Effect of hydroxypropyl cellulose (HPC), polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) on Nd-TiO₂/graphene oxide nanocomposite for removal of lead(II) and copper(II) from aquatic media

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ABSTRACT

In order to investigate the effect of hydroxypropyl cellulose (HPC), polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) on adsorbing capacity of nanosorbent Nd-TiO₂/GO, Nd-TiO₂/HPC/GO, Nd-TiO₂/PVP/GO and Nd-TiO₂/PEG/GO nanocomposites were synthesized. Studies by Fourier transform infrared spectroscopy confirmed the expected structure and X-ray diffraction results confirmed the formation of crystalline phase of anatase titania and also graphene oxide (GO). Scanning electron microscopy pictures and energy dispersive X-ray spectroscopy analysis showed the formation of Nd-TiO₂ nanoparticles. These nanocomposites were used for removal of lead(II) and copper(II) from water and the effective factors on removal were optimized. The results showed that the maximum removal for all three nanocomposites was at pH = 7. The amount of adsorbent and contact time for Nd-TiO₂/HPC/GO and Nd-TiO₂/PVP/GO nanocomposites was equal to 0.02 g and 20 minutes respectively, but they were equal to 0.01 g and 15 minutes for Nd-TiO₂/PEG/GO nanocomposite. Investigating the effect of interfering ions showed they had no considerable effect on removal efficiency. In order to investigate the effect of photocatalytic activity in optimal conditions and in the presence of visible-ultraviolet light, the removal process was performed. The results showed an increase in removal efficiency. Furthermore, the ability of synthesized nanosorbents to decompose organic compounds available in water was confirmed and their energy band gaps were calculated.

Key words | Cu(II), graphene oxide, nanocomposite, Pb(II), removal, titania

INTRODUCTION

Through the growth of different industries, a variety of toxic materials and pollutants have been introduced to the environment; as a result, water pollution by heavy metals has become one of today's world problems. Lead and cadmium ions are very toxic elements which are used in battery industries, paint and rubber manufactures, and even in agricultural fertilizers, and they enter the human body through various means, including water. The arrival of these heavy metals in the body cause various complications such as liver disease, bone cancer and anemia (Bánfalvi 2011). Therefore removal of them from water is very important. There are different methods to remove them, such as oxidation (Hudlický 1996), reduction (Hudlický 1996), deposition (Baldwin & Marshall 1999), membrane filtration (Koros et al. 1996), ion exchange (Sanjiumsak & Punrattanasin 2014) and adsorption. Among these methods, use of adsorbents is highly regarded and extensive research has been done to prepare or improve their adsorption capacity (Kuilla et al. 2010).

In recent decades, different nanocomposites have been synthesized by using nanotechnology, and have attracted attention in many different aspects, because of their high-performance, cost-effectiveness and easy processing (Deng et al. 2010). Many nanocomposites are able to adsorb heavy metal ions from water and are used as high-performance nanosorbents (Provenzano & Holtz 1995).
Nanoparticles of titanium dioxide are the most important and widely used photocatalyst for the destruction of organic materials (Ozoemena et al. 2001). Photocatalytic activity of TiO₂ is improved by decreasing particle size, due to the increasing of specific surface area (Wang & Hong 1999). The band gap of titania is about 3.2 eV and UV radiation area is needed for photocatalytic properties. There are several ways to transfer this ability to the visible region (Umebayashi et al. 2002). Doping of some elements to titanium dioxide improved its photocatalytic activity and transferred it to the visible region. Doped ion not only reduces energy gap of titanium dioxide, but also, by trapping holes or electrons, increases the lifetime of the electron–hole system. Titania, has the ability to adsorb heavy metal ions, in particular TiO₂/graphene oxide (GO) nanocomposite (Mark et al. 1992). TiO₂/GO nanocomposite, due to suitable functional groups and high specific surface area, has been considered for removal of heavy metal ions from water (Ozoemena et al. 2001).

GO is a flat and monolayer substance consisting of carbon atoms. These atoms are connected to each other in a hexagonal grid and hive-like (honeycomb) and also they have hydroxyl, epoxy and carboxylic functional groups (Novoselov et al. 2005). GO sheets strongly combine with different polymers. So GO can be used as an adsorber with the proper combination capability in nanocomposites (Zhao et al. 2011).

