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Reduced graphene oxide-metal/metal oxide composites: Facile synthesis and application in water purification

T.S. Sreeprasad¹, Shihabudheen M. Maliyekkal¹, K.P. Lisha, T. Pradeep*

DST Unit on Nanoscience, Department of Chemistry and Sophisticated Analytical Instrument Facility, HSB Block, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600 036, India

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ABSTRACT

This paper describes a versatile, and simple synthetic route for the preparation of a range of reduced graphene oxide (RGO)-metal/metal oxide composites and their application in water purification. The inherent reduction ability of RGO has been utilized to produce the composite structure from the respective precursor ions. Various spectroscopic and microscopic techniques were employed to characterize the as-synthesized composites. The data reveal that the RGO-composites are formed through a redox-like reaction between RGO and the metal precursor. RGO is progressively oxidized primarily to graphene oxide (GO) and the formed metal nanoparticles are anchored onto the carbon sheets. Metal ion scavenging applications of RGO-MnO₂ and RGO-Ag were demonstrated by taking Hg(II) as the model pollutant. RGO and the composites are found to be about an order of magnitude higher compared to parent RGO and GO for this application. A methodology was developed to immobilize RGO-composites on river sand (RS) using chitosan as the binder. The as-supported composites are found to be efficient adsorbent candidates for field application.

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1. Introduction

A great challenge for this century lies in cleaning-up the waste generated during industrial, domestic and agricultural activities. Water, an essential fluid on which all life depends, is heavily affected by such activities. Among the various contaminants found in water, heavy metals require special attention because of their toxic effect on humans and the environment, even at very dilute concentrations [1]. Technologies like adsorption, precipitation, membrane separation, amalgamation, and ion-exchange have been used to remove such contaminants from water [2]. However, adsorption is proved to be economical and efficient over other technologies, especially for removing pollutants from dilute solutions [1–3]. The efficacy and utility of adsorbents greatly depend upon the affinity of target contaminants towards the adsorbents.

Carbon is a versatile adsorbent that is heavily used in the removal of various pollutants including heavy metals from aqueous solutions [2,4-8]. Various forms of carbon and their composites have been investigated to improve the adsorption efficacy [9-12]. Graphene [13], the latest member of the carbon family is believed to

be one of the most interesting materials of this century. Graphene and its composites offers utility in several applications due to its unique two-dimensional nature and associated band structure [14-16]. Most of these composites were proposed either for catalytic or electronic applications [17-23]. The most important and widely used application of bulk carbon is in environmental remediation. Features like large surface area and presence of surface functional groups make single sheets of carbon and their composites an attractive adsorbent candidate for water purification. However, the use of graphenic materials for large-scale and down to earth applications like water purification is limited. This is mainly because of the difficulty in large-scale synthesis. The ability to make GO through chemical methods [24] and its subsequent reduction to reduced graphene oxide (RGO) opened up the possibility for the mass production of graphene in solution phase [25-27]. The properties of GO or RGO can be easily enhanced through chemical modifications. Several attempts have been made to produce GO and RGO-composites [17-23]. Recent literature suggests that RGO, GO and their composites are getting into environmental remediation [12,28-30]. RGO-magnetite and GO-ferric hydroxide composites were used for the removal of arsenic from water [28,30]. Iron based oxides and hydroxides are known to remove arsenic from drinking water [31-33]. The reports show that RGO and GO supported materials have higher binding capacity compared to free nanoparticles [28]. A study by Hu et al. also showed that RGO is antibacterial

^{*} Corresponding author. Tel.: +91 44 2257 4208; fax: +91 44 2257 0545/0509. *E-mail address*: pradeep@iitm.ac.in (T. Pradeep).

¹ These authors contributed equally to this work.

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Fig. 1. UV/vis spectra of RGO after the addition of metal ions. (A) KMnO₄, (B) Au³⁺, (C) Ag⁺, and (D) Pt²⁺. Spectral changes are marked.

[29] and this property may help in preventing the development of biofilm on the filter surface due to bacterial growth, which can cause unwanted tastes and odors or prematurely clogging of filters [34].

Important aspects to be considered for the large-scale production of RGO-composites are ease of synthesis and post synthesis purification. In most of the existing methods of composite preparation, constituents were separately prepared and mixed or external aids were employed for the production of composites, which has many limitations in large-scale synthesis. Another aspect for using such composites for application such as water purification is the ease of solid–liquid separation and post treatment-handling. Laborious processes like high speed centrifugation, membrane filtration, or magnetic separation are not practical for many end-users. A practical adsorbent material has been demonstrated here which shows that RGO-based materials are also field adaptable.

