

Graphene-Based 3D Xerogel as Adsorbent for Removal of Heavy Metal Ions from Industrial Wastewater

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ABSTRACT: Graphene-based 3D porous xerogel was designed through molecular self-assembly of graphene oxide on chitosan matrix and its application in removal of different heavy metal ions from wastewater was investigated. The synthesized xerogel was characterized through FTIR, SEM, XRD and BET surface area analysis. Heavy metal ions, including Pb(II), Cd(II), and Hg(II), were removed from wastewater using this graphene-chitosan (GO-Cs) xerogel and the removal efficiency was monitored through inductively coupled plasma mass spectrometry (ICP-MS). The effect of GO-Cs composition and pH on adsorption efficiency as well as the kinetics of adsorption was studied in detail. The study exhibited that this xerogel is more suited for the removal of Pb(II) than Cd(II) and Hg(II). It was demonstrated that the large surface area and highly porous structure of this nanomaterial make it a suitable candidate for the remediation of industrial wastewater pollutants.

KEYWORDS: Graphene xerogel, nanomaterials, remediation of pollutants, adsorption, ecotoxicity

1 INTRODUCTION

Water pollution due to the indiscriminate disposal of industrial and domestic wastes poses a serious environmental hazard both nationally and internationally. Worldwide, 780 million people still lack easy access to clean potable water [1]. According to a recent report, it is estimated that around 37.7 million Indians are affected by waterborne diseases annually, with an estimated 1.5 million children dying from diarrhea alone, and 73 million working days are lost due to waterborne diseases each year [2]. Industrial sewage from common industries like chemical and fertilizer manufacturing units, as well as mining and battery manufacturing sectors, add toxic and heavy metal ions like lead (Pb), mercury (Hg), etc., into ground water [3]. Moreover, almost 80% of the water supplied for domestic use comes back as wastewater, which contains untreated metal ions [4]. The presence of such chemicals in water make it unsuitable for drinking as well as for other domestic purposes as they cause serious health hazards, including renal dysfunction, bone defects, central nervous system damage and lung diseases, etc. [5]. Most of these are

also carcinogenic in nature according to World Health Organization (WHO) specifications [5]. Moreover, their bioaccumulation at different stages in a food chain further disrupts the ecosystem [5].

As a result, removal of these heavy metals ions from water is one of the major concerns of the scientific community today. It is proposed that 4% of the common disease burden can be relaxed by proper advancement of a water supply system with sanitation and hygiene to maximize the health benefits [6].

Different physical, chemical and biological methods have been utilized for the removal of these metal ions [7–13] like semiconductor photocatalysis [8], chelating task-specific ionic liquids [10], adsorption on zeolite and cold fly ash [11], diamine-functionalized SBA-15 [9], carbon aerogel [13], to name a few. However, development of a cost-effective, large-scale and on-site removal modality is still far from reality and needs to be addressed on an urgent basis. Recently, graphene, a two-dimensional carbon allotrope-based adsorbent, has gained a lot of scientific interest due to its large surface area and adsorption potential [14]. Together with chitosan, a biocompatible and inexpensive biopolymer which has also been previously used as adsorbent [9], graphene can form a porous 3D network. Moreover, in many cases, chitosan has been reported as a skeleton for different adsorbents [15]. Herein, we report a highly porous Graphene Oxide–Chitosan

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Xerogel (GO-Cs xerogel) as a potential adsorbent for heavy metal ions (Pb, Cd & Hg). The xerogel is formed from the self-assembly of graphene oxide nanosheets and chitosan ribbons. Inductively coupled plasma mass spectrometry (ICPMS) has been used to monitor the removal efficiency of the xerogel from wastewater.

