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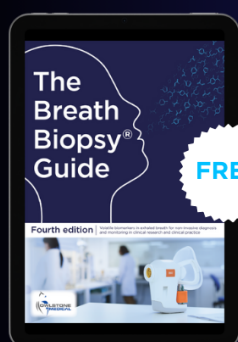
A novel synthesis of TiO_2/GO nanocomposite for the uptake of Pb^{2+} and Cd^{2+} from wastewater

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A novel synthesis of TiO₂/GO nanocomposite for the uptake of Pb²⁺ and Cd²⁺ from wastewater

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Keywords: ionic liquids (IL), cadmium, lead, graphene oxide (GO), titanium oxide (TiO₂)

Abstract

Ionic liquids attract attention in the last years due to its powerful solvation properties. For this reason, in current study 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM-BF₄] ILs was used for the synthesis of high surface TiO₂/GO nanocomposite, as an active material for heavy metal removal from aqueous media. FT-IR, transmission electron microscopy (TEM), scanning electron microscope (SEM), and x-ray diffraction (XRD) techniques were employed for identification of the novel nanocomposite. Batch experiments were conducted for Cd²⁺ and Pb²⁺ uptake from wastewater by the synthesized nanocomposite. The effect of parameters affecting adsorption capacity, such as contact time, pH, nanocomposite dosage and the initial concentration of heavy metals were examined for Cd²⁺ and Pb²⁺ removal by the prepared nanocomposite. The removal efficiency of Cd²⁺ and Pb²⁺ was 69.36% and 89%, respectively, under optimal conditions confirming the ability to use the prepared nanocomposite for wastewater treatment from heavy metals with high efficiency.

1. Introduction

Heavy metals are naturally occurred metal with high density, high atomic mass and exhibit toxicity at low concentrations [1]. Those metals are resulted from various sources, such as vehicle traffic emissions, cosmetics, electronics, pesticides, plastics, paints, herbicides, food, etc [2, 3]. The association of heavy metals with different sources allows them to expose the environment and global community to a real toxic threat [4]. The heavy metals risk arises from their ability to accumulate inside food chains and organisms bodies. It is demonstrated that heavy metals are able to cause serious health complications through adsorption into lungs, and skin [5, 6]. In order to control heavy metal risks, different policies related to the permissible concentrations in water of heavy metals have been recommended. For example, according to world health organization (WHO), the recommended limit for iron, mercury, cadmium and lead are 0.3–3 mg l⁻¹ and 1 µg l⁻¹, 3 mg l⁻¹, and 0.01 mg l⁻¹ respectively [7, 8]. While, as suggested by the American Environmental Protection Agency (EPA), the arsenic and copper acceptable limit is 0.01 mg l⁻¹ for arsenic [9] and 1.3 mg l⁻¹ for copper [10]. Thus, better human health required the wastewater treatment of heavy metals.

Many treatment techniques, such as adsorption, precipitation, filtration membranes and ion exchange were explored on heavy metals (e.g. Cd, Cu and Pb) removal from water [11–15]. Recently, the adsorption technique and bioremediation, using nano-adsorbent for heavy metals removal, have been widely applied [16, 17]. The preference of adsorption is due to its simplicity, efficiency at very low concentrations, and economical properties [16, 17]. For instance, nanostructured TiO₂, due to its chemical stability, versatility, effectiveness, and cheapness, is well known as a reliable and efficient heavy metal adsorbent [18, 19]. As another example, carbon-based nanomaterials, (e.g. graphene) have gained scientific interest in this respect, as a result of their high available surface, excellent thermal stability and outstanding mechanical strength. Further example is graphene oxide (GO) which gained great interest because it revealed superb mechanical, chemical, electric, thermal and surface properties [20, 21]. Additionally, the main benefits of graphene oxide are the inclusion on the edges and the surface of GO in various oxygen-containing functional groups.

