intra-particle diffusion model is the best model to identify the adsorption diffusion mechanism. According to this model, if the line passing through origin, then the adsorption process is controlled by intra-particle diffusion, while if the data exhibit multi linear plot but does not passing through origin, then more steps involved the adsorption process [112, 113]. Figure 10(c) shows three straight lines which indicate more than one steps are involved in the adsorption mechanism. The first straight line ascribe to outer surface adsorption that means Chromium (VI) diffuses through the solution to the outer adsorbent surface. The middle line corresponds to the

### Table 1: Kinetic parameters for Chromium adsorption on GO-Fe\textsubscript{3}O\textsubscript{4}-APTES powder.

| Parameter                  | Pseudo-first-order | Pseudo-second-order | Intraparticle diffusion model |
|----------------------------|--------------------|----------------------|-------------------------------|
| $q_e$ (mg g\textsuperscript{-1}) |                   |                      |                               |
| $K_1$                       |                   |                      |                               |
| $R^2$                       |                   |                      |                               |
| $q_e$ (mg g\textsuperscript{-1}) |                   |                      |                               |
| $K_2$                       |                   |                      |                               |
| $R^2$                       |                   |                      |                               |
| $k_p$ (mg g\textsuperscript{-1} min\textsuperscript{0.5}) |                   |                      |                               |
| $C$ (mg g\textsuperscript{-1}) |                   |                      |                               |
gradual adsorption reflecting intra-particle diffusion as the rate-limiting step. The final plateau relates out the equilibrium stage and surface adsorption, since the diffusion mechanism starts to slow down and level out \[114, 115\]. From the above results, it could be inferred that the diffusion mechanism was involved in the multi adsorption process.

3.2.7. Adsorption isotherm

The adsorption isotherm models such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevic (D-R) and Elovich were selected to define the adsorption process.

Langmuir isotherm is used for assuming the adsorption of Chromium (VI) on homogeneous planes by monolayer adsorption. The mathematical expression for Langmuir isotherm is written as follows.

\[
\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m}
\]

Here, \(c_e\) represents the Chromium (VI) concentration (mg l\(^{-1}\)) at equilibrium, \(q_e\) is the capacity of equilibrium adsorption (mg g\(^{-1}\)), \(q_m\) is the maximum adsorption capacity (mg g\(^{-1}\)) and \(b\) is the Langmuir constant. The values of \(q_m\), \(b\) and \(R^2\) was calculated by using the slope and intercept of the plot \(\frac{c_e}{q_e}\) versus \(c_e\).

The value of \(R_L\), which is the dimensionless constant can also be considered to know the favourability or unfavourability of the process of adsorption. \(R_L\) can be evaluated by using the following equation.

\[
R_L = \frac{1}{1 + bc_0}
\]

The calculated value of \(R_L\) was found to be less than 1 (<1). This designates that the adsorption process of Chromium (VI) was favourable for this isotherm.

Freundlich isotherm is utilized for assuming the adsorption of Chromium (VI) on heterogeneous planes by multilayer adsorption. This isotherm model can be expressed as follows,
Here $q_e$ is the adsorbed amount of Chromium (VI) per unit weight of adsorbent (mg g\(^{-1}\)) at equilibrium, $n$ is the density of adsorption, $c_e$ is the concentration of Chromium (VI) in solution at equilibrium time (mg l\(^{-1}\)). The values of $K_F$ (Freundlich constant), $n$ and $R^2$ were determined by using the slope and intercept of the plot $\ln q_e$ versus $\ln c_e$.

The electrostatic force of attraction between the adsorbent and the adsorbate were shown by Temkin isotherm. The Temkin isotherm is written as follows,

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

$$B_1 = \frac{RT}{B}$$

Here, $B_1$ is the Temkin constant which is related to the adsorption of heat, $K_T$ is the isotherm constant, $R$ is the gas constant and $T$ is the absolute temperature. The parameters like $B_1$, $K_T$, $R^2$ are evaluated by plotting the graph between $q_e$ versus $\ln c_e$.

Elovich isotherm model suggested multilayer adsorption. The mathematical expression for Elovich isotherm is expressed as follows, which depend on the kinetic principle presuming that the adsorption side exponentially increases with adsorption.

$$\ln \frac{q_e}{c_e} = \ln K_E q_m - \frac{q_e}{q_m}$$

Here $q_m$ is the maximum capacity of adsorption (mg g\(^{-1}\)), $K_E$ is the Elovich constant. The values of $q_m$, $K_E$ and $R^2$ were calculated by using the plot between $\ln (\frac{q_e}{c_e})$ versus $q_e$.

Dubinin-Radushkevich isotherm model is used to express the mechanism of adsorption onto a heterogeneous surface with an energy distribution. This isotherm model is fitted in the intermediate range of concentrations as well as solute activities. The equation for this model is,

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2$$

Here, $q_e$ is the equilibrium concentration of Chromium (VI) on the adsorbent, $q_m$ shows the saturation capacity of theoretical isotherm, $K_{DR}$ is the constant for Dubinin-Radushkevich model, $\varepsilon$ is the isotherm constant for Dubinin-Radushkevich model.

