

# Adsorptive behavior of Ni (II) on phosphoethanolamine functionalized titanium dioxide

## Abstract

Nickel has been identified as an environmental toxin and occupational pollutant leading to infertility, birth defects, and nervous system defects. That is why the adsorption of Ni (II) from aqueous solutions by functionalized nano powders of titanium dioxide was studied. The surface of adsorbent was functionalized using phosphoethanolamine and characterized. The maximum adsorption of Ni (II) was observed to occur at pH 6.0 in 90 minutes. Kinetic experimental data were fitted well by the pseudo-second-order model. According to the equilibrium data, Ni (II) adsorption was well described by Langmuir isotherm model. According to the evaluated thermodynamic parameters, the adsorption was a spontaneous ( $\Delta G < 0$ ) and endothermic ( $\Delta H > 0$ ) process. The presence of interfering cations (Mg and Ca) with a concentration of  $50 \text{ mg g}^{-1}$  caused no considerable lowering effect on the Ni (II) adsorption. Regeneration of adsorbent was performed using  $\text{HNO}_3$  ( $0.1 \text{ mol L}^{-1}$ ).

**Keywords:** : surface fictionalization, heavy metal removal, phosphoethanolamine

Volume 2 Issue 2 - 2018

**Effat Iravan**

Nuclear Science & Research Technology Institute, Iran

**Correspondence:** Effat Iravani, Nuclear Science & Research Technology Institute, Tehran, Iran, Email eiravani@aeoi.org.ir

**Received:** November 14, 2017 | **Published:** March 26, 2018

## Introduction

Heavy metal pollution is a serious problem with a lot of environmental and health consequences. Heavy metals are defined on the basis of their toxicity and specific weight. However, it was suggested, "heavy metals" would be better to be defined on the basis of the periodic table of the elements and classified to (a) transition elements; (b) rare earth elements subdivided into the lanthanides and the actinides; (c) a heterogeneous group including the metal bismuth, the elements forming amphoteric oxides including aluminum, gallium, indium, thallium, tin, lead, antimony and polonium, along with the metalloids germanium, arsenic and tellurium.<sup>1</sup> It is believed, that heavy metals exposure, even at trace level, is a risk for human beings.<sup>2-4</sup> Animals and plant are not protected from the harmful effects of heavy metals. Trace elements in very low concentration are necessary to provide a normal metabolic functions, but high levels of their concentration lead to severe interference with physiological processes.<sup>5</sup> Negative influence on the kinetic properties of enzymes and metabolism, and oxidant stress are two way, how heavy metals like nickel can affect plants.<sup>5</sup> There are some various resistance mechanisms developed by plants against metal stress. Lipid composition can be changed, enzyme activity profile can be adapted, contents of some biological compounds like proteins or even gene expressions can undergo a change.<sup>6</sup> Among the first group of heavy metals, nickel (Ni) is known as trace element, which in higher concentration than needed affects plants metabolism negatively.<sup>7</sup>

The ability of various plants is drastically different from each other to deal with nickel toxicity and that is why the threshold concentration of nickel leading to its toxicity level depends on the type of plant.<sup>8</sup> Water is one of the most important way to adsorb the heavy metals by plants and affect both directly and indirectly the human health negatively. Effective removal of undesirable metals from water systems is still a challenging task. Numerous methods have been applied to remove heavy metals from waters, including but not limited to chemical precipitation, ion exchange, adsorption, membrane filtration and electrochemical technologies.<sup>9-12</sup> Flexible design, easy

operation, regenerating of adsorbent for multiple use, high efficiency, and low cost are some important factors making adsorption process among the other techniques forefront as a major way and more favorable for heavy metal removal.<sup>13,14</sup> In this project, nano powder of titanium dioxide was surface modified using Phosphoethanolamine, characterized via various spectroscopic analysis methods<sup>15</sup> and was utilized to investigate the removal of Ni (II). The effects of pH of solution, adsorbent dosage, contact time, initial concentration of Ni (II), and temperature were studied. The adsorption kinetic models were determined and compared to the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. The Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) equations were used to fit the equilibrium isotherm. The adsorption measurements were done at different temperatures to evaluate thermodynamic parameters. Effect of interfering cations on the adsorption of Ni (II) was investigated and finally, the reusability of the functionalized titanium dioxide was also determined.