2 EXPERIMENTAL

2.1 Materials

All reagents were of analytical grade without further treatment. Distilled water was used for preparation, dilution, and analytical purposes in all experiments. The main reagents used in the experiment were: graphite powder, sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), concentrated sulphuric acid, hydrogen peroxide (H_2O_2), glacial acetic acid, chitosan powder (deacetylation > 75%, mol wt 190000–375000 Da), sodium hydroxide (NaOH), and salts of metal ions ($(\text{CH}_3\text{COO})_2\text{Pb}$, $(\text{CH}_3\text{COO})_2\text{Cd}$, HgCl_2). All chemicals were purchased from Rankem Pvt Ltd (apart from chitosan). Chitosan was purchased from Sigma-Aldrich.

2.2 Preparation of Graphene Oxide (GO)

The graphene oxide was prepared from natural graphite powder by Hummer's method. A mixture of graphite powder (3 gm, 1 wt equivalent) was mixed with NaNO_3 (0.5 wt equivalent) followed by addition of 69 ml concentrated H_2SO_4 , and the mixture was cooled to 0 °C. KMnO_4 (3 wt equivalent) was added in small portions to keep the reaction temperatures below 20 °C. Then the reaction was heated to 35 °C and stirred for 30 min. The reaction mixture gets thicker and brownish. After that, water (138 ml) was added slowly, producing a large amount of heat (exotherm). The temperature was externally stabilized to 98 °C and maintained for 15 min (no stirring). Then the reaction mixture was cooled in a water bath for 10 min. Additional water (420 ml) and 30% H_2O_2 (3 ml) were added, again causing an exothermic reaction. The solution is now a yellowish-brown color. After air cooling the mixture was centrifuged several times with HCl, water and ethanol to remove the ions and adjust the pH to neutral. Then the filtrate was vacuum dried to give GO as yellowish-brown powder.

2.3 Preparation of GO-Cs Xerogel

In this study, 2.0 wt% of chitosan solutions were obtained by mixing chitosan powder in glacial acetic acid solution and stirring overnight. Homogeneous suspension of GO (4 mg/ml) was obtained after ultrasonication of the GO powder in deionized water

for 2 hours. It is well known that mixing of GO and chitosan solutions in acidic medium leads to an immediate sharp increase in viscosity, leading to inhomogeneity of the hydrogel [16]. Thus, instead of directly mixing the GO and chitosan solution, the GO is first adjusted to a basic pH (by addition of 1M NaOH solution). Then different amounts of chitosan solution were added to the GO suspension to obtain two different hydrogels of GO:Cs mass ratio 5:1 (GO-Cs_5) and 10:1 (GO-Cs_{10}). In a few minutes the solution shows formation of viscous hydrogels which can be further stabilized by adding glacial acetic acid to the solution. Finally, the mixtures were heated to 90 °C for 24 hours to form GO-Cs hydrogels. These resulting hydrogels were freeze dried to obtain the porous graphene-chitosan xerogels.

2.4 Characterizations

The surface morphologies of GO were analyzed by Quanta 200 FEG field emission-scanning electron microscope (FE-SEM), while that of GO-Cs Xerogels were analyzed by LEO 435 VP scanning electron microscope (SEM). All samples were coated with gold to avoid the sample charging effect. The X-ray diffraction patterns of GO and GO-Cs xerogels were obtained using a Bruker DA advanced XRD equipped with $\text{Cu K}\alpha$ radiation at room temperature. The FTIR spectra were obtained using an FTIR Nicolet 6700 spectrometer at a resolution of 2cm^{-1} . The surface areas of GO-Cs xerogels were obtained with a NOVA 2200e BET surface area analyzer. The adsorbent particle size was determined by Zetasizer Nano ZS90 DLS (dynamic light scattering) set up. The metal ion concentrations were measured using the (Perkin Elmer) ELAN DRC-e ICPMS setup.