The value of epsilon ($\varepsilon$) can be derived by applying following equation.

$$\varepsilon = \frac{RT}{c_e} \ln \left(1 + \frac{1}{c_e}\right)$$

Here, $R$ is the gas constant and $T$ is the absolute temperature.
The value of $E$ can be computed by using the formula,

$$E = \frac{1}{\sqrt{2KD_R}}$$  \hspace{1cm} (14)

All isotherm models are demonstrated graphically in figure 11 and the isotherm parameters are listed in table 2. Among five isotherm models, Langmuir isotherm model ($R^2 = 0.99$) is more appropriate as compare to $R^2$ value. The Langmuir isotherm model agree to the formation of monolayer adsorption in between Chromium

---

**Table 2.** Isotherm parameters for the adsorption of Chromium (VI) on to GO-Fe$_3$O$_4$-APTES powder at room temperature ($25$ °C).

| Isotherm Model                  | $q_{max}$ (mg g$^{-1}$) | $b$ (mg g$^{-1}$) | $R^2$ |
|--------------------------------|-------------------------|------------------|-------|
| Langmuir                       | 60.53                   | 4.45             | 0.99  |
| Freundlich                     | 8.60                    | 5.88             | 0.96  |
| Temkin                         | 357.66                  | 1.56             | 0.90  |
| Dubinin-Radushkevich           | 12.94                   | 3.05             | 0.92  |
| Elovich                        | 236.57                  | 2.18             | 0.88  |

**Table 3.** Comparison of performance of proposed method with some previously reported Chromium (VI) adsorption systems.

| Adsorbent                                      | Langmuir $q_{max}$ (mg g$^{-1}$) | References |
|------------------------------------------------|----------------------------------|------------|
| Polyethylenimine facilitated ethyl cellulose   | 36.8                             | [118]      |
| Graphene oxide montmorillonite nanocomposite   | 12.86                            | [119]      |
| Magnetite polyethyleneimine-montmorillonite    | 8.8                              | [120]      |
| Activated carbon                              | 3.46                             | [121]      |
| Neurospora crassa (acetic acid pretreated)     | 15.8                             | [122]      |
| Brown coal                                    | 50.9                             | [123]      |
| Olive oil industry waste                       | 13.9                             | [124]      |
| Fucus vesiculosus (brown algae)               | 42.7                             | [125]      |
| Ulva lactuca (green algae)                    | 27.6                             | [125]      |
| Ulva spp. (green algae)                       | 30.2                             | [125]      |
| Polysiphonia lanosa (red algae)               | 45.8                             | [125]      |
| Palmaria palmate (red algae)                  | 33.8                             | [125]      |
| Saccharomyces cerevisiae                      | 32.6                             | [126]      |
| Alternanthera philoxeroides                   | 17.7                             | [127]      |
| GO-Fe$_3$O$_4$-APTES                          | 60.53                            | Present study |
(VI) on the surface of GO-Fe₃O₄-APTES. The maximum adsorption capacity \( q_m = 60.53 \) is higher than other reported adsorbent are shown in table 3. The calculated \( R_q \) value (0.011) with in the range between 0 to 1 which was shows favourable adsorption of Chromium (VI) on GO-Fe₃O₄-APTES [91]. From Freundlich isotherm model, it was observed that the value of \( l/n \) is 0.169, which is less than 1. It Shows favorable adsorption of adsorbate and adsorbent [116]. Temkin isotherm model is favourable for adsorption of Chromium (VI), because it shows smaller value of Temkin constant \( b_1 = 1.56 \) [117].

3.2.8. Influence of co-existing ion
The studies on Chromium (VI) removal were observed in the presence of different ions such as Sulphate, Phosphate, carbonate, bicarbonate, fluoride, nitrate and chloride, which is shown in figure 12. The adsorption procedure was carried out in presence of these ions keeping other parameters constant i.e. adsorbent dosage 0.3g, initial Chromium (VI) concentration 20 mg l⁻¹, pH of the solution is 3, shaking speed 160 rpm and an optimum time 10 h. About 20 ml of each anion having a concentration of 20 mg l⁻¹ was added to the polyethylene bottle and the adsorption efficiency was measured. Carbonate, fluoride and phosphate had more impact whereas nitrate, chloride, bicarbonate and sulphate had little impact on the Chromium (VI) adsorption. The more changes were observed due to change in solution pH caused by the anions. The adsorption capacity of Chromium (VI) increased in the order of chloride > nitrate > sulphate > bicarbonate > phosphate > fluoride > carbonate.

3.2.9. Reusability of adsorbent
The primary purpose of reusability is to recover the depleted material. This study is a very chief parameter to study the regeneration or effectiveness of the adsorbent. We have noticed that at lower pH maximum adsorption of Chromium (VI) occurs. Hence for the reusability study higher pH values were needed. Desorption of Chromium (VI) was carried out by washing Chromium (VI) with distilled water and various concentrations of Na₂CO₃, NaHCO₃ and NaOH. The desorption efficiency of H₂O, Na₂CO₃ and NaOH was noticed to be 1%, 83%, 74% and 92% respectively (figure S3(a)). Hence for the desorption process 0.5 M of NaOH solution was used. The plot shows desorption of Chromium (VI) having different pH conditions. Some distilled water was used in this experiment to remove undesirable ions present on the surface of the adsorbent (figure S3(b)). From the plot it was noticed that after 5 cycles, adsorption efficiency decreases up to 51%. This is shown that the reusability of the material was highly efficient.

3.2.10. Adsorption mechanism
The FT-IR peak of after adsorption of Chromium (VI) on GO-Fe₃O₄-APTES material was shown in figure S4. Comparing to the FT-IR data of before and after adsorption of chromium (VI), the N–H bending vibration was shifted from 1570 cm⁻¹ to 1577 cm⁻¹ and –CO–NH– was shifted from 1650 cm⁻¹ to 1664 cm⁻¹ with high intense peak which attributes the bonding between the nitrogen and chromium. The presence of one new peak at 943 cm⁻¹ was ascribing to stretching of Cr–O in CrO₇²⁻ groups [74]. These changes in the FT-IR spectrum after adsorption shows chromium (VI) successfully adsorb the synthesized material. The surface morphology of
GO-Fe₃O₄-APTES was aggregated after adsorption of chromium (VI) (figures S5(a), (b)). The presence of Chromium on the GO-Fe₃O₄-APTES was further confirmed by EDS analysis. Figure S5(c) shows the EDS mapping of the material after adsorption of chromium (VI). It was clearly seen the chromium adsorbed uniformly on the surface of GO-Fe₃O₄-APTES. Based on the above results, the possible mechanism for Chromium (VI) was the protonated amine groups and hydroxyl groups of GO-Fe₃O₄-APTES by electrostatic interaction (shown in scheme S1).