## Experimental

### Materials

Titanium dioxide nano powder (21 nm average particle size, 99.5%) and phosphoethanolamine (98%) were purchased from Degussa and Merck (Germany), respectively. Appropriate amounts of nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , 99%) purchased from Merck were used to prepare Ni (II) solutions with needed concentrations in distilled water. The other chemicals such as calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ , 99%), magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , 98.5%), nitric acid (69%), and sodium hydroxide ( $\geq 99\%$ ) were obtained from Merck. Distilled water was used for the reaction and washing process.

### Methods

The metal ion concentrations were determined by an inductive coupled plasma atomic emission spectrophotometer (ICP-AES, Optima, Model 7300DV American). The pH values of the aqueous solutions were adjusted in the range of 2–6 using appropriate amount

of HNO<sub>3</sub> or NaOH and monitored utilizing a pH meter (Sartorius PB-11). Mse Mistral 1000 centrifuge and GFL 1083 shaker water bath were also used for adsorption experiments.

### Surface fictionalization of Titanium Dioxide nano powders

The mixture of phosphoethanolamine and Titanium dioxide nano powders with a 1:10 molar ratio in distilled water was stirred for 24 h at room temperature. After centrifuging, the resulted powders were eluted in a Soxhlet extractor with distilled water for 12 h to remove the physically adsorbed modifying agent and probable titanium phosphates. Afterward, the powders were dried in an oven at 100 °C for 12h. The detailed process of surface fictionalization and characterization was thoroughly discussed elsewhere.<sup>15</sup>

### Adsorption experiments

Stock solution of Ni (II) was prepared by dissolving 4.9544 mg L<sup>-1</sup> of Ni(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O in 500 mL distilled water and dilution to 1000 mL to obtain an aqueous solution (1000 mg L<sup>-1</sup>) to prepare the other solutions with less concentrations. The appropriate amount of adsorbent (SFT) was added to 30 mL Ni (II) solution with needed concentration and the mixture was stirred for specific time at a needed temperature. After centrifuging, the solution was separated from the adsorbent. Then the initial and final concentrations of Ni (II) were measured using ICP analysis to obtain adsorption percentage and capacity.

## Results and discussion

### The effect of Initial pH and adsorbent dosage

The initial pH value shows one of the major effects on the adsorption due to pH dependency of the various complex formations or electrostatic interactions at the surface.<sup>16,17</sup> Since phosphoethanolamine with its zwitterion structure possesses two kinds of functional groups including phosphate, and amine, pH dependency of the Ni(II) ions adsorption should be investigated. Considering equilibrium solubility constant of Ni (OH)<sub>2</sub> (Log K=-16.1±0.1) leading to precipitation at pHs higher than 7<sup>18</sup>, the pH effect on the adsorption of Ni (II) ions was examined by varying the initial pH values in the range of 2–6. The adsorption percentages were found to be high at more basic pH values, probably due to the competition of H<sub>3</sub>O<sup>+</sup> ions with Ni (II) ions for the same active adsorption site on the surface of adsorbent at acidic pHs. Lessening of H<sub>3</sub>O<sup>+</sup> concentration in solution as a result of increasing pH made probably the surface less positive and consequently electrostatic attraction between the Ni (II) ions and the surface starker. Also, the maximum adsorption reached the value 95.6% at the pH value 6 Figure 1. The adsorption percentage was increased from 72.21% to 98.64% by increasing the adsorbent amount in the range of 0.05–0.21 g Figure 2. Higher amount of SFT showed no more performance in adsorption percentage of Ni (II).

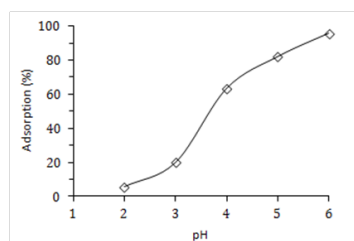


Figure 1 The effect of pH on the Ni (II) adsorption on SFT.