In this report, we propose a simple strategy to synthesize monodispersed and uncapped nanoparticles of silver, gold, platinum, palladium and manganese oxide on the surfaces of RGO. An in situ homogenous reduction strategy utilizing the inherent reducing properties of RGO to produce composite materials was explored, at room temperature without any external aids. The simple methodology adopted here permits to make largescale composites with good control over the particle size. The process uses the inherent reduction ability of RGO, simplifying the post-synthesis treatment and thereby increasing the viability in commercial applications. Among the materials prepared, one metal (Ag) and one metal oxide (MnO₂) based composites were selected, considering their possible utility in mitigating range of contaminants from water [3,35]. The applicability of RGO-Ag and RGO-MnO₂ were demonstrated for removing heavy metals from water. Hg(II), one of the most toxic metals found in the environment [10], was used as the model pollutant. The effects of mercury on humans and the environment have been documented [1,36]. Considering the practical difficulty in using RGO and its composites as such in water purification, a simple methodology was developed to immobilize the composites on a cheap and inert support like river sand (RS). Chitosan (Ch), an abundantly available and environment-friendly biomaterial was used as a binder for this process. The supported RGO-composites were also demonstrated for Hg(II) uptake and their applicability in the field of water purification. Various microscopic and spectroscopic techniques were used to probe the composite formation and attachment of Hg(II) onto the composites.

1.1. Preparation of various RGO-composites

GO synthesis from graphite powder was carried out based on the modified Hummers method [24,37] (Supplementary data S1a and b). The GO reduction to RGO was carried out similar to a procedure reported by Li et al. [27] (Supplementary data S1c). For making RGO-composites, 25 mL of RGO (0.01 wt%) were taken in a 50 mL beaker and calculated volumes of the metal ion precursors (KMnO₄, HAuCl₄, AgNO₃, H₂PtCl₆, PdCl₂) were added such that the final concentrations in the solution were 0.01, 0.025, 0.05, 0.1, and 0.3 mM. This was incubated undisturbed for 12 h at 30 ± 2 °C under ambient conditions. No mechanical stirring or sonication was used. Later, all the solutions were put for dialysis against distilled water. After dialysis, the samples were stored in glass bottles for further use.

1.2. Preparation of chitosan-RGO-composites@RS

In order to support RGO-composites on RS, the following protocol was adopted. Initially, the as-prepared RGO-MnO₂/RGO-Ag and chitosan solution (0.8% chitosan in 1.5% acetic acid) were mixed in 1:1 ratio. The mixture was stirred thoroughly to obtain a homogenous dispersion. 25 mL of the homogeneous dispersion was added to 10 g of RS and mixed thoroughly. The mixture was dried at 40 °C under constant stirring to ensure uniform coating. To stabilize the coating, the dried samples were soaked in ammonia solution (35%) for 1 h and subsequently washed with distilled water, until the pH of the wash water become nearly neutral. The materials were dried at 40 °C overnight and stored in glass bottles for further use.

1.3. Adsorption experiments

RGO-MnO₂ and RGO-Ag, both in supported and unsupported form, were evaluated for their utility in Hg(II) removal from water. The Hg(II) uptake capacities of various other adsorbents, including RGO, activated carbon (AC), Ag impregnated carbon (AC-Ag), MnO₂ impregnated carbon (AC-MnO₂), RS, and Chitosan (Ch) were compared with RGO-composites. For this, batch adsorption experiments were carried out in 20 mL glass bottles and the working volume was maintained as 10 mL. Homogenous adsorbent dispersions were taken in the reactor and the target pollutant was spiked into this solution to get the required concentration $(1 \text{ mg } L^{-1})$ of Hg(II). For RGO-composites immobilized on RS, 250 mg of adsorbent was weighed and added to 10 mL of 1 mg L^{-1} of Hg(II) solution. In all the experiments, solutions were kept for stirring at 30 ± 2 °C. The samples were collected at predetermined time intervals and analyzed for residual mercury. The solid-liquid separation was done either by membrane filtration or by simple settling depending upon the adsorbents employed. The filtration protocol consists of filtering adsorbent dispersion through a 200 nm membrane filter paper (Sartorius Stedim Biotech, Sartorius Biolab Products) followed by 100 nm anodized filter paper (Whatman, Schleicher and Schuell). For conducting adsorption experiments in real water, the water was simulated by spiking $\sim 1 \text{ mg L}^{-1}$ of Hg(II) into a groundwater sample collected from Kotlapalli, Puttaparthi, Andhra Pradesh, India. The water quality characteristics are given in Supplementary data S2, Table 1. The Hg(II) concentrations present in solution were determined by using a PerkinElmer 5300 DV series Inductively Coupled Plasma (ICP-AES) analyzer.