Hydroxypropyl cellulose (HPC), polyvinylpyrrolidone (C₆H₉NO)n and polyethylene glycol (C₂nH₄nOₙ₋₁) polymers, due to their organic natures and for having functional groups in their structure, have the ability to adsorb different ions (Yao et al. 2012). Use of GO has recently attracted the attention of scientists in production of nanocomposites with various polymeric matrices. This relates to the polymer's high capability for adsorption and the distribution of graphene layers in the polymer matrix. Increasing the surface connection of the polymer and graphene enhances the polymer–graphene properties (Deng et al. 2010). The advantages of adding polymer to titanium dioxide is the creating of thermodynamic stability, reducing of susceptibility of colloidal stability to impure ions and pH, and formation of a thin and uniform film of titanium dioxide nanoparticles with high uniform porosity (Yao et al. 2012).

In this paper, the effect of organic polymers such as HPC, polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) in increasing the adsorption capacity of TiO₂/GO nanocomposite was studied and important factors in the removal process such as pH, adsorbent dosage, contact time and temperature have been studied and optimized.

**MATERIALS AND METHODS**

**Materials**

Graphite flake, PVP, PEG, and HPC were obtained from Sigma-Aldrich; KClO₃, H₂SO₄, HNO₃, CH₃COOH, Nd (CH₃COO)₃, xH₂O₂, C₂H₅OH, and alpha tetraisopropyl orthotitanate (TTIP; C₁₂H₂₈O₄Ti) analytical grade were obtained from Merck, and deionized water was used.

**Characterization**

Characterization analysis was done using a Tensor 27 Bruker Fourier transform infrared (FT-IR) spectrophotometer, Philips PW 1800 diffractometer for X-ray diffraction (XRD), EM-3200 scanning electron microscope (SEM) and an energy-dispersive X-ray spectrophotometer (EDS) manufactured by KYKY, and a 990 flame atomic absorption spectrophotometer manufactured by PG in the United Kingdom.

**Synthesis of TiO₂/polymer/GO nanocomposite**

GO was synthesized by Staudenmaier method. Briefly, 9 mL of nitric acid and 18 mL of sulfuric acid were mixed by magnetic stirrer in an ice bath and kept constant at a temperature of 0–3 ℃. Then 1 g of powdered graphite gradually was added to acidic mixture under stirring. Next, 11 g potassium chloride was slowly added to the mixture for 3 hours in a way that its temperature did not exceed 10 ℃. Then, it was stirred in the ice bath for an hour. The resulting solution was removed from the ice bath and mixed with vigorous stirring for 10 days at room temperature. Finally, in order to purify the mixture, the pasty black composition was washed with deionized water to reach a pH of 7. At the end, the sediments was dried in a vacuum oven for 2 hours at 60 ℃ to obtain graphite oxide. Next, 0.1 g of graphite oxide was dispersed in 40 mL of deionized water and 40 mL of ethanol under ultrasonic condition for 2 hours and then the solution was centrifuged and placed in the vacuum oven for 2 hours to dry. This causes the separation of graphite oxide layers and formation of GO. The characterization of this compound was performed by FT-IR spectroscopy and XRD. For synthesis of nanocomposites, at first 10 mg of GO was poured into a beaker and then 70 L of absolute ethanol and 7 mL of glacial acetic acid were added. The above mixture was placed in an ultrasonic bath for 1 hour until well dispersed. Then 0.28 g of HPC polymer and 0.0015 g of neodymium acetate as a doping factor of
titania were added into the dispersed mixture and placed in the ultrasonic bath for complete mixing. 0.01 mL of TTIP was slowly added to the resultant mixture, which was then placed in the ultrasonic bath for 4 hours. Then, the mixture was transferred to a 100 mL Teflon autoclave for 24 hours at 115 °C. The resulting mixture was then centrifuged and washed with distilled water and ethanol several times and placed in a vacuum oven for 48 hours at 50 °C to dry. In order to synthesize crystalline TiO2/GO, samples were subjected to heat treatment in the oven for 1 hour at 400 °C. An amount of 0.28 g of HPC, PVP or PEG polymers was added to TiO2/GO with absolute ethanol 10 mL separately and placed in an ultrasonic bath for 2 hours and in a vacuum oven for 48 hours at 50 °C to dry and then milled by a planetary ball mill and then stored for tests.