2.5 Removal of Metal Cations

To study the adsorption abilities of the prepared xerogels for the proposed metal cations, lead acetate, cadmium acetate and mercuric chloride salts were utilized. Known amounts of these salts were directly dissolved in the deionized water to obtain the test solutions. Xerogel (5 mg/10 ml) was added to each of the solutions. The following studies were performed:

1. pH-based study
2. Composition of xerogel-based study
3. Time-based study (kinetics)

All experiments were done at room temperature (25 °C). The initial concentrations of metal cations were determined to be 100 ppb each using ICP-MS set up (except the time-based study). The adsorbent particle

size was in the range 200 nm to 10 μm . The contact time for adsorption was 24 hours for all measurements apart from the time-based study (kinetics). The final concentration of metal ions was measured and the amount of adsorbed ions was obtained from the difference between initial and final concentration by the following equation:

$$\sigma = (C_o - C_e) \cdot V/m \quad (1)$$

Here σ (mmol/g) is the amount of metal ion adsorbed by the adsorbent, V (L) is the volume of the solution, m (g) is the mass of adsorbent, C_o (mmol/L) is the initial concentration of metal ion in the solution and C_e (mmol/L) is the final concentration after adsorption.

3 RESULTS AND DISCUSSIONS

The formation of graphene oxide nanosheet was monitored through field emission scanning electron microscope (FE-SEM) and XRD. Figure 1 shows the FE-SEM images of the synthesized GO. The wrinkled structure of GO nanosheets is immediately evident from the figures. Due to the electrostatic repulsion between the consecutive layers (Figure 2), it was also easily dispersed in water [17].

Figure 3 shows the XRD pattern for GO. It exhibited a strong peak at 10.75° corresponding to an interlayer spacing of about 0.82 nm. This indicates the presence of oxygen functionalities, which cause exfoliation of the sheets in water.

The GO-Cs xerogel can be easily formed by the direct mixing of GO aqueous dispersion and chitosan solution in different weight ratios. The epoxy groups in GO nanosheets form hydrogen bonds with the NH_2 groups in chitosan ribbons, resulting in the 3D self-assembly. The highly porous structure

resulting from the 3D self-assembly is shown in the SEM images of GO-Cs xerogel in Figure 4. The porous structure is further confirmed by the BET surface area measurement as shown in Table 1.

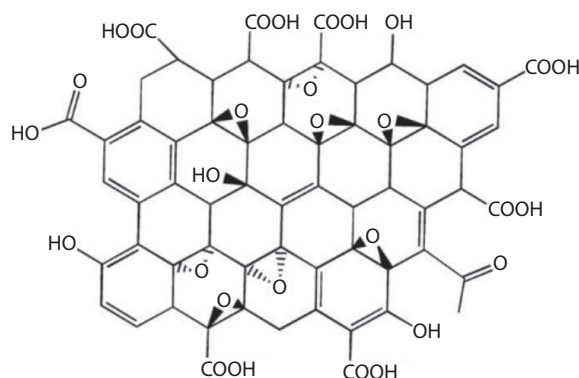


Figure 2 Structural formula of GO.

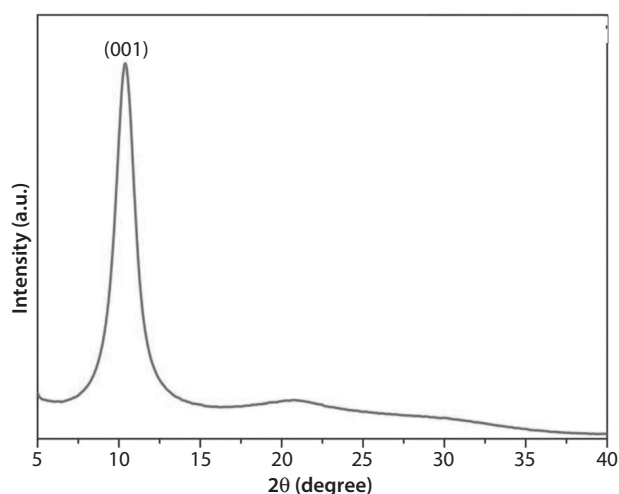


Figure 3 XRD of GO.