1.4. Distribution coefficient (K_d) measurements

The binding ability of a surface to an ion can be calculated from the distribution coefficient, K_d and it is a frequently used tool to compare the adsorbent performance [38,39]. It is defined as the mass-weighted partition coefficient between the liquid supernatant phase and the solid phase and can be express as:

$$K_{\rm d} = \frac{(C_{\rm i} - C_{\rm f}) \times V}{C_{\rm f} M}$$

where K_d is the distribution coefficient (mLg⁻¹); C_i is the initial concentration of the target pollutant and C_f is the final concentration of the pollutant in aqueous medium; V is the solution volume (mL), and M is the mass of the adsorbent (g).

2. Results and discussion

2.1. Characterization and mechanism of RGO-composites formation

Fig. 1 shows the UV/vis spectral (Lambda 25 Spectrometer, Perkin-Elmer, USA) changes accompanied by the addition of different metal ions to RGO suspensions. Fig. 1A shows the spectral changes observed after the addition of KMnO₄. All the spectral features are marked in the figure. KMnO₄ is known to show



Fig. 2. TEM images of $RGO-MnO_2$ (0.05 mM) at various magnifications showing nanoparticles attached to RGO. Folded RGO sheets are marked with arrows in (A).

two prominent features in the UV/vis spectrum [40,41]. The first absorption is in the visible region, situated at $17,700 \text{ cm}^{-1}$, or about 525 nm, which corresponds to yellow. The second band is at 29,500 cm⁻¹, or around 340 nm and is in the UV range [40,41]. We can see both of these bands in the UV/vis spectrum (Fig. 1A). At lower concentrations, there is no peak corresponding to KMnO₄. The graphenic peak at 270 nm as well as a broad peak characteristic of metal oxide (around 400 nm), in this case MnO₂, can only be seen. Spectral changes indicate the reduction of KMnO₄ to colloidal MnO₂ nanoparticles [42]. The KMnO₄ feature at 525 nm begins to appear when the concentration of KMnO₄ reaches 0.1 mM. It shows that at this concentration onwards, the reduction is incomplete. There is a blue shift for the graphenic peak, at higher concentration of KMnO₄ added. This blue shift is an indication of the oxidation of RGO to GO [27,43]. These results can be interpreted as the oxidation of RGO by



Fig. 3. TEM images of RGO-Ag (0.05 mM) showing well dispersed nanoparticles over a RGO sheet.

KMnO₄, which gives GO and MnO₂. The UV/vis spectra of the redoxreaction were recorded with respect to time (Supplementary data S3). There is a clear isosbestic point, emphasizing the simple redoxlike nature of the reaction. We extended the process to understand the reductive capacity of RGO with Ag. Fig. 1C shows the UV/vis spectral characteristics for the reduction of Ag⁺ by RGO. The characteristic plasmon of Ag nanoparticles around 410 nm is visible. More prominent plasmon peaks are observed at higher precursor loadings. The studies were extended to other metals such as Au³⁺, Ag and Pt²⁺ as well. RGO was able to reduce all the tested ions and showed blue shift in the graphenic peak upon increasing the concentration of the precursor ion added, pointing to oxidation of RGO [27,43].