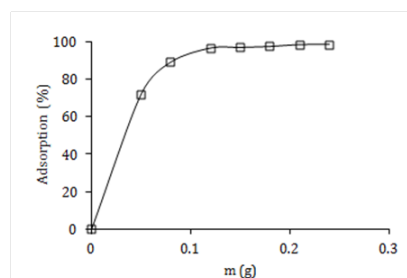


Figure 2 The effect of adsorbent dosage on the Ni (II) adsorption on SFT.

### The effect of initial concentration of Ni (II) ions and temperature

The initial concentrations of Ni (II) were varied from 25 to 100 mg L<sup>-1</sup>. Higher initial concentration led to lower equilibrium concentrations of Ni (II) ions after adsorption due to higher accessibility of Ni (II) ions per unit surface area of adsorbent in the solution. In this way, the probability of surface adsorption increases and can lead to decrease the equilibrium concentration. Increasing initial concentration from 25 to 100 mg l<sup>-1</sup> resulted in the adsorption capacity increase from 9.97 to 24.41 mg g<sup>-1</sup>. It seems, increasing initial concentration of Ni (II) ions provides a larger driving force needed to overcome the total mass transfer resistance of the Ni (II) ions between the liquid and solid phases, so resulting in higher collision between adsorbents and surface of adsorbent.<sup>18,19</sup> Adsorption capacities were improved also with increasing temperature, attributed to increasing mobility of Ni (II) ions leading to increase their tendency to be adsorbed from the aqueous solution. Accordingly, the adsorption of Ni (II) ions was an endothermic process (Figure 3).

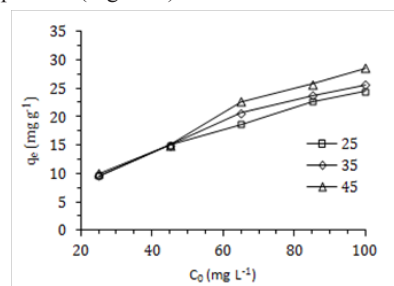


Figure 3 The effect of initial concentration and temperature on the Ni(II) adsorption on SFT.

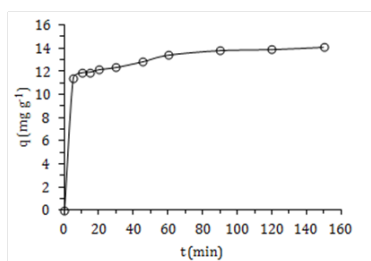
### Adsorption kinetics

Important information about the mechanism and the rate-limiting step could be provided from kinetic studies of adsorption process. The pseudo-first-order kinetic model (Lagergren equation) assumes that the adsorption rate is proportional to the number of unoccupied sites.<sup>20,21</sup> The pseudo-second-order kinetic model considers that the adsorption rate is related to the square of the number of free sites.<sup>22</sup> According to pseudo-first-order and pseudo-second-order kinetic model, chemical reaction may be considered as the rate-limiting step. The intra-particle diffusion kinetic model is based on the assumption that diffusion phenomenon is the rate-controlling step.<sup>23</sup> The adsorption amount of Ni (II) was measured in a range of 0–150 min. Adsorption capacity after 5 min was obtained about 11 mg g<sup>-1</sup> due to availability of many free sites. Over time, the free sites were occupied gradually making Ni (II) ions diffusion hard in order to connect to free sites, which needed more time. Adsorption amount showed no considerable

increase after 90 min (13.798 mg g<sup>-1</sup>). So, the equilibrium time for the rest of experiment runs was assumed 90 min Figure 4. The kinetic parameters for Ni (II) adsorption onto surface functionalized titanium dioxide were evaluated Table 1. The coefficient of correlation for pseudo-second order kinetic model (R<sup>2</sup>≈ 0.9983) was higher than the pseudo-first-order and intra-particle diffusion kinetic models. The calculated adsorption capacity (q<sub>e</sub>) according to pseudo-second-order kinetic model is close the experimental data. Also, higher correlation coefficient and closer adsorption capacity to the experimental data confirmed that the pseudo-second-order kinetic model successfully described the kinetics of Ni (II) ions adsorption onto the functionalized titanium dioxide.

