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Adsorption of lead over Graphite Oxide

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Abstract

The adsorption efficiency and kinetics of removal of lead in presence of graphite oxide (GO) was determined using the Atomic Absorption spectrophotometer (AAS). The GO was prepared by the chemical oxidation of graphite and characterized using FTIR, SEM, TGA and XRD. The adsorption efficiency of GO for the solution containing 50, 100 and 150 ppm of Pb²⁺ was found to be 98, 91 and 71% respectively. The adsorption ability of GO was found to be higher than graphite. Therefore, the oxidation of activated carbon in removal of heavy metals may be a viable option to reduce pollution in portable water.

Keywords

Graphite oxide; Lead; Adsorption; Graphite

1. Introduction

Today, one of the most important environmental issues is ground water contamination [1], arising primarily from humans and animals as well as other biological activities [2]. Among the wide diversity of contaminants affecting water resources, heavy metals are particular concern because of their toxicities in relatively low concentrations and tendency towards bioaccumulation [3-5]. Heavy metal pollution is associated with the areas of intensive industry and industrial waste water are main pollutants of ground waters.

Hydrometallurgical, electroplating, tanning, artificial fertilizers and herbicides production as well as dyeing, textile, electrochemical, motor, energetic industries are considered to be largest sources of heavy metals in waste water [6]. The industrially generated waste water mainly contains heavy metals such as Cr(III,VI), As(III,V), Cd(II), Pb(II), Cu(II), Zn(II) and Hg(II), which are particularly dangerous for the environment and living organisms. Among these, Pb (II) is particularly emphasisable due to its non-repairable harmful effect. For instance low level of lead could cause kidney damage and nervous system damage, while its high level can cause high blood pressure, muscle and joint pain, harm to fetus, and fertility problem in both men and women.

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Currently various methods are available for removing the heavy metals such as reduction, adsorption, ion exchange, evaporation, reverse osmosis, precipitation and co-precipitation/adsorption [6,7]. However, most of these methods have their own drawbacks like high capital and operational cost and problems in disposal of residual metal sludge [7]. Now a day, sorption of heavy metal ions onto different solid supports such as ion exchange resins, activated charcoals, zeolites, and ion chelating agents immobilized on inorganic supports is the most common route applied for decontamination of wastewater and industrial effluents. The employed sorbent is highly effective, economical [8, 9] and can be easily regenerated. Moreover, solid sorbents can be easily incorporated into automated analytical procedures for determination of trace metal ions in natural waters [10]. Therefore, efforts dedicated to exploring new effective sorbents have continued to grow.

The carbonaceous materials have been proved to be effective sorbents for removal of metal ions as well as their complexes because of their high sorption capacity which is linked to their well developed internal pore structures, a large specific surface area, and the presence of a wide variety of surface functional groups [11-13]. Activated carbon (AC) is a common sorbent consisting of graphene sheets randomly substituted with hetero-atoms. The characteristics of the obtained AC depend particularly on the precursor and the activation technique employed in its preparation process [12,13]. Amongst the characteristics of sorbents that make them effective in the removal of heavy metals and complexes in waste water, their polar nature and high surface energy which are responsible for their ability to form a strong adhesive force between their surface and that of the polar substances are of great importance.

Recent reports show that oxidation treatment of a carbon surface can introduce many functional groups and increase its hydrophilicity [14-16]. In particular, oxygen-containing groups can improve the adsorption capability of metal ions [17], so that oxidation of graphite to graphite oxide (GO) can help to introduce the required functional groups that could enhance the removal capability of metal ions and their complexes from water. Further, GO can be recycled and reusable. In consideration of the mentioned benefits, in this paper, graphite oxide was prepared and studied its adsorption efficiency at different concentrations of lead and compared with sorption rate of graphite. Prior to adsorption study the GO was characterized using FTIR, RAMAN, SEM, TGA and XRD.

2. 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).

2.1. Preparation of Graphite Oxide

Graphite oxide (GO) was prepared from graphite according to the Hummers method [18]. In detail, graphite powder (1.0 g), NaNO_3 (0.5 g) and KMnO_4 (3.0 g) were slowly added to concentrated H_2SO_4 (23 mL), which was cooled by ice bath and the mixture was vigorously stirred at room temperature for 2 hr. After DI water (46 mL) was added and the temperature of the mixture was stirred at 98 °C for 30 min. Then the temperature of the mixtures was

reduced to 60 °C by addition of more water (140 ml). This follows the addition of H₂O₂ (30%, 10 ml) and the reaction was further stirred for 1 hr. Thus obtained GO separated by centrifugation and washed with 4% HCl solution (5 times). Further it was washed with DI water (3 times). Finally, the resulting GO was dried in vacuum at 45°C.

2.2. Characterization

FTIR spectrum was recorded using Thermo-Nicolet IR 2000 spectrometer and the 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. TGA was performed with a TGA Q500 instrument under nitrogen environment at a heating rate of 10 °C/min. Powder XRD patterns were recorded on scintag X-ray diffractometer (PAD X), equipped with Cu K α photon source (45kV, 40mA) at scanning rate of 3°/min. SEM measurements were carried out with a JEOLJXA-8900 microscope and adsorption capability was studied using a Varian spectraAA 220FS atomic absorption spectrometer operated with an air–acetylene flame at the wavelength of 217nm.