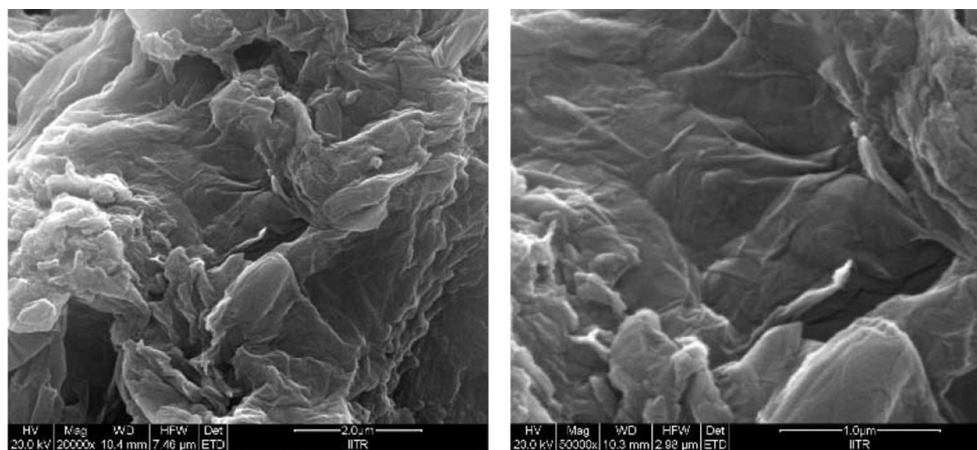


Figure 1 FE-SEM images of GO.

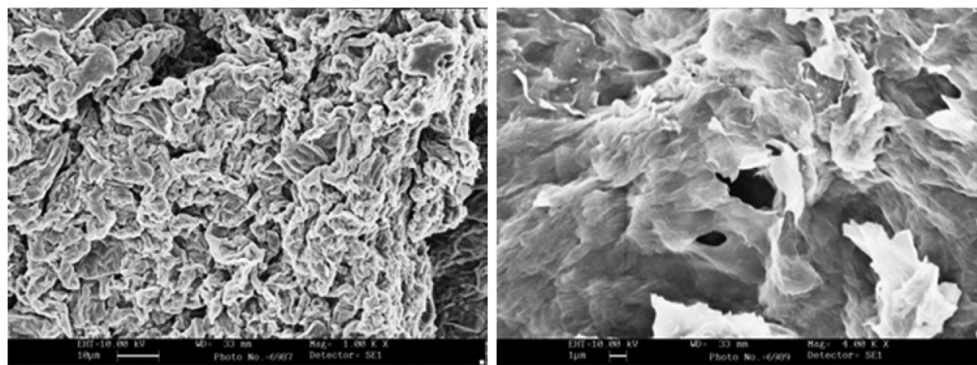


Figure 4 SEM images of GO-Chitosan xerogel.

Table 1 Different types of xerogels with obtained surface area.

Type of xerogel	Surface area
GO-Cs ₅	121.992 m ² /g
GO-Cs ₁₀	135.199 m ² /g

It is evident from the BET data that the surface area of GO-Cs₁₀ is more than the surface area of GO-Cs₅. This can be attributed to more graphene content in the GO-Cs₁₀ over GO-Cs₅.

Figure 5 shows the FTIR spectra for the GO-Cs xerogels. The spectra of both the xerogels were identical. The peaks at different intensities correspond to different stretches as 3438.60 (OH stretch, H-bonded), 2164.77 (C-triple bond-C stretch), 1646.01 (C-double bond-C), 1562.48 (C-C stretch), 1313.86 (amide stretch) and 1112.92 (C-N stretch). This is expected due to the interaction of different functional groups like -COOH, -OH, -O-, and -NH₂ of GO nanosheets with Cs. The stretch at 1021.63 results from the contribution of the absorption bands 1082 and 1032 cm⁻¹ (skeletal vibrations involving the C-O stretching), confirming the saccharide structure of chitosan. The evidence of H-bonding between GO sheets and Cs chains is also reconfirmed through FTIR.