Fig. 2 shows the TEM (JEOL JEM 3010, Japan) images taken from the sample containing 0.05 mM of KMnO₄. We can see large islands of MnO₂ nanoparticles on the RGO sheets. In Fig. 2A, folded RGO sheets can be seen on which particles are attached. The graphenic nature of the composite can be seen from the characteristic wrinkles present on the sheets [44,45] (Fig. 2, Supplementary data S4). Moreover, the edges and wrinkles were measured to be around \sim 1–1.5 nm thick, which is close to a bilayer thickness [45]. Even after the formation of the composites, the structure of the RGO sheets remained same (with wrinkles). Fig. 2B shows a higher magnification image, showing definite islands of nanoparticles of around 10 nm in size. Individual nanoparticles of smaller size regime (\sim 5 nm) can also be seen. Inset of Fig. 2B shows a lattice resolved image of the nanoparticle formed. The lattice was indexed to $\{100\}$ and $\{110\}$ planes of δ -MnO₂ with a spacing of 0.25 nm, and 0.14 nm, respectively [46,47]. Fig. 3 shows the TEM micrographs of RGO-Ag sample (0.05 mM). The large area image (Fig. 3A) shows that the particles are well separated, devoid of aggregation and in the size range of 10-15 nm. Fig. 3B shows a lattice resolved image of the nanoparticle. The {111} plane with a d-spacing of 0.235 nm [48], characteristic of cubic Ag, is marked in the figure. Typical of the nature of Ag nanoparticles, some polydispersity can be seen at places (Supplementary data S5).

The precursor concentration dependent TEM images were recorded (Fig. 4). As the concentration of added KMnO₄ increases, the density of MnO₂ islands increased (Fig. $4A_1-A_3$). In all the samples, the size of the island and the nanoparticle sizes are constant. In the case of RGO–Ag, with increase in AgNO₃ concentration, size of the nanoparticles formed also increased. Fig. $4B_1-B_3$ clearly shows this aspect. At the lowest concentration, the particle size is around 3–5 nm. As the concentration increased to 0.025 mM, the

size increased to 5–8 nm and at 0.05 mM the size was 10–20 nm. Similar observations are seen in case of all the metals studied (Supplementary data S6, S7, S8, S9 and S10).

Raman spectrum is a powerful tool for the characterization of carbon based materials. We explored our composites with Raman spectroscopy (WiTec GmbH CRM 200, Germany). The spectrum of RGO-MnO₂ showed features of RGO and MnO₂ (Supplementary data S11). The presence of Mn–O vibration at 632 cm⁻¹ confirmed the presence of MnO₂ in the composite and based on previous reports, the phase present may be δ -MnO₂ [49]. Fig. 5 shows the expanded view of the Raman spectra of the composites, in the region of characteristic D- and G-band of RGO, with different metal/metal oxide loading. In a typical synthesis, GO showed Dband at 1345 cm⁻¹ and G-band at 1598 cm⁻¹. After the reduction to RGO, the D-band remained the same but G-band shifted to lower frequency region (1580 cm^{-1}) , confirming the reduction [43,50]. The Raman spectra of the composites show interesting observations. From the spectra we can see that the D-band remained the same irrespective of the KMnO₄ concentration. However, the Gband shifted to higher frequency region with respect to RGO. As the concentration reached 0.1 mM, the G-band position is more or less similar to that of GO implying the oxidation of RGO to GO by KMnO₄ [43,50]. This confirms a redox-like reaction between RGO and KMnO₄, which results in the oxidation of RGO to GO and the reduction of KMnO₄ to MnO₂ nanoparticles. Similar observations are seen in the case of RGO-Ag composite as well. However, the extent of oxidation was lesser for the same concentration of metal content, compared to KMnO₄. This is understandable, since the reduction of Ag(+1) to Ag(0) requires only lesser number of electrons compared to the reduction of Mn(+7) to Mn(+4).

The redox reaction was characterized by XPS (ESCA Probe TPD of Omicron Nanotechnology, polychromatic Mg K α (hv = 1253.6 eV) was used as the X-ray source) as well. Fig. 6 shows the XPS spectra of sample containing different loadings of Mn. In all the samples, Mn 2p_{3/2} peak is centered around 641.8 eV while the Mn 2p_{1/2} peak is around 653.5 eV with ΔJ of 11.7 eV, indicating the reduction of KMnO₄ to MnO₂ nanoparticles [51]. As the concentration of added KMnO₄ increased, the feature of Mn(IV) in the spectra become more prominent (Fig. 6C₁–C₃). The corresponding oxidation of RGO can be seen in carbon and oxygen regions. In the first sample, the carbon spectrum is having only very less extent of oxidation (Fig. 6A₁). But, as the concentration of KMnO₄ added increased, the signatures of oxidation in the carbon also increased. In the first sample (0.025 mM), only two components are seen, the