Recently, extensive efforts have applied to prepare graphene oxide constructed hybrid nanocomposites [22–24]. Nevertheless, there is still a technological void in research for which ideal porosity has to be reached for adsorption. In general and because of their cost effectiveness besides ease of processing, solutions-phase processing routes are usually preferred. Recently, spending the ionic liquids (IL) with its unique solvation features and ionic conductivity, as a template for the preparation of nanostructured materials attracts attention [25, 26]. Furthermore, permittivity and high viscosity of ILs prevent the accumulation of nanostructured graphene oxide. In particular, the power of Vander Waals plays a magnificent role for the distribution of nanoparticles on carbon nanomaterial [27]. Many researchers have used ionic liquids for nanomaterials preparation to benefit from their solvation properties. As examples for the prepared materials are phosphate-based microporous zeolites [28], nanostructured zinc oxide [29], CoPt nanorods [30], and mesoporous SrCO_3 spheres [31]. Moreover, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) was used as a solvent for the preparation of TiO_2 -Reduced Graphene Oxide Composites via One-Step Hydrothermal method [32].

In light of the advantages of the use of IL as a solvent in the synthesis of nanostructured metal oxides and graphene oxide diffusion, it would be an ideal trial to model the IL-supported porous GO- TiO_2 composite as a unique adsorbent. IL can help to disseminate the graphene oxide and TiO_2 assembly and thus regulate them successfully. In this study, IL-supported nanocomposite GO- TiO_2 was explored as a possible adsorbents for effective heavy metals removal. However, the excellent applications of ILs confront with it is biologically active solvents which may cause different environmental problems [33]. Therefore, the challenge is expected to focus on the reduction of the pollutant linked to ILs.

This study reflects that IL, as a unique solvent, can efficiently assist the synthesis of nanostructured materials of graphene oxide (GO) and titanium oxide (TiO_2) that would exhibit better adsorbent features. Each component of the proposed nanocomposite plays an important role in its application as adsorbent. For example, GO will be used as a support to distribute TiO_2 and increases its surface area and efficiency. TiO_2 is a well-known as an adsorbent for the removing of pollutants, and ILs solvent enhances the driving force for the dispersion and stabilization of nanomaterials, which further boosts the surface area of nanocomposite.

Herein, the Hummers method and hydrothermal method were used for the preparation of nanostructured graphene oxide and titanium oxide, respectively. Then, the GO/ TiO_2 nanocomposite was synthesized using IL (1-ethyl-3-methylimidazolium tetrafluoroborate) by sol-gel method. TEM, SEM, FT-IR, and XRD techniques were used for GO/ TiO_2 GO, and TiO_2 characterization. Then, the prepared nanocomposite efficiency toward heavy metals removal was studied and discussed.

2. Experimental

2.1. Chemicals

1-Ethyl-3-methylimidazolium tetrafluoroborate (97%) ionic liquid and hydrofluoric acid (HF) were purchased from Sigma-Aldrich while titanium tetrabutoxide, ethanol, besides graphite supplied from Sinopharm Chemical Reagent Co., Ltd (China). Sulfuric acid (H_2SO_4 , 98 wt%), cadmium chloride, Potassium permanganate (KMnO_4 , 98 wt%), lead nitrate and sodium nitrate (NaNO_3) were purchased from Al-Nasr Co., Egypt. Without further purification, all chemicals were used as obtained. For all preparations, deionized water was used.

2.2. Titanium dioxide (TiO_2) preparation

The hydrothermal technique was employed for the preparation of titanium dioxide (TiO_2) [34]. In a typical method, 0.6 ml of hydrofluoric acid (HF, 45 wt%) that responsible for the formation of TiO_2 (101) plane was added drop by drop to a mixture of 2.0 ml titanium tetrabutoxide ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) and 82.0 ml anhydrous ethyl alcohol. After stirring for half an hour, a 100 ml autoclave was used for heating the mixture for 19 h at 180 °C. The autoclave was left at room temperature to cool down then the mixture was centrifuged. The resulting powder was washed several times with deionized water and tracked with anhydrous ethyl alcohol. Finally, the synthesized white TiO_2 was dried at 65 °C for four h under vacuum.

2.3. Graphene oxide (GO) preparation

Graphene oxide (GO) was synthesized through a modified method of Hummers [35]. The method was as follows: 12.0 g potassium permanganate (KMnO_4) was added to a mixture of 95 ml of sulfuric acid (H_2SO_4 , 98 wt%), 2.0 g of sodium nitrate (NaNO_3), and 2.0 g graphite in 200 ml beaker with continuous stirring. Then, an ice bath was used to implement the reactants at 5 °C for two h, followed by heating to 60 °C for 1.5 h. After heating, 85.0 ml of deionized H_2O was added slowly over a half-hour to the mixture, then 16.0 ml hydrogen peroxide (H_2O_2 , 30%) was added in order to remove the excess potassium permanganate. For dilution, about

205 ml of deionized H₂O was added to the mixture, followed by centrifugation and washing several times with deionized H₂O, while the pH value was adjusted at 7. The neutral mixture was distributed in deionized water after ultra-sonication for half an hour followed by removing the GO aqueous colloidal supernatant which is centrifuged to get the GO powder. The powder was washed several times with 10% HCl and deionized H₂O to obtain the graphene oxide (GO) as a final product.