Metal ion removal studies were performed with lead(II) acetate (Pb(CH₃COO)₂), cadmium acetate (Cd(CH₃CO₂)₂) and mercury(II) chloride (HgCl₂) metals salts with the freeze dried xerogel as the adsorbent. Here pH plays an important role in affecting the adsorption rate as the change of solution pH directly affects the available sites of the adsorbents. The initial study was done on both types of xerogel (GO-Cs₅ and GO-Cs₁₀). The pH of the solution was adjusted from 7 to 9, keeping xerogel amount fixed for these two different GO-Cs formulations. The basic pH was chosen as it is expected that in basic

medium the adsorption should increase owing to the increased negative charge of GO sheets (which will attract more metal ions) [18]. Figures 6a and 6b show the effect of pH on removal efficiency for GO-Cs₁₀ and GO-Cs₅ respectively.

As evident from the figures, the adsorption rate increased for both the xerogels when pH was increased from 7 to 9, strengthening the hypothesis that basic medium is more suited for adsorption. Thus, basic pH is favorable for removal of these heavy metals.

To study the extent of the effect of GO in the xerogel on its adsorption capacities, the xerogels of both types were added to the pollutant solution at pH 9 (more effective pH) for 24 hours (Figure 7). The retention capacity of the two types of xerogels is shown in Table 2.

Consequently, the GO-Cs₁₀ acts as a better adsorbent than GO-Cs₅ for each of the metal ions. Therefore, the metal ion adsorption capacity increases with an increase in the amount of GO in xerogel. This is as expected because in aqueous medium GO tends to develop a partial negative charge [18], while chitosan a partial positive charge [19]. The negative charge on GO attracts the metal ions into 3D pores, resulting in better adsorption. This confirms our hypothesis that chitosan acts more as a 3D skeleton than adsorbent on the xerogel.

Similarly, the effect of xerogel exposure time on metal pollutant was studied keeping pH and GO weight percent constant. The adsorption capacities with exposure time were studied at neutral pH at room temperature (25 °C) with GO-Cs₁₀ xerogel for different time intervals of 10 min, 2 h, 8 h, 16 h and 24 h. The change in concentrations with time is shown in Figure 8.

The concentrations of all the metal ions decrease gradually with time to reach the equilibrium value. The decrease is very sharp for the first 2 hours for Hg, 8 hours for Pb and gradual for Cd. The removal

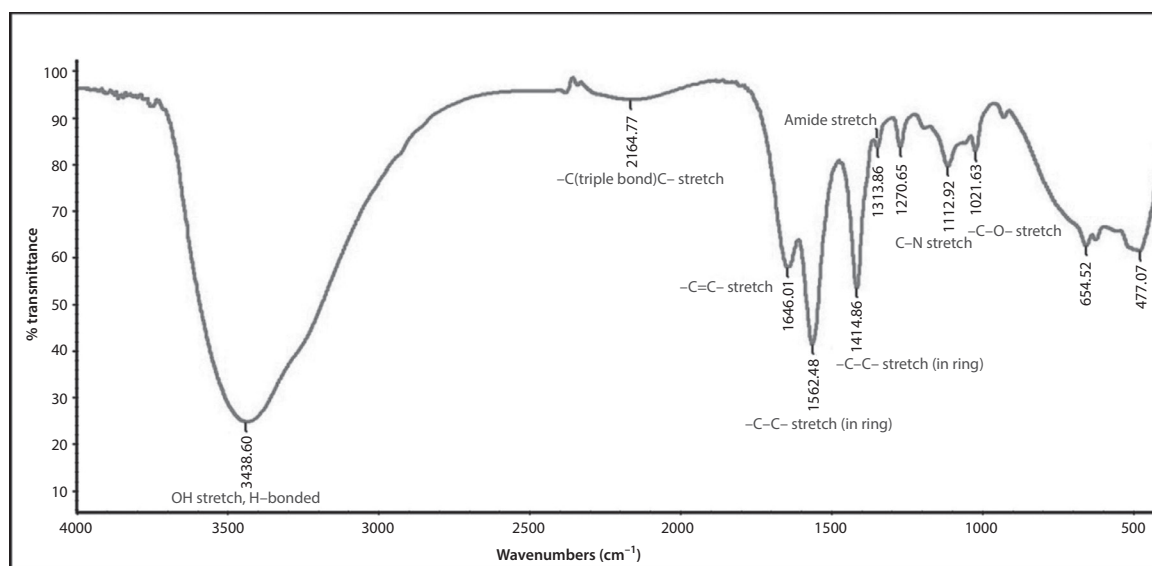


Figure 5 FTIR spectra of GO-Chitosan xerogel.