RESULT AND DISCUSSION
The effect of HPC, PVP and PEG polymers on the microstructure

FT-IR was used to identify the functional groups in a compound. FT-IR spectra of GO, Nd-TiO2/HPC/GO, Nd-TiO2/PVP/GO, Nd-TiO2/PEG/GO, in the range of 400–4,000 cm⁻¹, are shown in Figure 1(a)–1(d), respectively. Two stretching vibration peaks assigned to C-O bond of carbon attached to the hydroxyl and carboxyl group can be seen at 1,453 cm⁻¹ and 1,037 cm⁻¹, respectively. The stretching vibration peak of C-O-C bond from epoxy groups was visible at 1,247 cm⁻¹. On the other hand, there were two stretching vibration peaks at about 1,649 cm⁻¹ and 1,747 cm⁻¹ which were assigned to C=O bond in the non-oxidized carbon and C=O bond in carboxyl group, respectively. Finally, a strong peak at 3,416 cm⁻¹, belonging to the stretching vibration of OH bond, can also be seen (Bánfalvi 2011; Yao et al. 2012).

Observing of the peaks assigned to graphene in Figure 1(b)–1(d) confirms the existence of graphene in synthesized nanocomposites. In the FT-IR spectrum of the three synthesized nanocomposites, the peak of C=N bond in amino group and also the stretching vibration of methylene group (CH₃) were visible at about 1,083 cm⁻¹ and 1,402 cm⁻¹, respectively. The peak at 662 cm⁻¹ was assigned to the stretching vibration of O-Ti-O bond, and the stretching vibration peak of Nd-TiO2 can be seen at around 475 cm⁻¹ (Bánfalvi 2011; Yao et al. 2012).

SEM images of GO, Nd-TiO2/HPC/GO, Nd-TiO2/PVP/GO, and Nd-TiO2/PEG/GO are shown in Figure 2(a)–2(d), respectively. The layer structure of GO can be fully observed in Figure 2(a) and its synthesis was confirmed. In Figure 2(b)–2(d), the layer structure of GO is quite clear and produced nanoparticles. The use of different polymers affects particle size and its distribution range. The smallest particle size and the lowest range of size distribution can be seen in the use of PVP polymer. It is worth mentioning that the smaller the particle size, the more increases in surface area will be observed, which is favorable for adsorption. The increasing of the thickness of GO after nanocomposite synthesis can be attributed to the HPC, PVP and PEG polymer existing on the surface of GO.

The EDS spectra of the three synthesized nanocomposites were similar. Therefore, as a sample, Figure 3 shows
The EDS spectrum of Nd-TiO$_2$/PVP/GO. The result confirms the presence of titanium and neodymium elements in all samples and can be linked to Nd-TiO$_2$ that formed on the GO sheets.

The crystal structure of GO and synthesized nanocomposites was evaluated by XRD analysis. XRD patterns of Nd-TiO$_2$/HPC/GO, Nd-TiO$_2$/PVP/GO and Nd-TiO$_2$/PEG/GO nanocomposites are given in Figure 4(a)–4(c), respectively. The broad peak located at $2\theta = 12.23^\circ$ was assigned to GO and the strong diffraction peak at $2\theta = 25.38^\circ$ can be attributed to anatase phase of titanium dioxide with reflection of the (101) plane. The other diffraction peaks at about $38^\circ$, $48^\circ$ and $55^\circ$ can be assigned to the reflection of the (004), (200) and (211) planes, respectively (Li et al. 2014). This confirmed the formation of nanocomposites. The use of different polymers – HPC, PVP or PEG – had no effect on the formation of titania or GO and the intensity of both peaks was almost identical in all samples.

Removal study by use of nanocomposites

In order to find optimal conditions in achieving maximum adsorption efficiency, effect of various factors such as pH, contact time, adsorbent dosage and volume of the solution was evaluated. One parameter was assumed as a variable and other parameters were considered constant.
Effect of pH

In the GO structure, the carbonyl and carboxylic groups are attached to the edges of the sheet and the hydroxyl and epoxy groups are found on the basal plane. These oxygen-containing functional groups make the GO surface negative. Although more carboxylate group is formed in alkaline media (Chen et al. 2013), highly negative charge surface is presented in the pH range of 7–11 (Kashyap et al. 2014). Moreover, the presence of oxygen in the structure of each of the three polymers and nitrogen in PVP makes their surface negative.