2.4. Synthesis of [EMIM-BF₄] assisted GO/TiO₂ nanocomposite

Firstly, an ultrasonic bath for three h was used for the distribution of 50.0 mg GO in 30.0 ml deionized H₂O followed by the addition of 10.0 ml [EMIM-BF₄] to the aqueous GO for the preparation of [EMIM-BF₄/GO] suspension. In order to remove H₂O from preparation of [EMIM-BF₄/GO] suspension. In order to remove H₂O from the prepared suspension, the suspension was dried at 80 °C for nine h under vacuum. Then, 30.0 mg of TiO₂ was prepared in 7.0 ml [EMIM-BF₄] and stirred for 1 h before mixed with [EMIM-BF₄/GO] suspension at a continuous stirring for another 1 h, to homogenize the mixture and pre-concentrate GO/TiO₂. Then, the mixture was left for two days at 50 °C and the [EMIM-BF₄/GO/TiO₂] composite was extracted using ethyl alcohol. The rotary evaporation was used for the elimination of the excess H₂O and ethyl alcohol at 75 °C. In order to improve the porosity of the prepared nanocomposite, to avoid oxygen elimination from surfaces of GO, and for the removing of impurities, the [EMIM-BF₄] assisted GO/TiO₂ nanocomposite was heated for nine h at 180 °C under air.

2.5. Preparation of synthetic wastewater and batch experiments

In order to study the efficiency of the prepared nanocomposite, synthetic wastewater was prepared in the laboratory and batch experiments were conducted. The composition of the synthetic wastewater consisted of Cd (II) and Pb (II) ions with concentrations of 0.157 and 0.336 mg l⁻¹, respectively. Ultrapure deionized water was used for the preparation of stock solutions which renewed every week. A flame atomic absorption spectrophotometer was used to analyze the Cd²⁺ and Pb²⁺ ions. The synthesized nanocomposite was allowed to react with the wastewater solution for different times (40, 30, 20, 10, and 5 min) to examine contact time influence. A Series of 200 ml beakers were used for all experiments. For constant stirring, a magnetic stirrer was used to mix solutions that centrifuged for 15 min. The supernatant was subsequently filtered through a Whatman-42 filter paper, then the solution was analyzed for Cd²⁺ and Pb²⁺ concentrations. The pH of all experiments was adjusted using stock solutions of 0.1 M HNO₃ or 0.1 M NaOH. The pH effect was examined by adjusting the pH value to 8.5, 7.5, and 6.5. Furthermore, the effect of nanocomposite concentration was also studied.

3. Results and discussions

3.1. Synthesized GO and [EMIM-BF₄] assisted GO/TiO₂ nanocomposite characterization

Morphological characterization of the prepared GO, and [EMIM-BF₄] assisted GO/TiO₂ nanocomposite were performed using SEM images (figures 1(a) and (b)). Figure 1(a) suggests that the sizes of the GO were in the range of 200 nm and the particles tend to form agglomeration. Figure 1(b) shows a well-distributed spherical shape of TiO₂ onto GO nanosheets. The presence of ILs media supports the formation of nanoparticles with high stability and porosity compared to other media [36]. The SEM images show the uniform deposition of TiO₂ over GO sheets which could be related to the effect of ILs.

TEM images of GO and TiO₂/GO nanocomposite were presented in figures 1(c) and (d) The TEM micrographs shows the structure of GO and TiO₂/GO at approximately 200 nm, and demonstrates that the TiO₂ particles were present within the GO at the produced nanocomposite with porosity in the nanoscale. The revealed high accumulation of TiO₂ over GO surface is related to the excellent growth and nucleation of GO, due to the presence of ILs medium. In conclusion, the SEM and TEM display partially transparent GO nanosheets with few layers although the exact layer number cannot be estimated from these images [37].