2.3. Adsorption of Lead

40 mg of GO was added to 25 mL of Pb²⁺ solution and the mixture was stirred for 2 hr at room temperature. Then, the GO was separated by filtration and the filtrate was subjected to AAS analysis to calculate the amount of Pb²⁺. Further the adsorption capacity q(mg/g) was obtained according to the equation: $q = [(C_o - C_f)V/m]$, where C_o and C_f are the initial and final concentrations (mg/L) of Pb²⁺ ions in the aqueous solution, respectively, V is the volume of Pb²⁺ ion solution, and m is the mass of sorbent.

2.3. Kinetic studies

GO (80 mg) was added to 50 mL aqueous solution of Pb²⁺ (100 ppm) and stirred at room temperature. Then the adsorption rate of Pb²⁺ was determined by estimation of the concentration of Pb²⁺ at each 20 min of interval for 3 hr. The concentrations of Pb²⁺ remained in the solution was measured using the AAS.

3. Result and Discussion

The FTIR spectrum of GO (Fig. 1) displayed a well resolved characteristic band of GO. The absorption peaks 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 [19-21]. The band at 1623cm⁻¹ is ascribed C=C aromatic vibrations and the band at 1057cm⁻¹ is assigned to C–O stretching vibrations mixed with C–OH bending [21]. The peak at 3390cm⁻¹ is attributed to O-H stretching vibrations. Raman spectroscopy was used as a complimentary technique to FTIR for the identification of vibrational modes. It is utilized to study the ordered/disordered crystal structure of GO. The Raman spectra of GO (Fig. 2) shows two prominent peaks at 1355cm⁻¹ (D-bands) and 1589 cm⁻¹ (G-band). The G-band is attributed to all sp² carbon forms and it provides the information on the in-plane vibration of sp² bonded carbon atoms [22]. While, the D-band is associated with the existence of defects in the hexagonal graphitic layers of GO [23].

Fig 3 shows the TGA analysis of GO. The reduction in mass around 100 °C is attributed to loss of adsorbed water on the surface of GO. The following major mass reduction observed around 200 °C is ascribed to the pyrolysis of oxygen-containing functional groups, generating CO, CO₂ and steam [24,25]. The further reduction in mass around 700°C is attributed to the combustion of carbon. The powder XRD pattern of GO (Fig. 4) displayed a characteristic peak at 2θ value of 12.2°, corresponding to (0 0 1) reflection of stacked GO nanosheets [24]. The diffraction peak around 25.2° related to graphite was not observed in Fig. 4 [24], which shows GO does not contain any unreacted graphite. The SEM image of GO (Fig. S1) reveals some wrinkles on the surface of the GO, which might favors in the enhancement of the adsorption of Pb²⁺ over the surface of GO.

Table-1 (Fig. S2) details the adsorption rate and adsorptivity of GO at different concentrations of lead. It was observed that the adsorption capacity of GO has been increased with the increase in its concentration, which could be due to the presence of a wide variety of surface functional groups, mainly –COOH groups [25]. Further, the adsorption of GO was compared with graphite in presence of 50 ppm Pb²⁺ solution and the results are given in Table 2. In this case it is clear that the adsorption efficiency of GO is notably higher than the graphite.

Fig. 5 shows the kinetic profile of adsorption of Pb²⁺ in presence of 100 ppm solution of Pb²⁺ on GO. It was observed that over 90% of the lead was adsorbed within 20 min, later the stirring of GO in presence Pb²⁺ solution did not show any significant adsorption. This observation is consistent with previous report such as, Dorota et al. investigated the effect of time on the sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with Glutamic acid diacetic acid (GLDA) and nearly 100% of the sorption capacity was reached within 10–20 min [6].

4. Conclusions

Various functional groups have been successfully introduced on the surface of GO by the process of oxidation. In the adsorption of lead over GO, functional groups exists on the surface of GO plays a crucial role. An adsorption efficiency of 98, 91 and 71% was observed for the solutions containing 50, 100 and 150 ppm Pb²⁺ respectively. The adsorption ability of GO was found to be higher than graphite. Hence, GO could be promising material for the removal of lead that present in waste water. Hence this study could find a important application in the purification of water polluted by heavy metals.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- Excellent removal of lead by graphite oxide
- Adsorption ability of graphite oxide was higher than graphite
- Functional groups exists on the surface of graphite oxide facilitates the adsorption of lead

Fig. 1.
FTIR spectrum of graphite oxide.

Fig. 2.
Raman spectrum of graphite oxide.

Fig. 3.
TGA analysis of graphite oxide.

Fig. 4.
XRD pattern of graphite oxide.

Fig. 5.
Kinetic study of the adsorption rate of 100 ppm Pb²⁺ solution by graphite oxide.

Table 1

Adsorption capacity and adsorptivity of graphite oxide for different concentration of lead.

Wt of GO (g)	[Pb] _o (mg/L)	[Pb] _f (mg/L)	Adsorption capacity, Q	Adsorptivity, q(%)
0.0405	50	1.19	0.0301	97.62
0.0403	100	9.23	0.0563	90.77
0.0405	150	43.64	0.0656	70.90

Table 2

Comparison of the adsorption capacity and adsorptivity of graphite to graphite oxide for 50 ppm solution of lead.

Wt of GO (g)		[Pb] ₀ (mg/L)		[Pb] _f (mg/L)		Adsorption capacity, Q		Adsorptivity, q(%)	
Graphite	GO	Graphite	GO	Graphite	GO	Graphite	GO	Graphite	GO
0.0401	0.0405	50	50	46.47	1.19	0.0022	0.0301	7.06	97.62