The organic polymers can be inserted into the layer of GO in three ways: (i) hydrogen-bonding interactions between oxygen or nitrogen of polymer molecules and the oxygen-containing functional groups of GO, (ii) protonation of the nitrogen of PVP by the weakly acidic sites of the GO, and (iii) nucleophilic substitution reactions between oxygen or nitrogen of polymers and the epoxy groups of GO surfaces (Bourlinios et al. 2003). Furthermore, the isoelectric point of TiO₂ is about 5–7 (Zuccaro et al. 2015). Thus it is deduced that the surface charge of nanocomposite is positive in acidic media and it is negative in basic conditions.

To investigate the effect of pH on lead(II) and copper(II) adsorption, the range of pH = 3–7 was studied. At pH greater than 7, these ions precipitate as hydroxide. Therefore this higher pH was not examined. The results of copper and lead ions removal by Nd-TiO₂/HPC/GO, Nd-TiO₂/PVP/GO and Nd-TiO₂/PEG/GO nanocomposites are shown in Figure 5(a)–5(c), respectively. As shown, with an increase in pH, ion removal by synthesized nanoadsorbents will increase and maximum removal rates can be seen at pH = 7. The protonation of active sites of nanocomposites could cause less adsorption of analytes in acidic conditions, due to the electrostatic repulsion. However, the higher negative charge of nanocomposite in neutral or basic media resulted in raising the removal levels. Of course the removal efficiency of copper(II) ions in all three types of nanocomposites was more than lead(II). As a result pH = 7 was considered as the optimal value for pH.

Effect of sorbent dosage

To investigate the effect of sorbent dosage on the removal of heavy metal ions from water, the removal process was repeated for 0.005, 0.007, 0.008, 0.01, 0.02 and 0.03 g of synthesized nanocomposites at pH = 7, separately. Removal results of both copper(II) and lead(II) by Nd-TiO₂/H!PC/GO, Nd-TiO₂/PVP/GO and Nd-TiO₂/PEG/GO nanocomposites are shown in Figure 6(a)–6(c), respectively. The highest percentages obtained for removal of copper(II) and lead(II) ions were for 0.02, 0.02 and 0.01 g for Nd-TiO₂/HPC/GO, Nd-TiO₂/PVP/GO and Nd-TiO₂/PEG/GO nanocomposites, respectively. It is clear that increasing nanosorbent dosage will increase active sites for the adsorption of ions and removal efficiency increases until all ions in the sample will be adsorbed; after that sorbent dosage increase has not no effect. The results show that the type of polymer has affected the removal efficiency of nanocomposites. So, using PEG polymer decreases the adsorbent dosage to 50 percent, which is affordable economically.
Figure 5 | Effect of pH on the removal of lead(II) and copper(II) ions by (a) Nd-TiO₂/HPC/GO, (b) Nd-TiO₂/PVP/GO, and (c) Nd-TiO₂/PEG/GO nanocomposites.

Figure 6 | The effect of sorbent dosage on the removal of lead(II) and copper(II) ions by (a) Nd-TiO₂/HPC/GO, (b) Nd-TiO₂/PVP/GO, and (c) Nd-TiO₂/PEG/GO nanocomposites.
**Effect of removal time**

For the adsorption of copper(II) and lead(II) ions, sufficient time was needed to deal with active sites on the adsorbent. Therefore the removal process of lead(II) and copper(II) was repeated at 10, 15, 20, 30, 40, and 60 minutes at the obtained optimum condition, separately. The results for removal of both Cu\(^{2+}\) and Pb\(^{2+}\) by Nd-TiO\(_2\)/HPC/GO, Nd-TiO\(_2\)/PVP/GO and Nd-TiO\(_2\)/PEG/GO nanocomposites are shown in the Figure 7(a)–7(c), respectively.

As is clear, the maximum amount of removal of copper(II) and lead(II) ions by Nd-TiO\(_2\)/HPC/GO, Nd-TiO\(_2\)/PVP/GO and Nd-TiO\(_2\)/PEG/GO nanocomposites was obtained at 20, 20 and 15 minutes, respectively. It is obvious that, by increasing the contact time, the removal efficiency was increased also, because ions in solution have more time to adsorb on the active sites, but after adsorption of ions, a further increase in time will have no effect on removal. The results show that the polymer type also affects the removal time. If the PEG polymer were used, the optimal time would be reduced in comparison to the other polymers used, which is highly desirable from an economic standpoint.