Fig. 4. Concentration dependent TEM images of RGO-MnO₂. (A_1) 0.01 mM, (A_2) 0.025 mM, and (A_3) 0.05 mM and RGO-Ag; (B_1) 0.01 mM, (B_2) 0.025 mM, and (B_3) 0.05 mM. Insets in all figures show the lattice resolved images taken from the same sample. All scale bars in the insets correspond to 5 nm.

nonoxygenated ring C 1s (284.7 eV) and carbonyl carbon (C=O) (288.4 eV). At higher concentrations of KMnO₄, more oxygenated peaks started showing up. In the second sample (0.05 mM), three components can be seen: the non-oxygenated ring carbon at 284.7, C in C=O at 286.4 eV and the C in C=O around 288.4 eV. In the third sample (0.1 mM), four components at 284.7 (non-oxygenated ring carbon), 286.4 (C in C=O bonds), 288.4 (carbonyl carbon, C=O)

and 289.2 (the carboxylate carbon, O–C=O) are seen [26,43,52]. All the oxygenated features increased in intensity as the concentration of KMnO₄ added into RGO increased. The same trend was observed in the O 1s spectra as well. On deconvolution, each sample showed three components. First component centered around 530 eV can be ascribed to O 1s feature of metal oxide [53]. Oxygen in carbonyl (C=O) and carboxylate functionalities (O=C-OH) in GO



Fig. 5. Raman spectra of (A) RGO-MnO₂ composite and (B) RGO-Ag composite, at different loading of MnO₂ and Ag. Peak positions are marked.

are also known to give features around 530 eV [52]. The second component centered around 532 eV is due to the hydroxyl oxygen (C–OH) in GO [52]. The third component around 533 eV may be due to adsorbed water or C–O [53]. These observations indicate the redox-like nature of the process.

The RGO–Ag composite was also analyzed by XPS (Supplementary data S12). The data showed that with increase in AgNO₃ loading, more and more RGO is getting oxidized. But, similar to the observation in Raman, the extent of oxidation was much lesser compared to the RGO–MnO₂ composite, supporting our proposition (Supplementary data S12). The metal composites were analyzed by EDAX (INCA, Oxford Instruments, UK) as well.

All the EDAX spectra showed metal content and the corresponding imaging showed a uniform distribution of particles on the RGO sheets, which has a one to one correspondence with the corresponding TEM images (Supplementary data S13 and S14).

To further strengthen the involvement of RGO in reaction process and to rule out the participation of residual hydrazine, GO was reduced hydrothermally. The hydrothermally synthesised RGO [54] (RGO_H) was utilized for the formation of composite. RGO_H also shows similar UV/vis features while the formation of the composite. TEM also reveals a similar structure (Supplementary data S15). This along with other experimental evidences clearly supports the claim about the reduction ability of RGO.



Fig. 6. XPS spectra of samples containing (1) 0.025 mM, (2) 0.05 mM, and (3) 0.1 mM KMnO₄. (A) C 1s, (B) O 1s, and (C) Mn 2p regions.



Fig. 7. SEM images of (A) Ch-RGO-Ag@RS, (B) Ch-RGO-MnO₂@RS; inset in 'A' shows a SEM image of bare sand particles, (C) Raman spectrum of (a) RS, (b) Ch, (c) Ch-RGO-MnO₂@RS, and (d) Ch-RGO-Ag@RS, (D) photograph of RS, Ch-RGO-MnO₂@RS and Ch-RGO-Ag@RS.

2.2. Characterization of supported RGO-composites

Fig. 7A shows the SEM image of Ch-RGO-Ag@RS. The particles are micrometers in size and can settle easily by sedimentation. Inset photograph shows the SEM image of RS. Fig. 7B shows the SEM image of Ch-RGO-MnO₂@RS. EDAX analysis reveals the presence of Ag and MnO₂ on the surface of RS (Supplementary data S17 and S18). The presence of chitosan is confirmed by the nitrogen signal in both composites (Supplementary data S16 and S17). The supported composites were also characterized by Raman spectroscopy (Fig. 7C). All composites showed a fluorescence background, indicating the presence of chitosan. The presence of Si–O bending (440 cm⁻¹) [55,56] in all the above composites confirm the presence of SiO₂. The clear features of RGO (broad D and G band) are evident in both Ch-RGO-MnO₂@RS and Ch-RGO-Ag@RS, indicating that RGO-composites are effectively immobilized on RS surface. Characteristic Mn–O (630 cm⁻¹) [49] vibration in Ch-RGO-MnO2@RS confirms the presence of MnO2 nanoparticles in the composite. Photograph in Fig. 7D shows clear change in color after the incorporation of composites.