**Table 1** Kinetic parameters for Ni (II) adsorption on SFT

Pseudo-second-order model		
R2	q (mg g <sup>-1</sup> )	K <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )
0.9983	15.002	0.022



**Figure 4** The effect of contact time on the Ni (II) adsorption on SFT.

### Adsorption isotherms

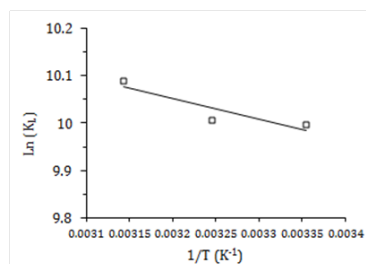
Knowing equilibrium adsorption isotherm is a helpful tool to investigate the kind of interaction between the adsorbate and adsorbent, necessary for design of new adsorption systems. Assuming that all adsorption sites are energetically identical, adsorption can be occurred homogeneously in a monolayer form and there will be no interaction between the adsorbed species.<sup>24,25</sup> Such a phenomenon is described well by Langmuir isotherm model. The Freundlich isotherm model assumes that the adsorption process occurs multilayer on heterogeneous surfaces and the distribution of adsorption heat will be non-uniform.<sup>26</sup> The type of the adsorption process (physical or chemical nature) can be specified by Dubinin–Radushkevich isotherm model.<sup>27</sup> Higher correlation coefficient showed that the experimental data could be described by Langmuir model better than Freundlich and Dubinin–Radushkevich models, which may be due to the homogeneous distribution of active sites on the nano adsorbent Table 2. The increasing values of K<sub>L</sub> by increasing temperature showed the enhancement of adsorption at higher temperatures. The Langmuir maximum adsorption capacity increased from 24.41 to 28.58 mg g<sup>-1</sup> with a rising temperature from 25 to 45 °C for Ni (II) ions. According to these results the adsorption process showed endothermic nature.

**Table 2** Isotherm parameters for Ni (II) adsorption on SFT

Langmuir Isotherm Model			
R <sup>2</sup>	KL (L mg <sup>-1</sup> )	q <sub>m</sub> (mg g <sup>-1</sup> )	Temperature (°C)
0.993	0.1038	24.41	25
0.996	0.1063	25.63	35
0.987	0.1146	28.58	45

### Adsorption thermodynamic

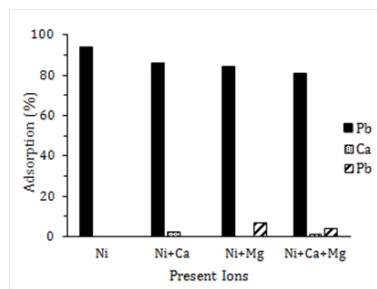
Thermodynamic parameters for the adsorption such as Gibbs free energy change (ΔG°, kJ mol<sup>-1</sup>), enthalpy change (ΔH°, kJ mol<sup>-1</sup>), and entropy change (ΔS°, kJ mol<sup>-1</sup> K<sup>-1</sup>) were determined using the Van't Hoff thermodynamic equations.<sup>26</sup> Adsorption of Ni(II) ions on the surface was confirmed to have endothermic nature due to calculated positive value of ΔH° (Figure 5) 3.819 kJ mol<sup>-1</sup>) (Moreover, the evaluated positive value of ΔS° (0.2360 kJ mol<sup>-1</sup> K<sup>-1</sup>) showed that the randomness at solid–liquid interface was increased during the adsorption of Ni (II) ions. The negative values of ΔG° (-56.2376, -58.3354, -59.9947 kJ mol<sup>-1</sup> at 25, 35, and 45 °C, respectively) at higher temperatures was increased. Accordingly, the adsorption process showed a feasible and spontaneous nature leading to better adsorption at higher temperatures.