XRD of GO, TiO₂, and TiO₂/GO were presented in figure 2. The XRD was investigated using (Cu Kα radiation, Panalytical X PertPro). The XRD pattern shows that graphite was completely oxidized to graphene oxide, which indicated by a sharp peak at 10.55 and the absence of a peak at 25 [37]. In addition, TiO₂ was characterized by the presence of peaks at 62.64, 54.99, 48, 37.78, and 25.29, all well matching with the peaks of anatase TiO₂ [38]. The XRD peaks of TiO₂/GO are similar to that of TiO₂, however, the graphene oxide peak disappears due to the destroying of GO nanosheets by interaction with TiO₂. In the range of 3750–400 cm⁻¹ FT-IR of GO, TiO₂ and TiO₂/GO spectrums are presented in figure 2(b). The GO range indicates the presence of the band at 1631 cm⁻¹ as C=C and the band with C–O–C stretching vibrations at 577 and 1071 cm⁻¹, respectively. The band with 1726 and 3382 cm⁻¹ is the oxygen-containing functional groups, such as C=O and OH, while the band with 1385 cm⁻¹ reflects C–OH bending vibration [39]. Therefore, the existence of these oxygen functional

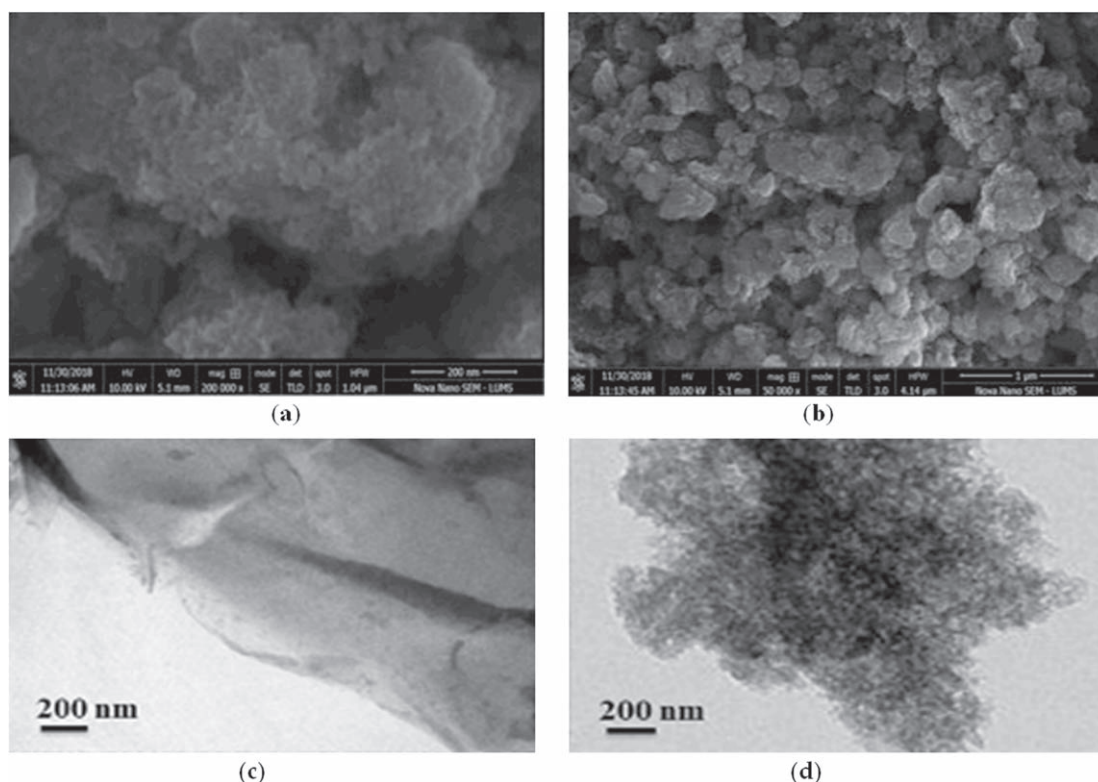


Figure 1. SEM images of GO (a), TiO_2/GO (b) and TEM images of GO (c) and TiO_2/GO nanocomposite (d).

