



Synthesis and characterization of surface modified graphene–zirconium oxide nanocomposite and its possible use for the removal of chlorophenol from aqueous solution

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ABSTRACT

The narrative adsorbent graphene zirconium oxide was synthesized and surface was modified with CTAB to enhance its adsorption capacity. The structural, functional, morphological, optical and thermal properties of synthesized adsorbent were performed using XRD, FTIR, electron microscopy, UV–vis spectroscopy and TGA/DSC techniques, respectively. The adsorbent showed excellent removal efficiency towards 4-chlorophenol from aqueous solution. Effects of concentration, contact time, pH and temperature were studied and it was found that adsorption process was spontaneous and exothermic. Maximum adsorption occurred at pH 1.0. Kinetic study showed that pseudo-second-order kinetic model was obeyed. The effect of interfering ions was found to be negligible on the adsorption of 4-chlorophenol. The analytical applicability was tested by desorbing the adsorbed chlorophenol with a mixture of methanol, 0.1 M sodium perchlorate (60:40) and >90% recovery of 4-chlorophenol was achieved by batch process.

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Introduction

The control of pollutants in the environment constitutes one of the greatest efforts in modern-day research. In this sense, there is a remarkable interest in developing, testing, and applying mechanisms that allow the elimination and control of harmful substances in natural resources. Chlorophenols (CPs) constitute an important category of phenolic contaminant compounds, which have one or more chlorine atoms in their structures. In 1975, EPA (United States Environmental Protection Agency) warned on the low control of the CPs distribution in the environment, and its danger on mammals due to its cancer-producing activity [1]. The potential damage of CPs is due to their low biodegradation, which allows its accumulation in live organisms, causing toxicity and mutagenic effects [1,2]. For these characteristics, CPs is used in production of dyes, papers, herbicides, defoliants, fungicides, and antibacterial agents [1]. Therefore, due to these uses, CPs which are frequently discharged in industrial wastewater, are accumulated in ground and water bodies, making necessary the implementation of processes that allows its treatment. To date several of approaches have been reported for removal of 4-chlorophenol (4-CP) from different sources. These approaches include the photocatalysis,

oxidative degradation, and adsorption [3–5]. Among them the adsorption approach is advantageous and successfully performed using carbon allotropes i.e., graphite, activated carbon, carbon nanotubes (CNTs), and graphene. Recently, an efficient method has been developed for the removal of CPs and other pollutants using graphene as adsorbent [6–8]. Graphene, which is a single layer of carbon atoms densely packed in a honeycomb crystal lattice, has attracted tremendous attention from both experimental and theoretical communities in recent years [9]. Its remarkable properties, such as huge surface area (with a calculated value of $2630 \text{ m}^2 \text{ g}^{-1}$), good chemical stability, and graphitized basal plane structure, allow it to have strong π – π interactions with the aromatic moieties present in many dyes [10]. Graphene has a large theoretical specific surface area and functional groups, indicating their potential for the adsorption processes. In the past few years, many studies have been focused on the applications of graphene or composites in removal of pollutants from air and water. Graphene shows hydrophobic surface and presents high adsorption to chemicals due to strong π – π interaction. Modification of graphene with metal oxides nanoparticles (NPs) can produce various nanocomposites, enhancing adsorption capacity [7]. Among the metal oxide NPs, ZrO_2 NPs have the high thermal stability, chemical inertness and low toxicity [11]. Moreover, various papers have been published recently on the graphene– ZrO_2 NPs nanocomposites applications, which includes the deoxyribonucleic acid sensing detection [12], organophosphorus agents [11],

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supercapacitor energy-storage application [13]. Researchers have also demonstrated that ZrO_2 has a strong affinity to negatively charge moieties [14], which motivated us to use graphene- ZrO_2 NPs nanocomposite as selective adsorbent for chlorophenols. Therefore, in this study we have chosen the use of graphene- ZrO_2 nanocomposite as an adsorbent for chlorophenols, which has not yet been reported. However, the synthesis of graphene- ZrO_2 nanocomposite has been reported in the literature [11], but the methods involved are usually multistep or require some rigorous conditions and toxic, expensive raw materials. Previous work has shown that solvothermal reduction is an effective method of lowering the oxygen content and defect level in graphene sheets [15]. Based on the above considerations, we report a simple one step strategy for producing graphene- ZrO_2 nanocomposite as an adsorbent for the removal of chlorophenols. The objectives of this study were to synthesize CTAB modified graphene- ZrO_2 nanocomposite (denoted as “CT-Gr@ZO-NC”) and to characterize them by UV-vis spectrophotometer, scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and differential scanning calorimetric (DSC); and to describe the adsorption of chlorophenols in general and 4-chlorophenol in particular.

Materials and methods

Materials

All chemicals and reagents used were of analytical grade. Graphite fine powder extra pure and Zirconium acetate [$Zr(CH_3COO)_2$] purchased from Loba Chemie Pvt. Ltd., Mumbai, India. Stock solutions (1000 mg L^{-1}) of chlorophenols (4, 2–4, 2–4–6) were prepared in methanol and were further diluted with deionized water.