**Figure 5** The Van't Hoff's plots for thermodynamic parameters of Ni (II) adsorption on SFT.

### The effect of interfering cations on the Ni (II) adsorption

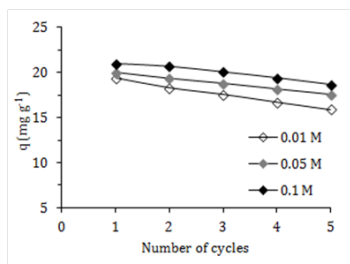
The effect of Ca and Mg cations (with a concentration of 50 mg L<sup>-1</sup>), founding commonly in aqueous solutions, was studied on the adsorption of Ni (II). The adsorption percentage of Ni(II) ions in the presence of Ca and Mg cations decreased from 93.82% to 86.33% and 84.42%, also 8.49% and 9.4% adsorption reduction respectively. Simultaneous presence of Ca and Mg cations led to an 11.36% decrease of Ni (II) adsorption percentage (Figure 6).



**Figure 6** The effect of interfering ions on Ni (II) adsorption on SFT.

### Desorption studies

Adsorbate releasing from the surface, also called desorption, is important to evaluate the economic justification for regeneration and reuse of the adsorbent. According to the results corresponding to the desorption experiments, 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> was more effective compared with 0.01 and 0.05 mol L<sup>-1</sup> HNO<sub>3</sub>. Increasing H<sub>3</sub>O<sup>+</sup> concentration led to more competition for the active sites where the metal ions hosted on the adsorbent. The adsorption amount was decreased about 20% after five cycles of adsorption–desorption (Figure 7).



**Figure 7** Five cycles of Ni (II) adsorption–desorption processes using  $\text{HNO}_3$  with different concentrations.

## Conclusion

The main aim of this study was to investigate Ni (II) removal from aqueous solution as a harmful heavy metal for environment and human. To achieve this goal, titanium dioxide nano powders were surface functionalized using Phosphoethanolamine and utilized as a novel adsorbent for Ni (II) ions. The best results were gained at a pH of about 6, using 0.2 g adsorbent for 90 min. The obtained kinetic and equilibrium data were described by the pseudo-second-order and Langmuir models for Ni (II), respectively. According to the Langmuir model, Maximum adsorption uptakes was obtained as 28.58  $\text{mg g}^{-1}$  for Ni (II). The surface modification led to the enhancement of the adsorption capacity for Ni (II) ions. According to calculated thermodynamic parameters, the adsorption process was spontaneous and endothermic in nature. Decrease of Ni(II) adsorption resulted from the presence of Ca and Mg cations was not significantly high (just about 8–11%). 0.1  $\text{mol L}^{-1}$   $\text{HNO}_3$  showed the best results as an agent for desorption and the results revealed about 3% decreased adsorption capacity over the studied five adsorption–desorption cycles. Due to high adsorption ability, and low-cost, the usage of phosphoethanolamine functionalized titanium dioxide as a novel adsorbent is promising for the removal of Ni (II) from contaminated aqueous solutions.

## Acknowledgement

None.

## Conflict of interest

The author dealer there is no any conflict of interest.