3.3. Antibacterial activity

Bactericidal activity of the synthesized material is dependent on the concentration of material and concentration of bacterial cell suspension [101]. Our study includes the initial bacterial load of 10⁶ cfu ml⁻¹ for interaction with GO-Fe₃O₄-APTES. Different concentration of GO-Fe₃O₄-APTES (10, 20, 40, 80, 160 μg ml⁻¹) was treated with bacteria (10⁶ cfu ml⁻¹) and bacterial growth inhibition was assessed. Disc diffusion assay reveals that the GO-Fe₃O₄-APTES shows the antibacterial activity at 160 μg ml⁻¹ and 80 μg ml⁻¹ with clear zone of inhibition at 160 μg ml⁻¹ but the zone of inhibition is not clearly visible at 20 and 40 μg ml⁻¹ against the E. coli and B. subtilis.

**Figure 13.** Image (A) shows the antibacterial activity of GO-Fe₃O₄-APTES against the E. coli at concentration 160 μg ml⁻¹ (a) with clear zone of inhibition but the zone of inhibition is not clear visible at 80, 40, 20 μg ml⁻¹ shown in (b)–(d) respectively. Image (B) shows the antibacterial activity of GO-Fe₃O₄-APTES against B. subtilis at concentration 160 μg ml⁻¹ (a) and 80 μg ml⁻¹ (b) with clear zone of inhibition but the zone of inhibition is not clear visible at 40, 20 μg ml⁻¹ shown in (c), (d) respectively. At middle shows the clear zone of inhibition for gentamicin against both the bacteria.

**Figure 14.** Shows the Concentration dependent effect of GO-Fe₃O₄-APTES, when 10, 20, 40, 80, 160 μg ml⁻¹ of GO-Fe₃O₄-APTES was incubated with E. coli and B. subtilis for 6 h. Percentage viability of bacteria at varying concentration of GO-Fe₃O₄-APTES was measured.
subtilis (figure 13). Antibacterial activity of GO-Fe₃O₄-APTES is dependent on the concentration and time of exposure with the bacteria. Assessment of bacterial growth inhibition by colony count method has suggested that the GO-Fe₃O₄-APTES shows the good antibacterial activity at 160 μg ml⁻¹ and its activity decreases gradually with decreasing concentration of the material (figure 14). Growth kinetics study of both the bacteria in the presence as well as in the absence of GO-Fe₃O₄-APTES suggested that the significant growth inhibition observed in treated one in comparison to control (figure 15). The proposed mechanism of antibacterial activity is supported by an increase in reactive oxygen species (ROS) generation at higher concentration 160 μg ml⁻¹ and it gradually decreases with decreasing concentration of the prepared material. To quantify the ROS generation the bacteria was treated with DCFDA which react with the ROS and produces the green fluorescence which is measured by the Fluorimeter (figure 16). Higher the fluorescence intensity higher is the amount of ROS generated from the bacteria in presence of GO-Fe₃O₄-APTES. ROS generated from the bacteria get mixed with the culture media which shows the fluorescence in presence of DCFDA. Bacteria show the ROS production in stress condition which could be observed in the control batch which is not treated with GO-Fe₃O₄-APTES. FESEM study also reveals the change in membrane integrity of bacteria with alteration in its morphology (figures 17 and 18).

Both gram positive and gram negative bacteria shows variation in the toxicity with respect to GO-Fe₃O₄-APTES bactericidal activity. In case of gram negative bacteria (E. coli) peptidoglycan layer is protected by an outer layer composed of lipopolysaccharide which helps to protect the bacteria from the chemical exposure [128]. Thus the bacterial death was less in E. coli in comparison to gram positive bacteria (B. subtilis). Direct contact of graphene material with the bacteria [59] increases oxidative stress [129] as the main mechanism responsible for bacterial growth inhibition and including this the iron oxide itself causes the increased oxidative
Figure 17. Antibacterial activity of GO-Fe₃O₄-APTES against *E. coli*, where (a) is FESEM image of *E. coli* and (b) is the *E. coli* treated with GO-Fe₃O₄-APTES, (c) is the EDS analysis showing the elements in bacteria and (d) is the element deposited in bacteria after GO-Fe₃O₄-APTES treatment.

Figure 18. Antibacterial activity of GO-Fe₃O₄-APTES against *B. subtilis*, where (a) is FESEM image of *B. subtilis* and (b) is the *B. subtilis* treated with GO-Fe₃O₄-APTES, (c) is the EDS analysis showing the elements in bacteria and (d) is the element deposited in bacteria after GO-Fe₃O₄-APTES treatment.
stress [130]. Increased oxidative stress is also responsible for the release of hydroxyl radical which bind to the carbonyl group of peptide linkage in the bacterial cell membrane which distorts the structure of cell membrane [131] (figure 18(b)). It is also reported that the bacterial cell membrane gets ruptured when it comes in contact with GO [132]. The GO binds to the water molecule by the help of carbonyl group and free radical sites and thus form the colloidal solution which enhances the easy accessibility of material to interact with the bacteria [133, 134].

4. Conclusion

Fe₃O₄-APTES was successfully fabricated on GO through organic transformation reaction followed by co-precipitation method. The functionalization, formation, morphology of the material, magnetic properties and surface area were characterized by FTIR, XRD, FE-SEM, TEM, HRTEM, Raman and BET technique. The synthesized GO-Fe₃O₄-APTES was identified as an efficient adsorbent for removal of hexavalent Chromium. Experimental results revealed that the removal efficiency was pH dependent and higher removal efficiency occurs at pH 3. Pseudo second order kinetics model was best fit for the adsorption process and shows chemisorptions’. Langmuir isotherm is best fit for Chromium (VI) adsorption on GO-Fe₃O₄-APTES with an adsorption capacity of 60.5 mg g⁻¹ at room temperature (25 °C). It has shown that the coexisting ions had no significant impact on adsorption efficiency. The adsorbed chromium could be effectively washed from the adsorbent in to the solution using 0.5 M of NaOH. It can be concluded that GO-Fe₃O₄-APTES material has got good reusable ability. GO-Fe₃O₄-APTES has shown inhibitory effect on the growth of E. coli and B. subtilis.