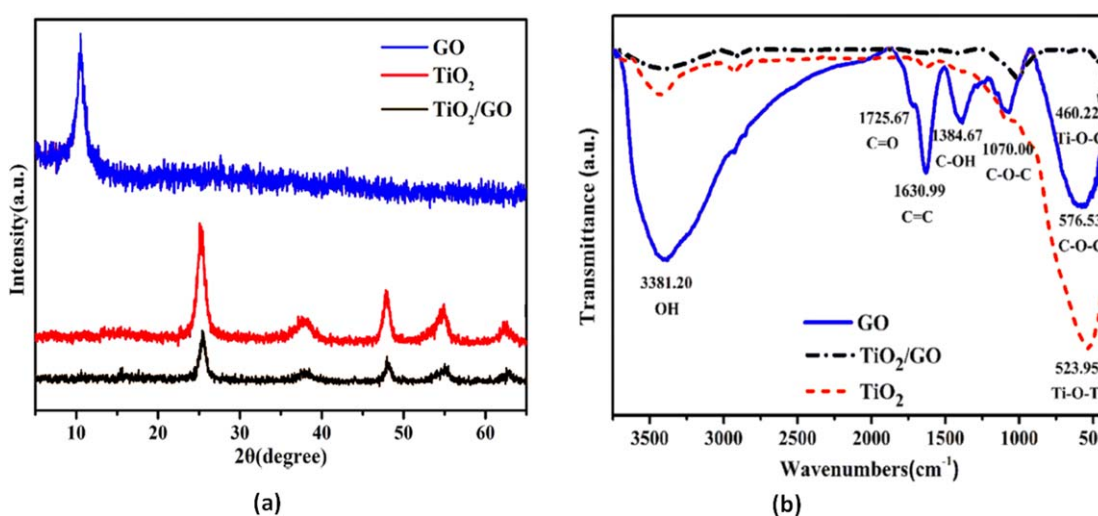
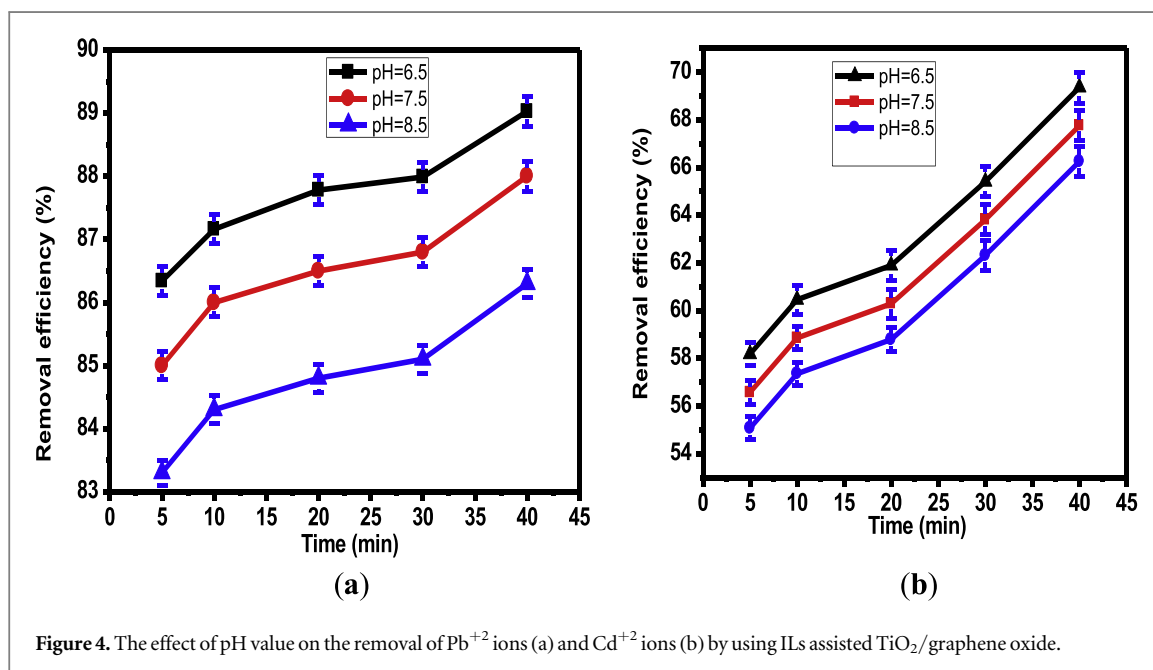
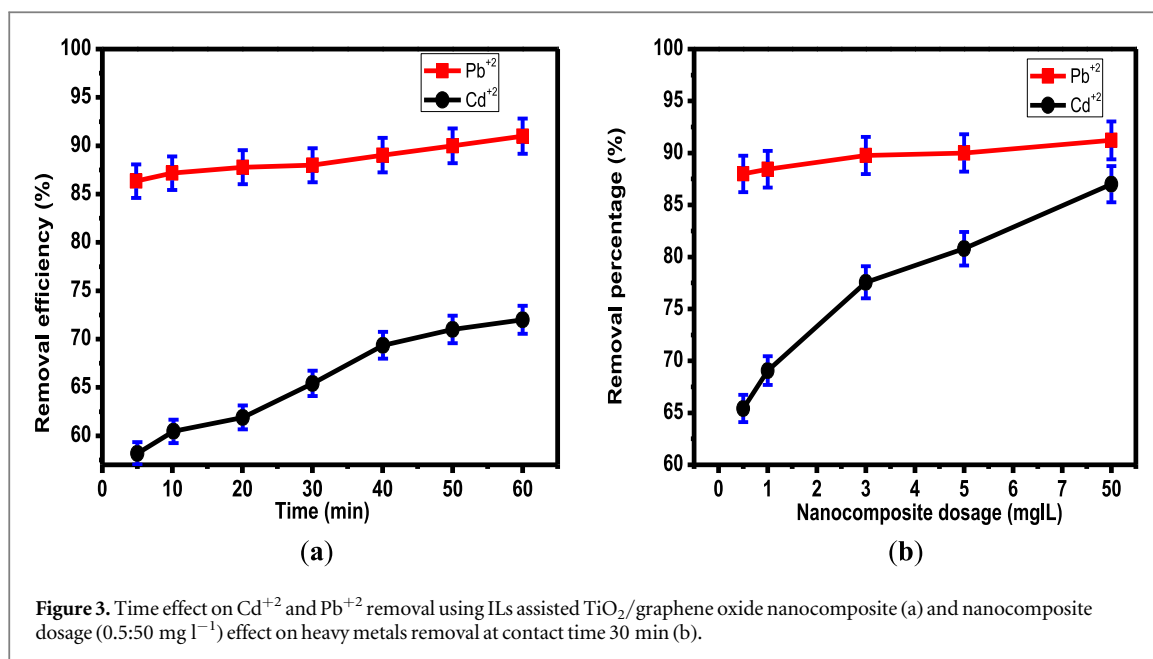


