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Synthesis and characterization of reduced graphite oxide-polymer composites and their application in adsorption of lead

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Abstract

Herein, we report the in-situ polymerization of 1,5-diaminonaphthalene (15DAN) and 1,4-diaminoanthraquinone (14DAA) on the surface of reduced graphite oxide (RGO). Synthesized RGO-P15DAN and RGO-P14DAA were characterized by FTIR, Raman, SEM, TGA and XRD. The adsorption capacity and adsorptivity of the synthesized composites were investigated by Atomic Absorption Spectroscopy (AAS) using 100ppm aqueous solution of Pb^{2+} ions. Further, we compared the results of the composites with those of poly 1,5-(diaminonaphthalene) (P15DAN), poly 1,4-(diaminoanthraquinone) (P14DAA), RGO, graphite oxide (GO) and graphite. Among the tested adsorbents, RGO-P15DAN demonstrated the high adsorptivity.

Graphical abstract

Herein, we report the *in-situ* polymerization of 1,5-diaminonaphthalene (15DAN) and 1,4-diaminoanthraquinone (14DAA) on the surface of reduced graphite oxide (RGO). Further, the adsorption capacity and adsorptivity of the synthesized composites were investigated by Atomic Absorption Spectroscopy using 100ppm aqueous solution of Pb^{2+} ions.

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Keywords

Reduced graphite oxide; poly 1, 5-(diaminonaphthalene); poly 1, 4-(diaminoanthraquinone); Lead; Adsorption

Introduction

Water pollution has been a critical issue for over a decade due to over exploring of natural resources and uncontrolled release of toxic pollutants such as heavy metal ions, organic dyes, herbicides, pesticides etc. [1]. These toxic pollutants, particularly heavy metals pose severe threats to ecological balance and human health [2]. Among the heavy metals, lead (Pb) has particular importance due to its non-repairable harmful effects [2–3]. Low level of Pb could cause kidney damage and nervous system damage, while high levels of lead can cause high blood pressure, muscle and joint pain, harm to fetus, and fertility problem in both men and women [1–3].

Adsorption process is one of the most efficient and economic method for purification of water due to the reversible nature of the process [4]. Over the past decades, commonly used adsorbents for the removal of heavy metal ions include activated carbon [5], zeolites [6] and clays [7]. Recently, graphene oxide (GO) and reduced graphene oxide (RGO) have been studied as adsorbents for the removal of heavy metals due to the presence of many functional groups such as –O–, –OH, and –COOH, which can form complexes with metal ions [8–10]. Graphene quantum dots have also been demonstrated as a probe to sense Hg^{2+} [11]. In our previous report, we demonstrated that adsorption efficiency of over 90% can be achieved for Pb^{2+} ions in an aqueous solution containing 100ppm Pb^{2+} [9]. Zheng et. al, also demonstrated the adsorption of Pb^{2+} ions from aqueous solution over low-temperature exfoliated graphene nanosheets [10]. In addition, RGO and RGO functionalized with metal oxides, such as Fe_3O_4 [12], MnO_2 [13], Al_2O_3 [14], TiO_2 [15] and ZnO [16], have also demonstrated the ability to reduce and remove heavy metal ions in aqueous solution. Siddhardha et. al., demonstrated the importance of the high surface area of graphene. They reported that the high surface area of graphene enhanced the catalytic activity of Au nanoparticles to decolorize dyes [17].

On the other hand, conducting polymers have been widely investigated in the past five decades but focus has been given to their potential applications in nanoelectronic devices, energy conversion and storage devices, sensors, catalysis, electrochromic devices, actuators and biomedicines [18–20]. Interestingly, amine ($-\text{NH}_2$) and imino ($-\text{NH}$) containing conducting polymers can also be exploited as adsorbent for use in remediation of water and removal of heavy metals from polluted water. This takes the advantage of the complexing ability and high sensitivity of amines to the metal ions, including Ag^+ , Cu^{2+} , Hg^{2+} , Pb^{2+} , VO^{2+} , and Cr^{3+} . The widely studied conducting polymers for adsorption of heavy metals includes polyaniline [21,22], polypyrrole [23,24], polythioamides [25], and polyethyleneimine [26]. However, very little information is available in the literature on adsorption capability of polymers derived from aromatic diamines, such as diaminonaphthalene and diaminoanthraquinone. These polymers are capable of chelating to

heavy metals exists in polluted water. It has been reported that poly 1,5 diaminonaphthalene (P15DAN) is one of the polymers, which capable of chelating metal ions with an extra free amine group with the other amine group used for coupling with another monomer unit [27]. Palys *et al.* also demonstrated the removal of heavy metal ions such as Ag^+ , Cu^{2+} , Hg_2^{2+} , and Hg^{2+} using P15DAN films [28].