Acknowledgments

The authors are extremely grateful and sincerely acknowledge NIT Rourkela for providing the central instrumental facilities. We are also thankful to the Board of Research in Nuclear Sciences (BRNS), Government of India, for providing financial assistance. SP is thankful to MHRD for financial support. MM is thankful to (BT/PR21857/NNT/28/1238/2017) for financial support.

ORCID iDs

Harekrushna Sahoo  https://orcid.org/0000-0003-2655-1196

References

[1] Mukherjee R, Bhunia P and De S 2019 Long term filtration modelling and scaling up of mixed matrix ultrafiltration hollow fiber membrane: a case study of chromium(VI) removal J. Membr. Sci. 570–571 204–11
[2] Rashid A, Bhatti H N, Iqbal M and Noreen S 2016 Fungal biomass composite with bentonite efficiency for nickel and zinc adsorption: a mechanistic study Ecol. Eng. 91 459–71
[3] Kausar A, MacKinnon G, Alharthi A, Hargreaves J, Bhatti H N and Iqbal M 2018 A green approach for the Sr(II) removal from aqueous media: kinetics, isotherms and thermodynamic studies J. Mol. Liq. 257 164–72
[4] Gu H, Lou H, Ling D, Xiang B and Guo Z 2016 Polystyrene controlled growth of zerovalent nanoiron/magnete on a spongelike carbon matrix towards effective Cr(VI) removal from polluted water RSC Adv. 6 11013–45
[5] Gao F, Gu H, Wang H, Wang X, Xiang B and Guo Z 2015 Magnetic amine-functionalized polyacryl acid-nanomagnetite for hexavalent chromium removal from polluted water RSC Adv. 5 560208–19
[6] Kausar A, Bhatti H N and MacKinnon G 2016 Re-use of agricultural wastes for the removal and recovery of Zrt(V) from aqueous solutions J. Taiwan Inst. Chem. E 59 330–40
[7] Zhang Z, Luo H, Jiang X, Jiang Z and Yang C 2015 Synthesis of reduced graphene oxide–montmorillonite nanocomposite and its application in hexavalent chromium removal from aqueous solutions RSC Adv. 5 47408–17
[8] Costa M 1997 Toxicity and carcinogenicity of Cr(VI) in animal models and humans Crit. Rev. Toxicol. 27 431–42
[9] Nogueira A E, Giroto A S, Neto A B S and Ribeiro C 2016 CuO synthesized by solvothermal method as a high capacity adsorbent for hexavalent chromium Colloids Surf. A 498 161–7
[10] Huang Z-N, Wang X-L and Yang D-S 2015 Adsorption of Cr(VI) in wastewater using magnetic multi-wall carbon nanotubes Water Sci. Eng. 8 226–32
[11] Mulwa A M, Leswiti T Y, Onyango M S and Maity A 2016 Magnetic adsorption separation (MAS) process: an alternative method of extracting Cr(VI) from aqueous solution using polypyrrole coated Fe₃O₄ nanocomposites Sep. Purif. Technol. 158 250–8
[12] Wang J, Pan K, He Q and Cao B 2013 Polycrylonitrile/polyppyrrole core/shell nanofiber mat for the removal of hexavalent chromium from aqueous solution J. Hazard. Mater. 244–245 121–9
[13] Rodrigues L A, Maschico I J, Silva R E D and Silva M L C P D 2010 Adsorption of Cr(VI) from aqueous solution by hydrous zirconium oxide J. Hazard. Mater. 173 630–6
[14] Naeem H, Bhatti H N, Sadaf S and Iqbal M 2017 Uranium remediation using modified Vigna radiata waste biomass Appl. Radiat. Isotop. 123 94–101
[15] Zeng Y, Woo H, Lee G and Park J 2010 Removal of chromate from water using surfactant modified Pohang clinoptilolite and Haruna chabazite Desalination 257 102–9
Sankararamakrishnan N, Dixit A, Iyengar L and Sanghi R 2006 Removal of hexavalent chromium using a novel cross linked xanthated chitosan Bioreour. Technol. 97 2377–82

Wu Z, Yuan X, Zeng G, Jiang L, Zhong H, Xie Y, Wang H, Chen X and Wang H 2018 Highly efficient photocatalytic activity and mechanism of Yb(III)/Tm(III) codoped In2S3 from ultraviolet to near infrared light towards Chromium (VI) reduction and rhodamine B oxidative degradation Appl. Catal. B 225 8–21

Zheng Y, Wang X, Li W, Cao Z, Wang H, Zhang C, Song W-G, Ma Y and Yao J 2012 Cubic nickel frames: one-pot synthesis, magnetic properties and application in water treatment Cryst. Eng. Comm. 14 7616–20

Rengaraj S, Joo C K, Kim Y and Yi J 2003 Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H 1500H and IRRN97H J. Hazard. Mater. 102 257–75

Rengaraj S, Yeon K H and Moon S H 2001 Removal of chromium from water and wastewater by ion exchange resins J. Hazard. Mater. 87 273–87

Tan M, Liu X, Li W and Li H 2015 Enhancing sorption capacities for copper(II) and lead(II) under weakly acidic conditions by 1-tryptophan–functionalized graphene oxide J. Chem. Eng. Data 60 1469–75

Hałez A and Młeharawy S 2004 Design and performance of the two-stage/two-pass RO membrane system for chromium removal from tannery wastewater Desalination 165 141–51

Modrzejewska Z and Kamiński W 1999 Separation of Cr(VI) on chitosan membranes Ind. Eng. Chem. Res. 38 4946–50

Tunali S, ve K and Akar T 2005 Chromium(VI) biosorption characteristics of Neurospora crassa fungal biomass Miner. Eng. 18 681–9