**Effect of interference ions**

To investigate the interference effects of other ions, the removal process for copper(II) and lead(II) was repeated in optimal conditions, in the presence of K\(^+\), Ni\(^{2+}\), Mg\(^{2+}\), Cd\(^{2+}\), Ag\(^+\), PO\(_4\)\(^{3-}\) and NO\(_3\) ions as interfering ions where their molar ratio was 100 times greater than lead(II) and copper(II) ions, separately. The results are shown in Tables 1 and 2. If the removal change in the presence of interfering ions was about ±5%, the impact was negligible. As the results indicate, the presence of various ions had no significant effects on the adsorption of lead(II) and copper(II) by nanocomposites and removal rate was appropriate and acceptable.

In other words, the synthesized nanocomposite is able to remove the Pb\(^{2+}\) and Cu\(^{2+}\) ions, without being affected by interference ions.

**Reproducibility of method**

To evaluate the reproducibility of the method, removal of the lead(II) and copper(II) ions was repeated five times using Nd-TiO\(_2\)/HPC/GO, Nd-TiO\(_2\)/PVP/GO and Nd-TiO\(_2\)/PEG/GO nanocomposites in optimal conditions, separately.
Removal efficiency at each stage was calculated and the relative standard deviation (RSD) values are shown in Table 3. The results were satisfactory and removal of lead(II) and copper(II) ions by all three nanocomposites shows a good reproducibility.

**Photocatalytic activity of nanocomposites**

In order to evaluate the photocatalytic effect, the removal process was studied in optimum conditions in presence of high vapor pressure mercury lamp radiation (Figure 8). Removal of lead(II) or copper(II) ions was determined by atomic absorption spectroscopy. The results in Table 4 show that in the presence of UV–visible (UV-Vis) light, removal rate of Pb$^{2+}$ and Cu$^{2+}$ ions increases.

On the other hand, there is much research on photodegradation of toxic dyes for water and wastewater treatment (Mousavinia et al. 2016; Mosleh et al. 2016). Therefore, the ability of synthesized nanocomposites was examined in the presence of light for removal of organic contaminants from water (such as color). For this purpose, methyl orange solution with concentration of 5 ppm was selected as organic polluting agent and its concentration change was evaluated using UV-Vis spectroscopy where wavelength was 460 nm. The results in Figure 9(a)–9(c) represent the change absorption of organic dye by Nd-TiO$_2$/HPC/GO, Nd-TiO$_2$/PVP/GO and Nd-TiO$_2$/PEG/GO nanocomposites, respectively. Photodegradation percentage of methyl orange solution under UV-Vis irradiation is listed in Table 5. As tabulated, photocatalytic degradation of organic dye increases with irradiation time. The maximum degradation of methyl orange was observed for Nd-TiO$_2$/HPC/GO and its minimum was with Nd-TiO$_2$/PEG/GO nanocomposites. So, the photocatalytic activity was influenced by the kind of organic polymer used in the synthesis of nanocomposites.

The energy band gap of the samples was evaluated by diffuse reflectance spectroscopy (Figure 10). The direct band gap of the Nd-TiO$_2$/HPC/GO ($\lambda = 520$ nm), Nd-TiO$_2$/PVP/GO

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**Table 1** | Investigation of interfering ions effect at concentration level of 5 mg/L on removal of lead(II) ion (molar ratios were 10 times greater than Pb$^{2+}$) by Nd-TiO$_2$/HPC/GO, Nd-TiO$_2$/PVP/GO, and Nd-TiO$_2$/PEG/GO nanocomposites

<table>
<thead>
<tr>
<th>Interfering ion</th>
<th>Nd-TiO$_2$/HPC/GO</th>
<th>Nd-TiO$_2$/PVP/GO</th>
<th>Nd-TiO$_2$/PEG/GO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^+$</td>
<td>31 ± 2.42</td>
<td>26 ± 1.25</td>
<td>25 ± 1.67</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>27 ± 1.68</td>
<td>23 ± 2.04</td>
<td>24 ± 1.98</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>17 ± 1.12</td>
<td>22 ± 2.41</td>
<td>26 ± 1.42</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>25 ± 2.01</td>
<td>27 ± 1.95</td>
<td>21 ± 1.53</td>
</tr>
<tr>
<td>K$^+$</td>
<td>19 ± 1.92</td>
<td>23 ± 2.05</td>
<td>24 ± 2.10</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>14 ± 1.32</td>
<td>19 ± 1.52</td>
<td>28 ± 1.87</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>24 ± 1.52</td>
<td>17 ± 1.62</td>
<td>23 ± 1.28</td>
</tr>
</tbody>
</table>