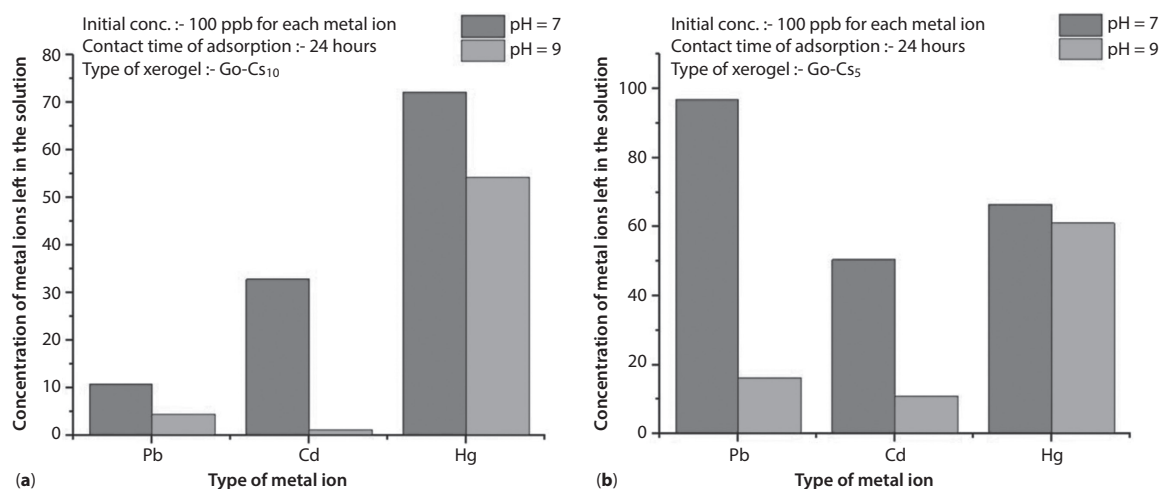


Figure 6 (a) pH-based study for GO-Cs₁₀, (b) pH-based study for GO-Cs₅.

Table 2 The retention capacity of the two types of xerogels.

Type of xerogel	Retention capacity(mg/g)		
	Pb	Cd	Hg
GO-Cs ₅	37.29	34.74	16.14
GO-Cs ₁₀	40.92	39.57	18.93

is most efficient in the case of Pb, followed by Cd and Hg respectively. This can be attributed to the higher electronegativity and larger size of Pb(II) cation as compared to others. Pb(II) can easily be bound in xerogel pores, resulting in better adsorption.

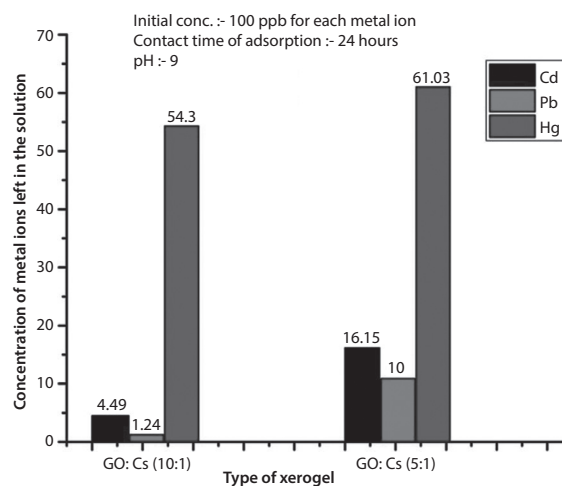


Figure 7 Composition of xerogel-based study.