Sari A, Tuzen M, zü D O U and Soyak M 2007 Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (Cladonia furcata) biomasses Biochem. Eng. J. 37 151–8

Sari A, Tuzen M and Soyak M 2007 Adsorption of Pb(II) and Cr(III) from aqueous solution on celtk clay J. Hazard. Mater. B 141 258–63

Yuusuf M, Khan M A, Otero M, Abdullaah E, Hosomi M, Terada A and Riera S 2017 Synthesis of CTAB intercalated graphene and its application for the adsorption of AR265 and AO7 dyes from water J. Colloid Interface Sci. 493 151–59

Wang H, Yuan X, Wu Y, Chen X, Leng L, Wang H, Li H and Zeng G 2015 Facile synthesis of polypropylene decorated reduced graphene oxide–Fe3O4 magnetic composites and its application for the Cr(VI) removal Chem. Eng. J. 262 597–606

Gupta V K, Agrawal S and Saleh T A 2011 Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes Water Res. 45 2207–12

Park D, Yun Y S, Lee D S and Park J M 2011 Optimum condition for the removal of Cr (VI) or total Cr using dried leaves of pinus densiflora Desalination 271 309–14

Li Z, Tang Q, Katsumi T, Tang X, Inui T and Imazumi S 2011 Leaf char: an alternative adsorbent for Cr(III) Desalination 264 70–7

Kılıç E, Font J, Pugí K and Colak S 2011 Chromium recovery from tannery sludge with saponin and oxidative remediation J. Haz. Mat. 183 156–62

Reddy K R, Park W, Sin B C, Noh J and Lee Y 2009 Synthesis of electrically conductive and superparamagnetic monodispersed iron oxide–conjugated polymer composite nanoparticles by in situ chemical oxidative polymerization J. Colloid Interface Sci. 335 34–9

Reddy K R, Lee K P and Gopalap Al 2008 Self-assembly approach for the synthesis of electro-magnetic functionalized Fe3O4/polyaniline nanocomposites: effect of dopant on the properties Colloids Surf. A 330 49–56

Reddy K R, Lee K P, Kim J Y and Lee Y 2008 Self-assembly and graft polymerization route to monodispersed Fe3O4/SiO2–polyaniline core–shell composite nanoparticles: physical properties J. Nanosci. Nanotechnol. 8 5632–9

Mi F, Chen X, Ma Y, Yin S, Yuan F and Zhang H 2011 Facile synthesis of hierarchical core–shell Fe3O4@MgAl–LDH@Au as magnetically recyclable catalysts for catalytic oxidation of alcohols Chemical Commun. 47 12804–6

Shen L H, Bao F, Wang D, Wang Y X, Chen Z W, Ren L, Zhou X, Ke X B, Chen M and Yang A Q 2013 One-step synthesis of monodisperse, watersoluble ultra-small Fe3O4 nanoparticles for potential bioapplication Nanoscale 5 2133–41

Gao M R, Jiang J and Yu S H 2012 Solution-based synthesis and design of late transition metal chalcogenide materials for oxygen reduction reaction (ORR) Small 8 1961–2124

Dong Y L, Zhang H G, Rahman Z U, Su L, Chen X J, Hu J and Chen X G 2012 Graphene oxide–Fe3O4 magnetic nanocomposites with peroxidase-like activity for colorimetric detection of glucose Nanoscale 4 3969–76

Mu J, Chen B, Guo Z, Zhang M, Zhang Z, P. Shao C and Liu Y 2011 Highly dispersed Fe3O4 nanosheets on one-dimensional carbon nanofibers: synthesis, formation mechanism, and electrochemical performance as supercapacitor electrode materials Nanoscale 3 5034–40

Wu H B, Chen J S, Hng H H and Lou X W 2012 Nanomaterial-based metal oxides as advanced anodes for lithium-ion batteries Nanoscale 4 2526–22

Patete J M, Peng X, Koenigsmann C, Xu Y, Karn B and Wong S S 2011 Viable methodologies for the synthesis of high quality nanostructures Green Chem. 13 482–519

Liu Y, Zhou L, Hu Y, Guo C, Qian H, Zhang F and Lou X W 2011 Magnetic-field induced formation of 1D Fe3O4/CaO coaxial nanochains as highly efficient and reusable photocatalysts for water treatment Journal of Materials Chem. 21 18359–64

Wang Y, Wang S, Niu H, Ma Y, Zeng T, Cai Y and Meng Z 2013 Preparation of polydopamine coated Fe3O4 nanoparticles and their application for enrichment of polycyclic aromatic hydrocarbons from environmental water samples Journal of Chromatography 20 20–6

Zhang D, Lu C, Ni Y, Xu Z and Zhang W 2013 A novel 3D chiral polyoxovanadate architecture based on breaking high symmetry of spiro[V15O36Cl]2+ cluster Crystal Engineering Communication 15 4593–6

Bhunia P, Kim G, Bask C and Lee H 2012 A strategically designed porous iron–iron oxide matrix on graphene for heavy metal adsorption Chemical Commun. 48 8988–90

A. L. H., J. H., Y. J., W. E., G. and Z. H. 2016 Aerosol–assisted in situ synthesis of iron–carbon composites for the synergistic adsorption and reduction of Cr(VI) RSC Adv. 6 56108–15

Kumar S, Umar M, Saifi A, Kumar S, Augustine S, Srivastava S and Malhotra B D 2019 Electrochemical paper based cancer biosensor using iron oxide nanoparticles decorated PEDOT:PSS Anal. Chem. Acta 1056 135–45

Zhu J, Wei S, Gu H, Rapole S B, Wang Q, Luo Z, Haldolaarachchige N, Young D P and Guo Z 2012 One-pot synthesis of magnetic graphene nanocomposites decorated with core–double-shell nanoparticles for fast chromium removal Environ. Sci. Technol. 46 977–85