*Remaining amount (µg/L).*

**Table 2** | Investigation of interfering ions effect at concentration level of 5 mg/L on removal of copper(II) ion (molar ratios were 10 times greater than Cu$^{2+}$) by Nd-TiO$_2$/HPC/GO, Nd-TiO$_2$/PVP/GO, and Nd-TiO$_2$/PEG/GO nanocomposites

<table>
<thead>
<tr>
<th>Interfering ion</th>
<th>Nd-TiO$_2$/HPC/GO</th>
<th>Nd-TiO$_2$/PVP/GO</th>
<th>Nd-TiO$_2$/PEG/GO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^+$</td>
<td>31 ± 1.25</td>
<td>34 ± 1.58</td>
<td>31 ± 1.15</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>35 ± 1.58</td>
<td>27 ± 1.24</td>
<td>35 ± 1.29</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>29 ± 1.69</td>
<td>24 ± 1.87</td>
<td>28 ± 1.56</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>32 ± 1.89</td>
<td>36 ± 1.29</td>
<td>27 ± 1.47</td>
</tr>
<tr>
<td>K$^+$</td>
<td>35 ± 1.39</td>
<td>31 ± 1.29</td>
<td>29 ± 1.82</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>34 ± 1.58</td>
<td>37 ± 1.52</td>
<td>30 ± 1.87</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>29 ± 1.92</td>
<td>26 ± 1.19</td>
<td>32 ± 1.98</td>
</tr>
</tbody>
</table>

*Remaining amount (µg/L).*

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**Table 3** | RSD of lead(II) and copper(II) ions removal by Nd-TiO$_2$/HPC/GO, Nd-TiO$_2$/PVP/GO, and Nd-TiO$_2$/PEG/GO nanocomposites

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>RSD Pb$^{2+}$</th>
<th>RSD Cu$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd-TiO$_2$/HPC/GO</td>
<td>1.62</td>
<td>2.24</td>
</tr>
<tr>
<td>Nd-TiO$_2$/PVP/GO</td>
<td>1.02</td>
<td>1.98</td>
</tr>
<tr>
<td>Nd-TiO$_2$/PEG/GO</td>
<td>1.32</td>
<td>2.16</td>
</tr>
</tbody>
</table>
\( \lambda = 510 \text{ nm} \) and Nd-TiO\(_2\)/PEG/GO (\( \lambda = 505 \text{ nm} \)) nanocomposites was calculated by Planck’s equation and found to be 2.34, 2.44 and 2.46 eV, respectively. These results showed that the photocatalytic activity of synthesized nanocomposites can be activated by visible light irradiation.

The photocatalytic ability of titania in reduction of heavy metal ions has been studied (Kabra et al. 2004). Increasing of removal of heavy metal ions and photocatalytic degradation of organic pollutant in presence of light may be related to interaction and chemical bonding between Nd-TiO\(_2\), GO and organic polymers. These interactions change the energy bands in such a way that the ability for heavy metal adsorption is improved besides the photodegradation of organic dye (Samadi et al. 2014).

This shows that using the three synthesized nanocomposites for water treatment not only can remove heavy metal ions with higher efficiency in the presence of light, but also can decompose the organic pollutants in the water. The combination of these two capabilities not only increases water efficiency but also reduces costs in total and is very affordable.

### Evaluation of adsorption isotherms

To describe the behavior of sorbent, different isotherms and equations have been developed. In this paper, the Langmuir and Freundlich isotherms were studied.

