

# Lead Adsorption onto Surface Modified Nano Titania: Kinetic and Thermodynamic Studies

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**ABSTRACT:** *The present work focused on the adsorption of Pb(II) from aqueous solutions by amino-functionalized nano titania in a batch system. Surface modification was based on immobilization of o-phosphoethanolamine on the surface. The effects of pH, adsorbent dose, contact time, initial metal concentration, and temperature on the adsorption process were examined. The maximum adsorption of Pb(II) was observed to occur at pH 6.0. Kinetic data showed that the adsorption process achieved equilibrium within 90 min and experimental data were fitted well by the pseudo-second-order model. According to the equilibrium data, Pb(II) adsorption was well described by the Langmuir isotherm model. According to the evaluated thermodynamic parameters at different temperatures, the adsorption was a spontaneous ( $\Delta G < 0$ ) and endothermic ( $\Delta H > 0$ ) process. The presence of Mg and Ca ions as interfering cations up to 150 mg/g caused no considerable lowering effect on the Pb(II) adsorption. In addition, the regeneration of the adsorbent was performed using  $\text{HNO}_3$  (0.1 mol/L). The obtained studies showed that amino-functionalized nano titania was successfully used as an efficient adsorbent for removal of the Pb(II) from aqueous solutions.*

**KEYWORDS:** *Functionalization; Nano titania; o-phosphoethanolamin; Pb(II).*

## INTRODUCTION

Heavy metals such as lead with high toxicity can be stored permanently in different body organs and cause

cumulative poisoning, different kind of cancer, kidney damage, and mental defect especially in young children

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in a wide range. Lead has a great affinity to certain radicals and functional groups such as amines. As a metabolic poison, lead can replace calcium in the bones. Chronic effects on the blood cells is another disease resultant from lead bioaccumulation [1]. Lead exists in elemental, inorganic, and organic forms and presents in trace amounts in all soils, water, and foods. It is soft, malleable, blue-gray in color, and is highly resistant to corrosion. These properties, along with the poor ability of lead to conduct heat and electricity, probably contributed to its use in mining, smelting, refining, battery manufacturing, soldering, electrical wiring, home demolition and construction, painting, ceramic glazing, and the making of stained glass [2]. Lead may release into the environment and water sources in a number of different ways such as mining or metallurgical processes, metal plating, lead storage batteries, electrodes, cables, ceramics, oil refinery, plumbing, building construction, leaded gasoline, lead based paints, pigments, and alloy industries. Drinking water is known as the main source of lead exposure [3, 4]. Lead removal in effluent is also necessary before discharging into the water. Lead can be removed via various processes including precipitation, ion exchange, electrolysis, reverse osmosis, adsorption, using bimetallic building blocks, phosphate aggregation, etc. [3, 5-7]. Numerous research projects are still in progress to remove lead cations from waste water due to its toxicity [7-11]. Cost, complexity, and efficiency are some important factors, which should be considered to choose a suitable way to remove heavy metals. Advantages and disadvantages of current treatment methods to remove heavy metals are listed in Table 1. Among the mentioned methods, considering the cost and industrial application feasibility, adsorption is regarded as the most competitive one [12]. Adsorption by nanoparticles is simple, sludge free and hence the most versatile technique for heavy metal removal. Low cost and effective contaminant removal are the other benefits of this method [13].

In the last two decades, surface modification of transition metal oxides has been devoted a lot of attention due to attractive catalytic, adsorptive, optical and dielectric properties. The purposive selection of the nanopatterned core and modifying agents plays an important role affecting the performance of nanoparticles in the needed applications. Chemical stability and low toxicity are also required. These requirements can be achieved via proper in-situ or post synthetic surface functionalization.

The main goal of this research was to study the adsorptive removal of Pb(II) ions from aqueous solutions and optimize the adsorption conditions using surface modified nano titania. Nano titania as an affordable commercial nano powder was selected as the core of adsorbent due to its chemical stability and low toxicity. Possible capping agents include alcohols, amines, organic acids, silanes, phosphoric acids and phosphonic acids [20]. Characteristics of some surface modifiers are presented in Table 2.

It has been shown in literatures that phosphonic acid, phosphoric acid and some of their derivatives are stable under ambient conditions for over a long time and usually form strong chemical bonds with metal oxide surfaces [28, 29]. Possessing soft and hard centers (amine and phosphate groups) simultaneously, o-phosphoethanolamine (OPA) was selected to modify nano titania surface. Also nano titania (Degussa P-25) was treated with OPA [30]. In this regard, the effects of important variable including pH, adsorbent dosage, contact time, initial metal concentration and temperature on the adsorption efficiency were examined. The pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models applied to investigate the kinetic mechanism of Pb(II) ions adsorption. The Freundlich and Langmuir isotherm models were utilized to study the equilibrium data obtained at different concentrations and temperatures. In addition, the regeneration ability of the adsorbent was studied.

## EXPERIMENTAL SECTION

### Materials

Nano titania (99.5%, 21 nm average particle size) and OPA (98%) were purchased from Degussa and Merck (Germany), respectively. Ethanol (99.5%) obtained from Bidestan (Iran).  $\text{Pb}(\text{NO}_3)_2$  (99%), and  $\text{HNO}_3$  (70%) were purchased also from Merck (Germany).