Lingamdinne I P, Koduru J R, Choi Y L, Chang Y Y and Yang J K 2016 Studies on removal of Pb(II) and Cr(III) using graphene oxide based inverse spinel nickel ferrite nano-composite as sorbent Hydrometallurgy 165 64–72
[51] He C, Yang Z, Ding I, Chen Y, Tong X and Li Y 2017 Effective removal of Cr(VI) from aqueous solution by 3-amino propyltriethoxysilane-functionalized graphene oxide Colloids Surf. A 520 448–58
[52] Das M R 2011 Synthesis of silver nanoparticles in an aqueous suspension of graphene oxide sheets and its antimicrobial activity Colloids Surf. B 83 16–22
[53] Bao Q, Zhan D and Qi P 2011 Synthesis and characterization of silver nanoparticle and graphene oxide nanosheet composites as a bactericidal agent for water disinfection J. Colloid Interface Sci. 360 463–70
[54] Liu Z, Robinson J T, Sun X and Dai H 2008 PEGylated graphene oxide nanomaterials for delivery of water-insoluble cancer drugs JACS 130 10876–7
[55] Chen H, Müller M B, Gilmore K J, Wallace G G and Li D 2008 Mechanically strong, electrically conductive, and biocompatible graphene paper Adv. Mater. 20 3557–61
[56] Premnathan M, Karthikeyan K, Jayasubramanian K and Maniannan G 2011 Selective toxicity of ZnO nanoparticles toward Gram-positive bacteria and cancer cells by apoptosis through lipid peroxidation Nanomed. Nanotechnol. Biol. Med. 7 184–92
[57] Sun X, Liu Z, Welscher K, Robinson J T, Goodwin A, Zaric S and Dai H 2008 Nano-graphene oxide for cellular imaging and drug delivery Nano Res. 1 203–12
[58] Nath A, Das A, Rangan I and Khare A 2012 Bacterial inhibition by CuO/Cu2O nanocomposites prepared via laser ablation in liquids Science of Advanced Materials 4 106–9
[59] Akharov O and Ghaderi E 2010 Toxicity of graphene and graphene oxide nanowalls against bacteria ACS Nano 4 5731–6
[60] Vecitis C D, Zdowor K R, Kang S and Elimelech M 2010 Electronic-structure-dependent bacterial cytotoxicity of single-walled carbon nanotubes ACS Nano 4 5471–9
[61] Liu S, Zeng T H, Hofmann M, Burcombe E, Wei I, Jiang R, Kong J and Chen Y 2011 Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: membrane and oxidative stress ACS Nano 5 6971–80
[62] Das M R, Sarma R K, Saikia R, Kale V S, Shelke M V and Sengupta P 2011 Synthesis of silver nanoparticles in an aqueous suspension of graphene oxide sheets and its antimicrobial activity Colloids Surf. B 83 16–22
[63] Bao Q, Zhan D and Qi P 2011 Synthesis and characterization of silver nanoparticle and graphene oxide nanosheet composites as a bactericidal agent for water disinfection J. Colloid Interface Sci. 360 463–70
[64] Zhang D, Liu X and Wang X 2011 Green synthesis of graphene oxide sheets decorated by silver nanoprisms and their anti-bacterial properties J. Inorg. Biochem. 105 1181–6
[65] Fan X, Peng W, Li Y, Li X, Wang S, Zhang G and Zhang F 2008 Deoxygenation of exfoliated graphite oxide under alkaline conditions: a green route to graphene preparation Adv. Mater. 20 4490–3
[66] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V and Grigorieva I V 2004 Electric field effect in atomically thin carbon films Science 306 666–9
[67] Stankovich S, Dikin D A, Dommett G H B, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 Graphene-based composite materials Nature 442 282–6
[68] Watcharotone S et al 2007 Graphene — silica composite thin films as transparent conductors Nano Lett. 7 1888–92
[69] Wang Y, Yu S, Jin J, Wang H, Alharbi N S, Alsaedi A, Hayat T and Wang X 2016 Application of graphene oxides and graphene oxide-based nanomaterials in radionuclide removal from aqueous solutions Sci. Bull. 61 1583–93
[70] Tang B, Yuan L, Shi T, Yu L and Zhu Y 2009 Preparation of nano-sized magnetic particles from spent pickling liquors by ultrasonic-assisted chemical co-precipitation J. Hazard. Mater. 163 1173–8
[71] Safari I and Zarnegar F 2014 Ultrasonically activated efficient synthesis of chromene using amino-silane modified Fe3O4 nanoparticles: a versatile integration of high catalytic activity and facile recovery J. Mol. Struct. 1072 53–40
[72] Xu Y, Sheng K and Shi C L 2010 Self-assembled graphene hydrogel via a one-step hydrothermal process ACS Nano 4 4324–30
[73] Carvalho L A, Ardisson J D, Lago R M, Vargas M D and Araujo M H 2015 Reactive porous composites for Chromium(VI) removal applications on post-consumer PET and iron oxide RSC Adv. 5 97248–55
[74] Weckhuysen B M, Wachs I E and Schoonheydt R A 1996 Surface chemistry and spectroscopy of chromium in inorganic oxides Chem. Rev. 96 3327–49
[75] Sahoo J K, Paikra S K, Mishra M and Sahoo H 2019 Amine functionalized magnetic iron oxide nanoparticles: synthesis, activity and rapid removal of Congo red dye J. Mol. Liq. 282 428–40
[76] Verma S, Munage P I, Kumar N, Choudhary S, Jain S L, Sain B and Khatri O P 2011 Graphene oxide: an efficient and reusable carbocatalyst for azo-Michael addition of amines to activated alkenes Chem. Commun. 47 12673–5
[77] Liu M, Wen T, Wu X, Chen C, Hu J, Li J and Wang X 2013 Synthesis of porous Fe3O4 hollow microspheres/graphene oxide composite for Cr(vi) removal Dalt. Trans. 42 14710–7
[78] Mohan S, Kumar V, Singh D K and Hasan S H 2016 Synthesis and characterization of RGO/ZrO2 nanocomposite for enhanced removal of fluoride from water: kinetics, isotherm, and thermodynamic modeling and its adsorption mechanism RSC Adv. 6 87523–38
[79] Waldron R D 1955 Infrared spectra of ferrites Phys. Rev. 99 1727
[80] Ma M, Zhang Y, Yu W, Shen H, Zhang H and Gu N 2003 Preparation and characterization of magnetite nanoparticles coated by amino silane Colloids Surf. A 212 219–26
[81] Guang-She L, Li-Ping L Jr, S R L and Inomata H 2001 Characterization of the dispersion process for NiFe2O4 nanocrystals in a silica matrix with infrared spectroscopy and electron paramagnetic resonance J. Mater. Sci. 560 87–93
[82] Bruni S, Cariati F, Casu M, Lai A, Musina A, Piccaluga G and Solinas S 1999 IR and NMR study of nanoparticle-support interactions in a Fe3O4·SiO2 nanocomposite prepared by a sol-gel method NanoStructured Mater. 11 573–86
[83] Xu Z, Liu Q and Finch J A 1997 Silanation and stability of 3-aminopropyl triethoxysilane on nanosized superparamagnetic particles: I. Direct silanation J. Appl. Surf. Sci. 120 269–78
[84] White L D and Tripp C P 2000 Reaction of (3-aminopropyl)dimethylethoxysilane with amine catalysts on silica surfaces J. Colloid Interface Sci. 232 400–7
[85] Hou W, Tang B, Lu L, Sun J, Wang I, Qin C and Dai L 2014 Preparation and physico-mechanical properties of amine-functionalized graphene/polyamide 6 nanocomposite fiber as a high-performance material RSC Adv. 4 4848–55
[86] Dehghanbazi B, Aghjeh M K, Rafeie O, Tavakoli A and Oskooie A J 2016 Synthesis and characterization of graphene and functionalized graphene via chemical and thermal treatment methods RSC Adv. 6 3578–85
[87] Zhao D, Gao X, Wu C, Xie R, Feng S and Chen C 2016 Facile preparation of amino functionalized graphene oxide decorated with Fe3O4 nanoparticles for the adsorption of Cr(VI) Appl. Surf. Sci. 384 1–9
[88] Heidarizad M and Şengin S S 2016 Synthesis of graphene oxide/magnesium oxide nanocomposites with high-rate adsorption of methylene blue J. Mol. Liq. 224 607–17
[89] Yang X, Chen C, Li J, Zhao G, Ren X and Wang X 2012 Graphene oxide–iron oxide and reduced graphene oxide–iron oxide hybrid materials for the removal of organic and inorganic pollutants RSC Adv. 2 8823–6