The Langmuir theory is based on single molecule adsorbed layers and mostly used for low pressures and
relatively high temperature adsorptions. For a sample containing adsorbate, with concentration of \( C_0 \) (mg/L or ppm), when in contact with the adsorbent for enough time, the concentration of analyte (with the same unit) is reduced. The parameter \( q_e \) is defined as the amount of moles per mass of adsorbent and can be expressed as:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

where \( V \) is volume of the solution in liter and \( W \) is the amount of adsorbent in gram. And it can be rearranged as Equation (2):

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \left( \frac{1}{K_L q_{\text{max}}} \right) \left( \frac{1}{C_e} \right)
\]

where \( q_{\text{max}} \) is mono layer adsorption capacity of adsorbent and \( K_L \) is the Langmuir adsorption equilibrium constant, which is related to free energy of adsorption. The Langmuir isotherm is one of the most used models for investigation of adsorption behavior in equilibrium systems. However, it should be noted that the Langmuir equation based on its assumptions cannot always be true, because in most cases there are structural defects in the surface of the adsorbent which prevents its uniformity. In addition, the molecules of adsorbate are not neutral. As a result, the interactions of these particles cannot always be ignored. On the other hand at high pressures of gas or at very high concentrations of solution, adsorbate particles can be adsorbed on the first layer molecules, physically.

When the adsorbent places are the same and surfaces are uniform, the Langmuir equation works well and is also consistent with experimental tests, but in the case of a heterogeneous surface, this equation cannot be appropriate.

Freundlich assumed that an adsorber was divided into smaller parts with different types. Also it can be assumed that each part has its specific heat of adsorption. Freundlich measured the amount of adsorbate in different pressures, and presented his empirical equation as Equation (3):

\[
\theta = kp^{1/n}
\]

where \( p \) is gas pressure, \( k \) and \( n \) both are constant values that are functions of temperature; \( k \) is proportional to the surface area and \( n \) is a heterogeneity factor of the surface.
In order to use the Freundlich isotherm in liquid adsorption on a solid surface, the above-mentioned equation can be written and rearranged as Equations (4) and (5):

\[ q_e = K_F \cdot C_e^{1/n} \]  \hspace{1cm} (4)

\[ \log q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e \]  \hspace{1cm} (5)

where \( K_F \) is the Freundlich constant related to the binding energy and \( 1/n \) represents the adsorption intensity or the heterogeneity of surface. If \( 1/n \approx 0 \), the surface is more heterogeneous; \( 1 > 1/n \) is similar to the Langmuir normal isotherm and \( 1 < 1/n \) represents the dependence of adsorption. Although in the Freundlich equation, the effect of heterogeneity has been assumed but increasing of concentration (P) will increase the adsorption capacities, whereas in practice there is not such a steady increase. This is a major drawback of the Freundlich equation (Hameed, 2003), Kavitha & Namasivayam (2007).

In order to investigate the adsorption isotherms of lead(II) and copper(II) ions on synthesized nanosorbents, at the optimum conditions, concentrations of 2–8 ppm were tested separately and \( C_0 \), \( C_e \) and \( q_e \) were calculated and shown in Tables 6 and 7. Based on the isotherms equations of Langmuir and Freundlich, related curves were plotted and Langmuir and Freundlich kinetics parameters were calculated and are presented in Table 8. The results show that adsorption of both lead(II) and copper(II) ions on synthesized nanocomposites comply with the Freundlich isotherm.

**CONCLUSIONS**

Providing a simple, effective, reproducible and inexpensive method to remove heavy metal ions was the primary objective of this article. In this study, Nd-TiO₂/HPC/GO, Nd-TiO₂/PVP/GO and Nd-TiO₂/PEG/GO nanocomposites were synthesized by using sol-gel and solvothermal methods. Nanocomposites structures were analyzed by XRD, SEM and FT-IR. XRD results showed that in all synthesized nanocomposites, TiO₂ has been formed as anatase phase and GO has been formed. FT-IR spectroscopy confirmed the fine structure and SEM images showed the layer structure of GO and formation of Nd-TiO₂ nanoparticles on it.

The synthesized nanocomposites were used as adsorbents for the removal of lead(II) and copper(II) ions.
Factors affecting the ability of adsorption, such as pH, contact time and adsorbent dosage were investigated and optimized. The survey showed that interference ions have not much impact on the extraction of lead(II) and copper(II) ions by synthesized nanocomposites and recovery percentage was appropriate and acceptable.

Study of photocatalytic properties of synthesized nanocomposites in the removal of Pb$^{2+}$ and Cu$^{2+}$ ions showed not only a slight increase in removal efficiency but also the ability of nanocomposites to remove organic contaminants from water, such as color. Experimental equilibrium data of Langmuir and Freundlich isotherms showed that the Freundlich isotherm was in good agreement with the experimental data.

**REFERENCES**


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