Figure 2. GO, TiO_2 , and TiO_2/GO XRD (a) and FT-IR (b).

groups saves the sites required for TiO_2 adsorption over the GO surface. For TiO_2/GO FT-IR, the bands related to oxygen functional groups were reduced. The appearance of the band at 460.23 cm^{-1} denotes Ti–O–C stretching bands, while the appearance of the band at 524 cm^{-1} denotes Ti–O vibration. Thus, FT-IR indicates the presence of oxygen functional groups in TiO_2/GO nanocomposite, which save sites for heavy metals removal [40].

3.2. The Time effect on heavy metals removal

A neutral (pH 7.5), ambient ($20 \pm 2^\circ\text{C}$) temperature and 0.5 mg l^{-1} of Cd (II) and Pb (II) concentration were studied for heavy metals uptake at a varying contact time of 40, 30, 20, 10, and 5 min, while other parameters were kept consistent at different levels. The concentration of nanocomposite was 0.5 mg l^{-1} . The detected deletion rates of heavy metal ions Cd^{+2} and Pb^{+2} are shown in figure 3(a). According to figure 3(a), heavy metals



removal increased by increasing the contact time with the prepared nanocomposite. It is observed that Cd²⁺ removal by the prepared nanocomposite increased from 58.18% to 69.36% as the time increased from 5 to 40 min. For Pb²⁺, the removal by the prepared nanocomposite increased from 86.3% to 89%, during the studied contact time. These results suggested that selective adsorption of heavy metals on the GO surface might be connected to the greater efficient removal of Pb²⁺ than Cd²⁺ [41].

The rate of heavy metals removal changes with the time was attributed to the change of the reaction progress with time. It is noticed from figure 4(a) that during period time of 30 min to 40 min, there was no efficient removal for heavy metals which could be due to the active sites overlapping. Therefore, 30 min was taken as the optimum removal time for Cd²⁺ and Pb²⁺ ions. Thus, the prepared nanocomposite serves as efficient material for heavy metals removal with maximum removal values of 70% for Cd²⁺ and 88.5% for Pb²⁺.