## References

- Appenroth KJ. Definition of Heavy Metals and their Role in Biological Systems. 2010;19:19–29.
- Khan S, Cao Q, Zheng YM, et al. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environ Pollut*. 2008;152(3):686–692.
- Singh A, Sharma RK, Agrawal M, et al. Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India. *Food Chem Toxicol*. 2010;48(2):611–619.
- Peng SH, Wang WX, Li X, et al. Metal partitioning in river sediments measured by sequential extraction and biomimetic approaches. *Chemosphere*. 2004;57(8):839–851.
- Yadav SS, Soni M, Sharma YK. Toxic level of Ni and its combination with micronutrient (B and Cu) on antioxidative enzymes and synthesis of sugar and protein in brinjal (*Solanum melongena* L.) metabolism. *Trop Plant Res*. 2016;3(2):375–379.
- Schützendübel A, Polle A. Plant responses to abiotic stresses: heavy metal-induced oxidative stress and protection by mycorrhization. *J Exp Bot*. 2002;53(372):1351–1365.
- Seregin IV, Kozhevnikova AD. Physiological role of nickel and its toxic effects on higher plants. *Russian Journal of Plant Physiology*. 2006;53(2):257–277.
- Manusadzianas L, Maksimov G, Darginaviciene J, et al. Response of the charophyte *Nitellopsis obtusa* to heavy metals at the cellular, cell membrane, and enzyme levels. *Environ Toxicol*. 2002;17(3):275–283.
- Hua M, Zhang S, Pan B, et al. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. *J Hazard Mater*. 2012;211–212:317–331.
- Wang YH, Lin SH, Juang RS. Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents. *J Hazard Mater*. 2003;102(2–3):291–302.
- O’Connell DW, Birkinshaw C, O’Dwyer TF. Heavy metal adsorbents prepared from the modification of cellulose: a review. *Bioresour Technol*. 2008;99(15):6709–6724.
- Kurniawan TA, Chan GYS, Lo WH, et al. Physico–chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*. 2006;118(1–2):83–98.
- Pan B, Pan B, Zhang W, et al. Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chemical Engineering Journal*. 2009;151(1–3):19–29.
- Mishra SP, Singh VK, Tiwari D. Radiotracer Technique in Adsorption Study: Part XIV. Efficient Removal of Mercury from Aqueous Solutions by Hydrous Zirconium Oxide. *Applied Radiation and Isotopes*. 1996;47(1):15–21.
- Iravani EA, Allahyari S, Shojaei Z, et al. Surface Modification and Spectroscopic Characterization of  $\text{TiO}_2$  with 2-Aminoethyl Dihydrogen Phosphate. *J Braz Chem Soc*. 2015;26:1608–1616.
- Ghasemi Z, Seif A, Ahmadi TS, et al. Thermodynamic and kinetic studies for the adsorption of  $\text{Hg(II)}$  by nano- $\text{TiO}_2$  from aqueous solution. *Advanced Powder Technology*. 2012;23(2):148–156.
- Shojaei Z, Iravani E, Moosavian MA, et al. Amino phosphate on the surface of nanotitania as attractive group to improve the adsorptive properties for lanthanides removal: adsorption, kinetic, equilibrium, and thermodynamic studies. *Desalination and Water Treatment*. 2016;57(57):1–14.
- Mattigod SV, Rai D, Felmy AR, et al. Solubility and Solubility Product of Crystalline  $\text{Ni(OH)}_2$ . *J Solution Chem*. 1997;26(4):391–403.
- Malkoc E, Nuhoglu Y, Dundar M. Adsorption of chromium (VI) on pomace--an olive oil industry waste: batch and column studies. *J Hazard Mater*. 2006;138(1):142–151.
- Chiron N, Guilet R, Deydier E. Adsorption of Cu(II) and Pb(II) onto a grafted silica: isotherms and kinetic models. *Water Res*. 2003;37(13):3079–3086.
- Da’na E, De Silva N, Sayari A. Adsorption of copper on amine-functionalized SBA-15 prepared by co-condensation: Kinetics properties. *Chemical Engineering Journal*. 2011;166(1):454–459.

22. Debnath S, Ghosh UC. Nanostructured hydrous titanium (IV) oxide: Synthesis, characterization and Ni (II) adsorption behavior. *Chemical Engineering Journal*. 2009;152(2–3):480–491.
23. Debnath S, Ghosh UC. Equilibrium modeling of single and binary adsorption of Cd(II) and Cu(II) onto agglomerated nano structured titanium(IV) oxide. *Desalination*. 2011;273(2–3):330–342.
24. Yang S, Li J, Shao D, et al. Adsorption of Ni (II) on oxidized multi-walled carbon nanotubes: effect of contact time, pH, foreign ions and PAA. *J Hazard Mater*. 2009;166(1):109–116.
25. Abbasizadeh S, Keshtkar AR, Mousavian MA. Sorption of heavy metal ions from aqueous solution by a novel cast PVA/TiO<sub>2</sub> nanohybrid adsorbent functionalized with amine groups. *Journal of Industrial and Engineering Chemistry*. 2014;20(4):1656–1664.
26. Vuković GD, Marinković AD, Čolić M, et al. Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes. *Chemical Engineering Journal*. 2010;157(1):238–248.
27. Unlu N, Ersoz M. Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. *J Hazard Mater*. 2006;136(2):272–280.