Recently, organic-inorganic hybrid polymers have been found promising candidates for removal of toxic contaminants of wastewater [4]. This kind of materials often provide the best properties of each of its components in a synergic way and have high performances of physical, chemical and mechanical properties [29]. Additionally, these functionalized hybrid polymeric materials can chemically bond to metal ions more effectively compared to individual polymer or adsorbents [4, 26–29]. Therefore, we believe functionalization of RGO with conducting polymers such as poly 1,5-diaminonaphthalene (P15DAN) and poly 1,4-diaminoanthraquinone (P14DAA) will result in strong binding affinities towards Pb^{2+} ions owing to complexing ability of the polymers and high surface area of RGO. In addition, both P15DAN and P14DAA have capability of in-situ reduction of GO to RGO. It has been reported that GO and RGO modified with polymers and organic molecules have also demonstrated good adsorption to heavy metal ions [23]. For instance, polypyrrole-RGO composite can adsorb Hg^{2+} ions selectively, with the adsorption capacity of 0.98 g g^{-1} [23,24]. Li *et al.* [18] synthesized a hierarchical nanocomposite by the polymerization of pyrrole arrays on the surface of graphene oxide nanosheets and used it as a superadsorbent for the adsorption of Cr(VI) oxyanion from water.

Owing to this, in this study, we report the polymerization of 1,5 diaminonaphthalene (15DAN) and 1,4 diaminoanthraquinone (14DAA) on the surface of RGO. The synthesized composites, RGO-P15DAN and RGO-P14DAA, were characterized by FTIR, RAMAN, SEM, TGA and XRD. In addition, we investigated the adsorption efficiency of the synthesized RGO composites with P15DAN, P14DAA and GO using 100ppm aqueous solution of Pb^{2+} ions.

Materials and methods

All the reagents were purchased from Aldrich and used without further purification unless otherwise noted. All the aqueous solutions were prepared with ultrapure water obtained from Milli-Q Plus system (Millipore).

Preparation of graphite oxide and reduced graphite oxide (RGO)

Graphite oxide was prepared from graphite powder according to the Hummers method and as detailed in reference [9]. Reduced graphite oxide was prepared by chemical reduction of GO using NaBH_4 . Then, 0.3g of GO was dispersed in 50ml of deionized water and 0.5g NaBH_4 was added to the mixture, and refluxed at 100°C for 24 h. After the reaction was completed, the mixture was centrifuged and repeatedly washed with DI water. Thus obtained product was dried in vacuum at 60°C .

The synthesis of Poly 1,5-diaminonaphthalene (P15DAN) and Poly 1,4-diaminoanthraquinone (P14DAA) and their deposition on reduced graphite oxide (RGO) have been carried out according to procedure provided in supplementary section.

Characterization

The FTIR spectra of the products in KBr were obtained using thermo-Nicolet IR 200 spectrometer and TGA were performed on a TA instruments TGA Q500 at a heating rate of 10°C/min under flowing nitrogen. Powder XRD patterns were recorded using Scintag X-ray diffractometer (PAD X), equipped with Cu K α photon source (45kV, 40mA) at a scanning rate of 3°/min. SEM measurements were carried out on a JEOL JXA-8900 microscope and Raman analysis was performed by a Renishaw R-3000QE system at room temperature in the backscattering configuration using an Argon ion laser at a wavelength of 785 nm. The concentrations of Pb remained in solution was measured using the Varian spectra AA 220FS atomic absorption spectrometer operated with an air–acetylene flame at the wavelengths 217nm.

Adsorption study of Pb

To determine the sorption capacity of Pb, 40mg of the adsorbents were stirred separately with 25 ml of 100ppm Pb²⁺ solution for 2hr at room temperature and the solution was centrifuged and filtered to remove the adsorbents. Then the filtrates were subjected to atomic absorption spectrophotometry analysis (AAS) to determine the concentration of Pb²⁺ and thereafter, sorption capacity q (mg/g) was obtained using the equation: $q = [(C_o - C_f)V/m]$, where C_o and C_f are the initial and final concentrations in mg/L of metal ions in the aqueous solution, respectively, V is the volume of metal ion solution in liters, and m is the mass of sorbent in grams.