3.3. The concentration effect of the nanocomposite on heavy metals removal

The nanocomposite dosage effect on the uptake of Pb²⁺ and Cd²⁺ were studied and shown in figure 3(b). The Cd²⁺ and Pb²⁺ content in the synthetic water was 0.5 mg l⁻¹ and they were studied with different dosage of ILs assisted TiO₂/graphene oxide nanocomposite (0.5, 1, 3, 5, and 50 mg l⁻¹) with a time of contact 30 min for the

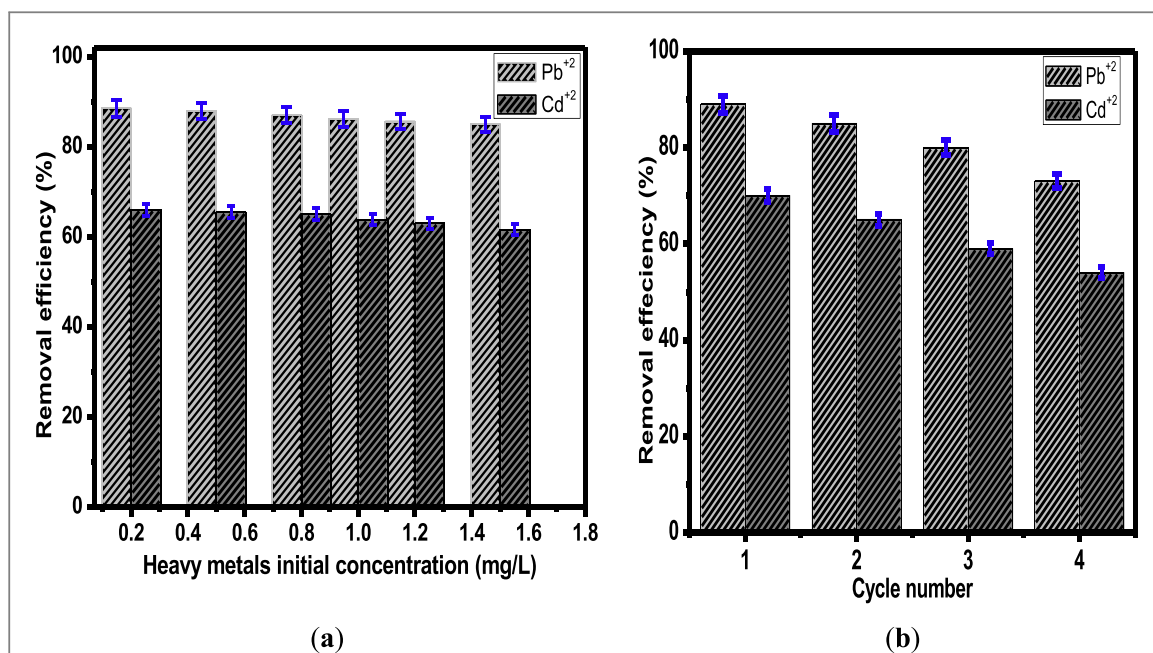


Figure 5. The removal efficiency of Cd^{+2} and Pb^{+2} ions at different initial concentrations of heavy metals with contact time 30 min, pH = 6.5, and nanocomposite dosage of 0.5 mg l^{-1} (a), and recycling test of nanocomposite for Cd^{+2} and Pb^{+2} ions removals.

carried-out experiments. According to figure 4(b), the Cd (II) and Pb (II) removals improved linearly by increasing of the nanocomposite dosage. The Pb^{+2} removals were 87 % at 0.5 mg l^{-1} of the nanocomposite dosage, while it was 91 % at 50 mg l^{-1} of nanocomposite dosage. The Cd^{+2} removals were 65 % at 0.5 mg l^{-1} of the nanocomposite dosage, while it was 87 % at 50 mg l^{-1} of nanocomposite dosage. This indicated that the available binding sites for heavy metal adsorption increased by increasing the dose of nanocomposite.