[90] Heidarzad M and Şengör S S 2016 Synthesis of graphene oxide/magnesium oxide nanocomposites with high-rate adsorption of methylene blue J. Mol. Liq. 224 607–17

[91] Sahoo S K and Hota G 2018 Surface functionalization of GO with MgO/MgFe2O4 binary oxides: a novel magnetic nanoadsorbent for removal of Fluoride ions J. Environ. Chem. Eng. 6 2918–31

[92] Naghizadeh A and Ghafari M 2017 Synthesis and performance evaluation of chitosan prepared from persian gulf shrimp shell in removal of reactive blue 29 dye from aqueous solution (isotherm, thermodynamic and kinetic study) Iran. J. Chem. Eng. Chem. Eng. 36 25–36

[93] Kamranifar N and Naghizadeh A 2017 Montmorillonite nanoparticles in removal of textile dyes from aqueous solutions: study of kinetics and thermodynamics Iran. J. Chem. Eng. Chem. Eng. 36 127–37

[94] Derakhshani E and Naghizadeh A 2018 Optimization of humic acid removal by adsorption onto bentonite and montmorillonite nanoparticles J. Mol. Liq. 59 76–81

[95] Naghizadeh A, Momeni F, Derakhshani E and Kamranifar M 2017 Humic acid removal efficiency from aqueous solutions using graphene and graphene oxide nanoparticles Desalinat. Water Treat. 100 116–25

[96] Naghizadeh A, Ghasemi F, Derakhshani E and Shahabi H 2017 Thermodynamic, kinetic and isotherm studies of sulfate removal from aqueous solutions by graphene and graphite nanoparticles Desalinat. Water Treat. 80 247–54

[97] Naghizadeh A, Momeni F and Derakhshani E 2017 Efficiency of ultrasonic process in regeneration of graphene nanoparticles saturated with humic acid Desalinat. Water Treat. 70 290–3

[98] Yang D 2009 Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy Carbon 47 145–52

[99] Zhao D, Gao X, Wu C, Xie R, Feng S and Chen C 2016 Facile preparation of amino functionalized graphene oxide decorated with Fe3O4 nanoparticles for the adsorption of Cr(VI) Appl. Surf. Sci. 384 1–9

[100] Lin Y, Xu S and Li J 2013 Fast and highly efficient tetracyclines removal from environmental waters by graphene oxide functionalized magnetic particles Chem. Eng. J. 233 679–85

[101] Dinda D and Saha S K 2015 Sulfuric acid doped poly diamino pyridine/graphene composite to remove high concentration of toxic Cr(VI) J. Hazard. Mater. 291 93–101

[102] Wu Z, Zhong H, Yuan X, Wang H, Wang L, Chen X, Zeng G and Wu Y 2014 Adsorptive removal of methylene blue by rhombloid-fun- damentalized graphene oxide from wastewater Water Res. 67 330–40

[103] Singh D K, Kumar V, Mohan S and Hasan S H 2017 Polylysine functionalized graphene aerogel for the enhanced removal of Cr(VI) through adsorption: kinetic, isotherm, and thermodynamic modeling of the process J. Chem. Eng. Data 62 1732–42

[104] He C, Yang Z, Ding J, Chen Y, Tong X and Li Y 2017 Effective removal of Cr(VI) from aqueous solution by 3-amino propyltriethoxysilane-functionalized graphene oxide Colloids Surf. A 520 448–58