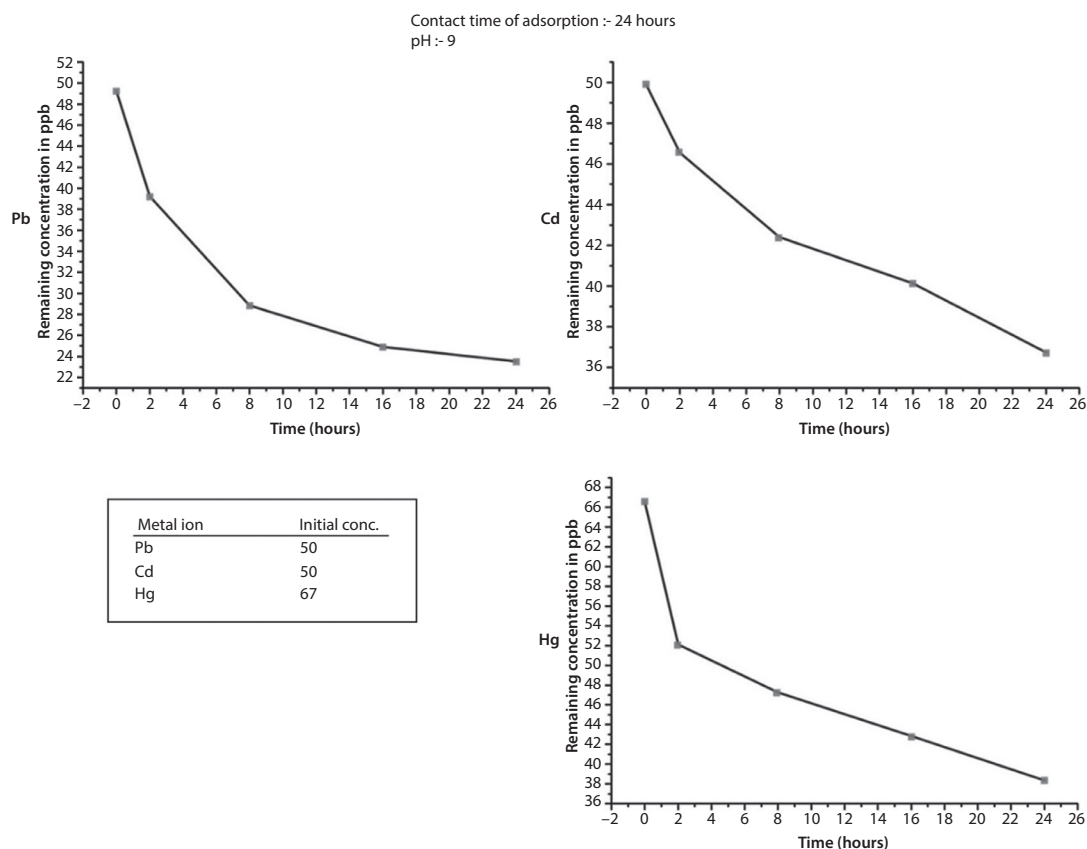


Figure 8 Kinetics of adsorption by GO-Cs10.

4 CONCLUSION

Graphene Oxide–Chitosan (GO-Cs) xerogels were prepared from graphene oxide sheets by incorporation of chitosan ribbons. The strong hydrogen bonds between GO and Cs result in the highly porous 3D self-assembly. Chitosan provides the skeleton while GO works as the prime adsorbing component. Consequently, these xerogels exhibit high adsorption capacity for the heavy metal ions, namely, Pb (40.92 mg/g), Cd (39.57 mg/g) and Hg (18.93 mg/g). The adsorption is more prominent at basic pH than at neutral pH and also the prime component for adsorption is GO. The kinetics showed that for all three cations the adsorption isotherms reached equilibrium (at considerably low values) within 24 hours. Thus, we believe that these xerogels will emerge as one of the most promising low-cost candidates for water purification.

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