2.3. Affinity of various adsorbents for Hg(II) uptake

Distribution coefficient, K_d is an important parameter to compare the affinity of a pollutant to an adsorbent. It is possible to compare the effectiveness of the adsorbent by comparing the magnitude of the K_d value. Higher the K_d value, the more effective the adsorbent material is. In general, the K_d values of above $1 Lg^{-1}$ are considered good, and those above $10 Lg^{-1}$ are outstanding [38,39]. The K_d values calculated at equilibrium clearly indicate that RGO–MnO₂ and RGO–Ag, both supported and unsupported forms, are excellent candidates for Hg(II) removal (Fig. 8A and B). The RGO composites outperformed all other materials studied. The importance of RGO as a substrate is also well demonstrated. K_d values showed that these nanoparticles in the supported state in RGO-composites are 10 times better candidates. On close comparison of K_d value (without considering the weight of sand), we see that RGO-composites in the supported form are also highly efficient in removing Hg(II).

2.4. Kinetics of Hg(II) adsorption

Kinetic study was performed to understand the time dependant removal of Hg(II) by few selected adsorbents. Fig. 8C shows that all the tested materials are capable of adsorbing Hg(II). Pristine RGO and GO shows similar kinetics of removal and does not show any significant variation in equilibrium uptake capacity. Normally one would expect more Hg(II) uptake by GO due the presence of large number of functional groups compared to RGO. However, no significant variation in equilibrium uptake capacity was observed. This indicated that a special type of functional group, which is present in both RGO and GO may be responsible for Hg(II) uptake, most probably the COO⁻ group. Carboxylic acid groups are known to have an affinity to Hg(II) [57], but more investigation is required to establish the same. Compared to the parent material, RGO-composites showed higher removal kinetics.

To quantify the uptake rate, the experimental kinetics data were analyzed with well-known reaction kinetic models such as Lagergren pseudo-first-order [58,59] and Ho's pseudo-second-order [60] equations. Mathematical representations of these models are given in the supplementary data (Supplementary data S18). A non-linear approach was used to find the best-fitting model and kinetic parameters [61]. The model predicted kinetic parameters and their associated error measurements show that pseudo-first-order equation is more appropriate in predicting the experimental data (Table 2, Supplementary data S19). The pseudo-first-order model



Fig. 8. Comparison of K_d values for the adsorption of Hg(II) on (A) unsupported RGO composites with other adsorbents (B) supported RGO composite with RS, Ch, Ch@RS, (C) kinetics of Hg(II) adsorption by various adsorbents, (D) performance comparison of RGO composites for removing Hg(II) from distilled water and real water.

predicted plots with experimental data are given in Fig. 9. The corresponding data for pseudo-second-order model is depicted in Supplementary data S20.

more investigations are needed to establish the extent of Hg(II) uptake.

2.5. Effect of co-existing ions on Hg(II) removal

In order to evaluate the Hg(II) removal capability of the RGOcomposites, both supported and unsupported, in real water, a groundwater sample spiked with $\sim 1 \text{ mg L}^{-1}$ of Hg(II) was prepared and tested for uptake. Control experiments were also conducted with $\sim 1 \text{ mg L}^{-1}$ Hg(II) spiked distilled water and the results are shown in Fig. 8D. The data show that complete (below detectable limit) removal of Hg(II) happened in both the systems. The co-ions present in the real water did not affect the removal, indicating that such a system can be employed for the field application. However, 2.6. Hg(II) removal mechanism and analysis of Hg(II) loaded adsorbents

RGO-composite samples after adsorption of Hg(II) were analyzed using TEM, EDAX and XPS. We can see that the size of the nanoparticles increases on exposure to Hg(II) (Supplementary data S21 and S22). Fig. 10 shows the EDAX spectrum as well as the elemental mapping of RGO–MnO₂ after Hg(II) adsorption. The spectrum clearly shows the presence of Hg along with the principal element Mn, indicating that Hg is adsorbed on RGO–MnO₂. EDAX mapping shows similar distribution for Mn, O and Hg, emphasizing that Hg is concentrated more on manganese oxide. Similar trend



Fig. 9. Pseudo-first-order kinetic plots with experimental data for adsorption of Hg(II) by GO, RGO and RGO composites (A) unsupported and (B) supported on sand (E – experimental, P – predicted).