[105] Lan G, Hong X, Fan Q, Luo B, Shi P and Chen X 2014 Removal of hexavalent chromium in wastewater by polyacrylamide modified iron oxide nanoparticle J. Appl. Polym. Sci. 131 14095–55

[106] Dotto G L and Pinto L A A 2011 Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: stirring rate effect in kinetics and mechanism J. Hazard. Mater. 187 164–70

[107] Naghizadeh A 2015 Comparison between activated carbon and multiwall carbon nanotubes in the removal of cadmium(II) and chromium(VI) from water solutions AQUA 64 64–73

[108] Naghizadeh A and Gholami K 2017 Bentonite and montmorillonite nanoparticles effectiveness in removal of fluoride from water solutions J. Water Health 15 555–65

[109] Naghizadeh A and Nabizadeh R 2016 Removal of reactive blue 29 dye by adsorption on modified chitosan in the presence of hydrogen peroxide Environ. Prot. Eng. 42 149–68

[110] Pourbehram S 2016 Effective removal of heavy metals from aqueous solutions by graphene oxide–zirconium phosphate (GO–Zr–P) nanocomposite Ind. Eng. Chem. Res. 55 5608–17

[111] Wu F C, I Tseung K and Jiang R S C 2001 Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization J. Hazard. Mater. 81 167–77

[112] Chaudhari H, Dash S and Sarkar A 2017 Single-step room-temperature in-situ syntheses of sulfonic acid functionalized SBA-16 with ordered large pores: potential applications in dye adsorption and heterogeneous catalysis Ind. Eng. Chem. Res. 56 2943–57

[113] Chaudhari H, Dash S, Gupta R, Pathak D D and Sarkar A 2017 Room-temperature in-situ design and use of graphene oxide–SBA-16 composite for water remediation and heterogeneous catalysis Chemistry Select 2 1835–42

[114] Chowdhury S and Saha P 2010 Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: equilibrium, kinetic and thermodynamic studies J. Chem. Eng. J. 164 168–77

[115] Saha P D, Chakraborty S and Chowdhury S 2012 Batch and continuous (fixed-bed column) biosorption of crystal violet by Artocarpus heterophyllus (jackfruit) leaf powder Colloids Surf. B 92 262–70

[116] Kausar A, Nowaz H and Mackinnon G 2013 Equilibrium, kinetic and thermodynamic studies on the removal of U(VI) by low cost agricultural waste Colloids Surf. A 114 123–33

[117] Choy K K H, Kay G M and Porter J F 1999 Sorption of acid dyes from effluents using activated carbon Resour. Conserv. Recycl. 27 57–71

[118] Qiu B et al 2014 Polyethyleneimine facilitated ethyl cellulose for hexavalent chromium removal with a wide pH range ACS Appl. Mater. Interfaces 6 19816–24

[119] Zhang Z, Luo H, Jiang X, Jiang Z and Yang C 2015 Synthesis of reduced graphene oxide–montmorillonite nanocomposite and its application in hexavalent chromium removal from aqueous solutions RSC Adv. 5 47408–17

[120] Larrasa I, Lo pez-Go nalez M, Corrales T and Marcelo G 2012 Hybrid materials: magnetite–polyethyleneimine–montmorillonite, as magnetic adsorbents for Cr(VI) water treatment J. Colloid Interface Sci. 383 24–33

[121] Selvi K, Pattabhi S and Kadirvelu K 2001 Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon Bioresour. Technol. 80 87–9

[122] Tunali S, ve I K and Akar T 2005 Chromium(VI) biosorption characteristics of Neurospora crassa fungal biomass Miner. Eng. 18 681–9

[123] God F and Pehlivian E 2006 Chromium(VI) adsorption by brown coals Energy Source 28 447–57

[124] Malkoc E, Nuhoglu Y and Dundar M 2006 Adsorption of chromium(VI) on pomace—an olive oil industry waste: batch and column studies J. Hazard. Mater. 138 142–51

[125] Murphy V, Hughes H and McLoughlin P 2008 Comparative study of chromium biosorption by red, green and brown seaweed biomass Chemosphere 70 1128–34
[126] Zer A O and Zer D O 2003 Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto S. cerevisiae: determination of biosorption heats J. Hazard. Mater. 100 219–29

[127] Wang X S and Qin Y 2006 Removal of Ni(II), Zn(II) and Cr(VI) from aqueous solution by Alternanthera philoxeroides biomass J. Hazard. Mater. 138 582–8

[128] Chen M L, Meng Z D, Zhu L, Choi J G, Park C Y, Lee S C, Hong D S, Lee J G, Jang W K and Oh W C 2011 Dispersion stability of metal (oxide)-graphene nanofluids with electrical and thermal properties Sci. Adv. Mater. 3 887–92

[129] Chang Y, Yang S T, Liu J H, Dong E, Wang Y, Cao A, Liu Y and Wanga H 2011 In vitro toxicity evaluation of graphene oxide on A549 cells Toxicol. Lett. 200 201–10

[130] Arakha M, S P, D S, Panigrahi T K, Mallick B C, Pramanik K, Mallick B and Jha S 2015 Antimicrobial activity of iron oxide nanoparticle upon modulation of nanoparticle–bacteria interface Sci. Rep. 5 14813

[131] Valko M, Leibfritz D, Moncol J, Cronin M T D, Mazur M and Telser J 2007 Free radicals and antioxidants in normal physiological functions and human disease Int. J. Biochem. Cell Biol. 39 44–84

[132] Hu W, Peng C, Luo W, Lv M, Li X, Li D, Huang Q and Fan C 2010 Graphene-based antibacterial paper ACS Nano 4 4317–432

[133] Krishnamoorthy K, Umasuthan N, Mohan R, Lee J and Kim S J 2012 Antibacterial activity of graphene oxide nanosheets Sci. Adv. Mater. 4 1111–17

[134] Park S and Ruoff R S 2009 Chemical methods for the production of graphenes Nat. Nanotechnol. 4 217–24