Methods

Preparation of graphene oxide (GO) and graphene-zirconium oxide nanocomposite (Gr@ZO-NC)

Graphene oxide (GO) was prepared according to the method described by Hummers and Offeman [16] from graphite fine powder. Briefly, $\sim 2 \text{ g}$ of graphite powder was mixed with 100 mL of H_2SO_4 and stirred in an ice-water bath for 40 min . In this mixture 5 g of $KMnO_4$ was slowly added and stirred for 1 h in the ice-water bath. The mixture was again stirred at room temperature until it became pasty brownish. This mixture was then diluted with slowly addition of 200 mL water. The reaction temperature increased rapidly to $90 \text{ }^\circ\text{C}$, and the colour changed to brown after 1 h . Finally, 10 mL of 30 wt\% aqueous solution of H_2O_2 was added to complete oxidation. The impurities were removed from the GO using 3 wt\% HCl aqueous solution by the repeated cycle of washing. The obtained GO was vacuum dried and stored for further characterization and applications. The synthesis of Gr@ZO-NC was carried out in two steps. In the first step, $\sim 3 \text{ g}$ of zirconium acetate and 200 mg of GO were dispersed into 200 mL of water and sonicated for 30 min . In the second step, sodium borohydride 20 mL (1% , w/v) solution [17] was added drop-wise into the solution mixture. The resultant mixture was stirred for 1 h , and then harvested by the centrifugation at 5000 rpm for 5 min and washed with 80% ethanol. The obtained sample was vacuum dried at $70 \text{ }^\circ\text{C}$ for 10 h and 1 g of dried sample was mixed with 100 mL of ethylene glycol under sonication in a 250 mL culture flask for 10 min . The resulting mixture was heated to $140 \text{ }^\circ\text{C}$ under vigorous magnetic stirring for 3 h . The synthesized Gr@ZO-NC suspension was centrifuged, washed by 80% ethanol three times to remove the remaining

ethylene glycol and soluble by-products, and dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ for 6 h . For surface modification a total of 100 mL Gr@ZO-NC solution (30 mg/mL , w/v) was placed into a 500 mL flask with a magnetic stirring beat and was placed onto hot plate without heating only for stirring. To this solution 100 mL solution of CTAB (cetyltrimethyl ammonium bromide, $C_{19}H_{42}BrN$) (1 mg/mL , w/v) was added, ultra sonicated for 5 min and the mixture was gently stirred for 2 h at room temperature. The CTAB modified Gr@ZO-NC (“CT-Gr@ZO-NC”) was centrifuged and washed with double distilled water (DDW). The obtained CT-Gr@ZO-NC was dried under vacuum at $65 \text{ }^\circ\text{C}$ and stored under dark condition until further use.

Characterization of GO and CT-Gr@ZO-NC

The synthesis of CT-Gr@ZO-NC nanocomposite in solution was monitored by measuring the absorbance (A) using UV-vis spectrophotometer (Perkin Elmer Life and Analytical Sciences, CT, USA) in the wavelength range of $200\text{--}800 \text{ nm}$. The vacuum dried CT-Gr@ZO-NC powder was stored in amber colour vials at room temperature under dry and dark condition form until used for further characterization.

For the morphological analysis transmission electron microscopy (TEM) of fine powder of CT-Gr@ZO-NC was carried out on JEOL 150/200 kV transmission electron microscope (JEOL, Tokyo, Japan) with an accelerating voltage of 80 kV . The thin film of the CT-Gr@ZO-NC was prepared on the borosilicate glass slide for the analysis of surface morphology on the light microscope at different magnifications. Scanning electron microscopy (SEM) was performed using the fine powder of the as synthesized CT-Gr@ZO-NC on a carbon tape in a JSM-6510LV scanning electron microscope (JEOL, Tokyo, Japan) at an accelerating voltage of 20 kV . The elemental analysis was carried out using the Oxford Instruments INCA X-sight energy dispersive X-ray (EDAX) spectrometer equipped SEM. The electron and light microscope images were obtained and converted into an enhanced meta file format. The X-ray diffraction (XRD) patterns of powder samples were recorded on MiniFlexTM II benchtop XRD system (Rigaku Corporation, Tokyo, Japan) operating at 40 kV and a current of 30 mA with $Cu K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The diffracted intensities were recorded from 5° to $80^\circ 2\theta$ angles. For the FTIR spectroscopic measurements CT-Gr@ZO-NC powder was mixed with spectroscopic grade potassium bromide (KBr) in the ratio of $1:100$ and spectra recorded in the range of $400\text{--}4000 \text{ wave number (cm}^{-1}\text{)}$ on Perkin Elmer FTIR Spectrum BX (PerkinElmer Life and Analytical Sciences, CT, USA) in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets. Thermal analysis of GO and CT-Gr@ZO-NC were measured by using thermal gravimetric analysis (TGA)/differential scanning calorimetry (DSC) (PerkinElmer Life and Analytical Sciences, CT, USA) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere [18,19].

Adsorption studies

Adsorption studies were carried out by batch process. Solutions of chlorophenols (20 mL) of desired concentrations ($10\text{--}100 \text{ mg L}^{-1}$) were equilibrated with 0.2 g of adsorbent (CT-Gr@ZO-NC) in 50 mL capped glass bottle. The mixtures were kept at room temperature for 24 h . Samples after equilibration were taken for UV-vis analysis. The samples were analyzed in triplicates and adsorption capacity values at equilibrium (q_e) were calculated by using the following relationship:

$$q_e = \left(\frac{C_0 - C_e}{W} \right) \times V \quad (1)$$

where C_0 is initial concentration of adsorbate (mg L^{-1}), C_e concentration of adsorbate at equilibrium (mg L^{-1}), V volume of the solution (L) and W is the mass of the adsorbent (g).

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