Results and discussion

The FTIR spectrum of GO (Fig. 1b) displayed the well resolved characteristic bands. The absorption peaks displayed at 1721, 1224 and 1384cm⁻¹ are assigned to C = O stretching of -COOH groups, epoxy symmetrical ring deformation vibrations and tertiary C–OH groups vibrations, respectively [9]. The band at 1623cm⁻¹ is ascribed to C=C aromatic vibrations and the band at 1057cm⁻¹ is assigned to C–O stretching vibrations mixed with C–OH bending [9, 30]. The peak at 3390cm⁻¹ is attributed to O–H stretching vibrations [30]. In the spectrum of RGO (Fig. 1a), the characteristic features of GO are almost disappeared showing the successful conversion of GO to RGO. The peak at around 3123cm⁻¹ in Fig. 1a is attributed to residual O–H stretching vibration and the new peak which appeared at around 1565cm⁻¹ is assigned to the skeletal vibration of the RGO sheets [31]. Fig. 1c shows the IR spectrum of 15DAN monomer, which displayed the characteristic peaks at 3416 and 3319cm⁻¹ and are ascribed to N–H stretching of the primary amino groups [32], these dual bands have turned into a single broad weak resolved band in the spectrum of P15DAN (Fig. 1d), and is centered around 3420cm⁻¹, which is ascribed to the N–H stretching vibration of secondary amino groups. This suggests that most of the free –NH₂ groups of 15DAN are converted to –N–H– groups or –N= groups after polymerization [33]. The decreased intensity in Fig. 1d might be due to decreased number of hydrogen atoms in P15DAN. In addition, the

peaks around 2922 and 2855 cm^{-1} in Fig 1c are assigned to the protonated species of the secondary amino and imino groups (NH_2^+ and $\text{C}=\text{NH}^+$), respectively [34]. The spectrum of RGO-P15DAN (Fig. 1e) displayed all the characteristic peaks found in the spectrum of P15DAN (Fig 1d) and RGO (Fig. 1a) except the broad peak around 3123 cm^{-1} related to O-H stretching. This suggests existence of strong interaction between the protonated terminal amino groups of P15DAN and the hydroxyl groups and/or carboxylic groups of RGO in RGO-P15DAN composite. In the spectrum of 14DAA (Fig 1e), the broad peaks centered around 3550 and 3700 cm^{-1} can be ascribed to the N-H stretching of primary amines in 14DAA. The peak at 1590 cm^{-1} corresponds to quinone carbonyl and the peaks around 1650 cm^{-1} corresponds to C=C stretching of aromatic [35]. The spectrum of RGO-P14DAA (Fig. 1g) displayed all the characteristic peaks found in the spectrum of P14DAA (Fig. 1f) and RGO. The broad O-H stretching peak around 3123 cm^{-1} of RGO has disappeared in the spectrum, which suggest the successful formation of RGO-P14DAA composite.

The Raman spectra of GO, RGO, RGO-P15DAN and RGO-P14DAA are presented in Figs 2a–d. The spectra of GO (Fig 2b) shows two prominent peaks at 1355 cm^{-1} (D-band) and 1589 cm^{-1} (G-band). The G-band is attributed to in-plane vibration of sp^2 bonded carbon atoms [36] while the D-band is associated with the presence of defects in the hexagonal graphitic layers [37]. After reduction of GO to RGO (Fig. 2a) using NaBH_4 , an increase in the intensity of the D/G ratio was observed. In addition, in Fig. 2a both D and G-bands have shifted to 1340 cm^{-1} and 1585 cm^{-1} respectively. These changes indicate the successful reduction of GO to RGO [38]. The spectra of RGO-P15DAN (Fig 2c) and RGO-P14DAA (Fig 2d) also show a shift in the G-band from 1589 cm^{-1} (in GO) to 1565 cm^{-1} and to 1569 cm^{-1} for RGO-P14DAA and RGO-P15DAN respectively. Moreover, the intensity ratio of D/G increased from 1.06 (for GO) to 1.12 for RGO-P14DAA and to 1.13 for RGO-P15DAN. This increase in intensity ratio of D/G implies the decreased size of sp^2 domains after chemical reduction to RGO [39].

TGA analysis (Fig 3e) of GO shows a mass reduction around 100°C, which can be attributed to loss of water. The major mass reduction around 200°C was caused by the pyrolysis of the oxygen-containing functional groups, generating CO, CO_2 and steam [31]. RGO (Fig. 3d) showed an enhanced thermal stability compared to GO. The weight loss exhibited by RGO between 580° and 700°C is attributed to the decomposition of RGO nanosheets [31]. The profile of both P14DAA (Fig. 3a) and P15DAN (Fig. 3c) show enhanced thermal stability compared to their monomers, 14DAA and 15DAN, respectively. The drastic reduction in the mass of 15DAN (Fig. 3f) and 14DAA (Fig. 3d) observed around 186 and 268°C respectively, correspond to the melting point of 15DAN and 14DAA.