Fig. 10. EDAX spectrum and elemental maps of RGO-MnO₂ sample after adsorption of Hg(II).

was seen in the case of RGO–Ag composite as well. Fig. 11 shows the EDAX spectrum and the elemental maps of RGO–Ag sample after treatment with Hg(II). We see that the distribution of Ag and Hg in the sample is the same, which proves that the metal is actively involved in the removal of Hg(II) and is enhancing the activity.

From TEM and EDAX measurements, it is clear that MnO₂ and Ag play significant roles in enhancing the Hg(II) uptake capacity of RGO. However, these data reveal little information about the removal mechanism. Thus, XPS measurements were carried out and the results are shown in Fig. 12. The survey spectrum in Fig. 12A shows the presence of Hg(II) in RGO–MnO₂ and RGO–Ag. The detailed scans of Mn 2p, Ag 3d and Hg 4f regions are shown in Fig. 12B–D. Mn in RGO–MnO₂ composites shows an Mn 2p_{3/2} peak at 641.8 eV with a ΔJ of 11.7 eV, which is in agreement with Mn(IV) in MnO₂ [51]. The Mn 2p spectrum after the adsorption of Hg(II) shows no noticeable shift and matches with the binding energies of Mn 2p_{3/2} and 2p_{1/2} of pristine RGO–MnO₂.

Detailed photoelectron spectra of Ag 3d and Hg 4f in the RGO-Ag system are also shown in Fig. 12. Hg 4f showed a Hg 4f7/2 binding energy of 101.0 eV and Hg 4f_{5/2} binding energy of 105.0 eV in Hg(II) exposed RGO-MnO₂. These peaks can be assigned to mercury in Hg(II) [51]. Ag in RGO-Ag system shows peaks at 368.3 eV (3d_{5/2}) and 374.3 eV (3d_{3/2}) [51]. These peaks can be attributed to elemental Ag. No significant variation in binding energies are observed after exposure to Hg(II); the $3d_{5/2}$ and $3d_{3/2}$ photoelectron peaks are observed at 368.2 eV and 374.2 eV binding energy, respectively. The Hg 4f in Hg(II) exposed RGO-Ag shows Hg $4f_{7/2}$ and Hg $4f_{5/2}$ at 101.0 eV and 105.0 eV, respectively. This is similar to the curve of RGO-MnO₂. Though many reports exist on the possible formation Hg-Ag amalgam as the reason for mercury uptake, the current evidence shows that adsorption of Hg(II) on silver nanoparticles is the governing mechanism in Hg(II) removal. It is in agreement with the observations of Katsikas et al. [62].



Fig. 11. EDAX spectrum and the elemental maps of RGO-Ag sample after adsorption of Hg(II).



Fig. 12. XPS analysis of composites before and after treatment with Hg(II). (A) Survey spectra showing the presence of Hg after treatment, (B) Mn 2p, (C) Ag 3d, and (D) Hg 4f regions. In B and C, (a) and (b) refer to the samples before and after Hg adsorption, respectively. In D (a) and (b) refer to Hg 4f in RGO–MnO₂ and RGO–Ag, respectively. The curves have been fitted to the spin–orbit components.

3. Conclusions

A facile synthetic route for the preparation of RGO-metal/metal oxide composites is reported. The method was found to be versatile and applicable for the syntheses of variety of RGO-composites. A redox-like reaction between RGO and the metal precursor was the prime cause for the composite formation. As the metal precursors are getting reduced, RGO is getting progressively oxidized primarily to graphene oxide and the formed metal nanoparticles are closely anchored onto the sheets. The size of the formed nanoparticles can be tuned by controlling the precursor concentration added. RGO and its composites (RGO-MnO₂ and RGO-Ag) showed excellent Hg(II) uptake capacity. The composites showed enhanced removal capability compared to the parent material. A methodology was successfully developed to immobilize RGO composites on inexpensive substrates like RS and the product was found to be an effective candidate for Hg(II) removal. The reported method uses the intrinsic reduction capability of RGO without the use of any external aids, which makes this method simple and eco-friendly. Apart from water purification, these kinds of composites open up wide application possibilities in diverse fields of science and engineering such as catalysis, fuel cells.

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Appendix A. Supplementary data

Detailed procedure for GO and RGO synthesis and post synthesis treatment, table showing the water quality parameters of real water used for testing, and additional microscopic and spectroscopic characterization. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.11.100.

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