3.4. Heavy metals removal at different pH values

To determine the pH change influence on the cadmium and lead ion removals from water using the ILs assisted TiO_2 /graphene oxide nanocomposite, batch experiments were performed at different pH values (8.5, 7.5, and 6.5), as shown in figure 4(a). The experiments were performed at initial 0.5 mg l^{-1} cadmium and lead ions and 0.5 mg l^{-1} nanocomposite doses with a 5 to 40 min contact time. From figures 4(a) and (b), it is appeared that the pH value has significant influence on removals of cadmium and lead. This may be related to the great influence of the acidity on the ILs assisted TiO_2 /graphene oxide nanocomposite active sites, besides its effect on the oxidation state of heavy metal ions in the solvent media. According to figures 4(a) and (b), the removal efficiency of Cd^{+2} and Pb^{+2} using ILs assisted TiO_2 /graphene oxide nanocomposite increased by decreasing the pH value, that matches with the literature [42]. For the studied pH range, greater than 89% of Pb^{+2} and 70 % of Cd^{+2} were removed using the synthesized nanocomposite. This result is an indication of the ability to use the ILs assisted TiO_2 /graphene oxide nanocomposite in the neutral pH conditions. The high removal of lead and cadmium was observed at pH value of 6.5 which indicate the optimum pH value for cadmium and lead removal.

3.5. Effect of heavy metals initial concentration

To determine the initial concentration of lead and cadmium ions on the efficiency of treatment using the prepared ILs assisted TiO_2 /graphene oxide, the initial concentrations of lead and cadmium ions used were 0.2, 0.5, 0.8, 1, 1.2, and 1.5 mg l^{-1} for each ion as figure 5(a) reveals. At an optimum pH and contact time of 30 min, the dose of nanocomposites was 0.5 mg l^{-1} . The efficiency of the removal of two heavy metals was reduced, according to figure 5(a), by increasing the initial heavy metal concentration, which was connected with the accumulation of adsorbed ions in the synthesized nanocomposite sites. The results of the removal efficiency in figure 5(a) indicated the ability to use the prepared nanocomposite for heavy metals removal from water at various concentration with high efficiency.

3.6. Reusability study of the nanocomposite

The ability to reuse the prepared nanocomposite for cadmium and lead removals was studied for four successive cycles as can be seen in figure 5(b). The nanocomposite was isolated from the reaction mixture at 6000 rpm and seven minutes by centrifugation of the reaction solution at 6000 rpm for seven minutes, then dried out for seven hours at 65°C in a vacuum. In figure 5(b), the treatment efficiency of cadmium and lead ions decreased with the

increase in cycle number. The maximum removal of Cd^{+2} and Pb^{+2} was achieved in the first cycle, which is 89% for Pb^{+2} and 70% for Cd^{+2} , respectively. After four successive cycles, the treatment efficiency of cadmium and lead ions was still acceptable, which possibly indicates the excellent stability of the prepared ILs assisted TiO_2 /graphene oxide. In order to indicate the efficiency of the ionic liquid in increasing the surface area and nanocomposite pores, the efficiency of TiO_2 /graphene oxide prepared in the absence of ionic liquid toward Cd^{+2} and Pb^{+2} removal found to be 50% and 75%, respectively. Interestingly, the removal efficiency of the prepared nanocomposite toward cadmium and lead ions is promising and competitive with the previously published studies [43–45].

4. Conclusions

In the present study, the presence of 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquids that have excellent solvation properties during the TiO_2 /graphene oxide nanocomposite synthesis facilitate a high surface generation and nanocomposites possess high number of available active sites. The synthesized composite was characterized using SEM, TEM, and FT-IR and the obtained results indicate the stability of the prepared nanocomposite. Different conditions, such as pH, contact time effect, initial heavy metal concentration, and nanocomposite dosage effect, were studied to evaluate the prepared nanocomposite efficiency toward heavy metal ions lead and cadmium ions uptake. The prepared high-surface nanocomposite showed extremely high removal efficiency for Pb^{+2} and Cd^{+2} , that measured at 89 and 69.36, respectively. TiO_2 /graphene oxide synthesized using ILs as a solvent provides a realistic solution to the problem of reducing sewages with high heavy metal ion concentrations that may led to human health improvements in the communities and recycle wastewater. Our perspective research, according to the obtained results, is that the prepared nanocomposite is a promising nanomaterial could be applied for the removal of additional pollutants such as dyes, pharmaceuticals, and other heavy metals. Furthermore, the prepared material could be used as a support for the immobilization of microorganisms.

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