The XRD pattern of GO (Fig. 4a) shows a characteristic peak at $2\theta=11.5^\circ$ which corresponds to (001) reflection of stacked GO nanosheets [29]. The pattern of RGO (Fig. 4b) shows two characteristic peaks at $2\theta=24.5^\circ$ and 43.0° which are ascribed to (002) and (100) reflection of stacked RGO nanosheets [31]. This confirms the successful reduction of GO to RGO in presence of NaBH_4 . The patterns for P15DAN (Fig. 4d) and P14DAA (Fig. 4f) displayed high intense peaks, which signify high crystalline nature of polymer matrix. This crystallinity is well maintained in the RGO-P15DAN (Fig. 4c) and RGO-P14DAA (Fig. 4e) composites also. In addition, almost disappearance of the characteristic diffraction

peaks of RGO at 24.5° and 43.0° have been observed in Figs. 4c and e. This can be ascribed to the inability of the RGO planes to form regular stacks due to high crystalline polymers [4, 36, 38].

The SEM images of GO, RGO, RGO-P15DAN and RGO-P14DAA are shown in Fig. 5. A visible difference has been observed in the images of GO, RGO, RGO-P15DAN and RGO-P14DAA composites. The images of RGO (Fig. 5c–d) consist of many stacked layers of RGO sheets. Fig 5e–h shows the morphology of RGO-P15DAN and RGO-P14DAA composites. The surface of RGO-P15DAN (Fig. 5e–f) and RGO-P14DAA (Fig. 5g–h) have rough surface compared to RGO. For RGO-P15DAN however, the polymer appears more like an interconnected threadlike structures on the surface of stacked RGO and some nanospheres-like structures were observed, which is consistent with literature reported for P15DAN [33]. For RGO-P14DAA, the polymer appears like nanospheres on the surface of the RGO with little threadlike structure.

Further, the adsorption capacity and adsorptivity of RGO-P15DAN and RGO-P14DAA have been estimated and those were compared with graphite, GO, RGO, P15DAN and P14DAA. Table 1 shows the adsorption capacity and adsorptivity of the different sorbents in 100ppm of Pb²⁺ solution. It was observed that P15DAN shows greater affinity for Pb²⁺ ions compared to P14DAA under identical conditions. Similar trend was observed with RGO-P15DAN and RGO-P14DAA. However, the result showed that the RGO has greater affinity in presence of P14DAA compared to P15DAN. As expected, low adsorptivity was observed for RGO, compared to GO. This can be ascribed to loss of functional groups following by reduction of GO to RGO. It has been reported that adsorption involve the strong surface complexation of metal ions with the oxygen-containing functional groups on the surface of GO [3,33]. Oxidation of graphite to GO introduces many oxygen-containing functional groups which increases the hydrophilicity of the carbon surface [9]. Hence, an increase in the adsorption ability of GO has been observed compared to RGO and graphite.

Conclusions

In conclusion, P15DAN, P14DAA, RGO-P15DAN and RGO-P14DAA were prepared and successfully applied for the removal of Pb. Combination of RGO with P15DAN and P14DAA having strong complexation ability would enhance adsorptive power of RGO-P15DAN and RGO-P14DAA. Hence, RGO-P15DAN and RGO-P14DAA hybrids can provide a good platform for removal of harmful heavy metal such as Pb present in contaminated water.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

1. In-situ reduction to reduced graphite oxide.
2. Promising candidates for removal of Pb.
3. High capability of adsorption of Pb.
4. Study of absorption of Pb using AAS.

Fig. 1.
FTIR spectra of (a) RGO (b) GO (c) 15DAN (d) P15DAN (e) RGO-P15DAN (f) 14DAA (g) P14DAA and (h) RGO-P14DAA.

Fig. 2.
Raman Spectra of (a) RGO (b) GO (c) RGO-P15DAN and (d) RGO-P14DAA.

Fig. 3. TGA profiles of (a) P14DAA (b) 14DAA (c) P15DAN (d) RGO (e) GO and (f) 15DAN.

Fig. 4. XRD patterns of (a) GO (b) RGO (c) RGO- P15DAN (d) P15DAN (e) RGO-14DAA and (f) P14DAA.

Fig. 5.
SEM images of (a) and (b) GO; (c) and (d) RGO; (e) and (f) RGO-P15DAN; (g) and (h) RGO-P14DAA.

Table 1

Adsorption capacity and adsorptivity of different sorbents using 100ppm of Pb^{2+} solution.

Adsorbent	$[\text{Pb}^{2+}]$ after 2 hr of adsorption (mg/L)	Adsorption capacity, Q	Adsorptivity, q (%)
Graphite	81.08	0.0116	18.92
GO	9.23	0.0563	90.77
P15DAN	10.65	0.0549	89.35
RGO-P15DAN	8.14	0.0564	91.86
RGO	18.00	0.0510	82.00
P14DAA	62.03	0.0233	37.97
RGO-P14DAA	25.39	0.0463	75.61