### Methods

The Pb(II) ions concentrations in aqueous solutions after the adsorption were determined by an inductive coupled plasma atomic emission spectrophotometer (ICP-AES, Optima, Model 7300DV American). Zeta potentials of the samples in the pH range of 2-6 were determined by a light scattering & zeta potential analyzer model SZ-100z (Horiba Jobin Jyovin). The pH values of the aqueous

**Table 1: A brief comparison of current treatment methods for heavy metal removals.**

	advantages	disadvantages
Precipitation [14]	<ul style="list-style-type: none"> <li>•Permanent and efficient</li> <li>•Multiple contaminants of concern</li> </ul>	<ul style="list-style-type: none"> <li>•High cost</li> <li>•Not applicable for all cases</li> <li>•Waste product formation</li> </ul>
Ion exchange [15]	<ul style="list-style-type: none"> <li>•Cost effective</li> <li>•Economical regeneration of resins</li> </ul>	<ul style="list-style-type: none"> <li>•Calcium sulfate and iron fouling</li> <li>•Organic and chlorine contamination</li> <li>•Bacterial contamination</li> </ul>
Electro-coagulation [16]	<ul style="list-style-type: none"> <li>•Low operation cost</li> <li>•Low demand for chemicals</li> <li>•Low sludge production</li> </ul>	<ul style="list-style-type: none"> <li>•Maintenance required Regularly</li> <li>•The electrode breaks down over time</li> <li>•Wastewater must has high conductivity</li> </ul>
Reverse osmosis [17]	<ul style="list-style-type: none"> <li>•No need for chemicals</li> <li>•No need for thermal energy</li> </ul>	<ul style="list-style-type: none"> <li>•Suspended particles fouling</li> <li>•Depositing particles on the membrane</li> <li>•Irreversible damages to the membrane</li> </ul>
Oxidation [18]	<ul style="list-style-type: none"> <li>•Rapid</li> </ul>	<ul style="list-style-type: none"> <li>•High energy cost</li> <li>•Byproduct generation</li> </ul>
Biological treatment [18]	<ul style="list-style-type: none"> <li>•Feasible in removing some metals</li> </ul>	<ul style="list-style-type: none"> <li>•Technology yet to be established</li> <li>•Technology yet to be commercialized</li> </ul>
Adsorption [19]	<ul style="list-style-type: none"> <li>•Simple to apply and design</li> <li>•Economical</li> <li>•Flexible working</li> <li>•High efficiency</li> <li>•High quality purified products</li> </ul>	<ul style="list-style-type: none"> <li>•Need for adsorbent regeneration</li> </ul>

**Table 2: Characteristics of some modifiers to functionalize the surface of adsorbents.**

Modifier	Advantages and Disadvantages
Thiols [21]	Improving the stability of noble metal nano particles. Rarely applicable for nano metal oxides.
Amines [22]	Stabilizing mostly metal nano particles. Weaker interaction with surface, compared with thiolate.
Phosphines [23]	Known as a good stabilizing ligand for noble metal nano particle. Using in excess can lead to nano metals dissolution in organic solvents.
Carboxylates [24]	Often utilized to modify metal oxide nanoparticles. Decreasing the size of nano particles leads to more chemisorption than the adsorption.
Silanes [22, 25]	May form oligosiloxane structure resulting in an ill-defined surface structure. Using chlorosilanes forms HCl leading to alter the nanoparticle.
Phosphonates [22, 26, 27]	Creating M-O-P bonds, stable toward hydrolysis in a large pH range. No formation of any P-O-P bonds. Probable multidentate attachment to the surface. Limited to none siliceous particles.

solutions were adjusted as needed (2–6) using appropriate concentration of HNO<sub>3</sub> and monitored using a pH meter (Sartorius PB–11). Mse Mistral 1000 centrifuge and GFL 1083 shaker water bath were also used for adsorption experiments.

#### Surface modification of nano titania with OPA

Surface modification and characterization of nano titania was explained in detail elsewhere [30], which is briefly described here. Nano titania (0.799 g, 0.01 mol) was added into the solution of OPA (0.141 g, 0.001 mol) dissolved in 100 mL distilled water and was stirred for 24 h to complete the reaction at room temperature to prevent

the polymerization of OPA. Then the mixture was centrifuged for 30 min with a ramp of 6000 cycle min<sup>-1</sup>. The resulted powders were eluted in a soxhlet extractor with distilled water for 12 h to separate any physically adsorbed OPA on the surface and dried in an oven at 100 °C for 12 h. SEM and HRTEM images (Fig. S1), XRD pattern (Fig. S2), and ATR-FTIR spectrum (Fig. S3) of synthesized OPA-nano titania are presented as supplementary materials for a quick accesses.

#### Batch adsorption experiments

Stock solutions of Pb(II) were prepared by dissolving appropriate amounts of Pb(NO<sub>3</sub>)<sub>2</sub> in deionized water,

and the initial concentrations ( $C_0$ ) were adjusted to 50 mg/L for each experiment. A mass of 0.2 g modified nano titania was added into a flask containing 30 mL Pb(II) solution at room temperature and was shaken for 90 min. Afterward the solutions were centrifuged at 6000 rpm for 15 min to separate the solid adsorbents from the liquid phases. After determining the optimal pH, the effect of adsorbent dose was investigated in the range of 0.05–0.5 g of adsorbent at 25 °C and optimum pH. Kinetic experiments were conducted by varying the contact time from 5 to 150 min (5, 10, 15, 20, 30, 45, 60, 90, 120 and 150 min) at room temperature and optimum pH. The adsorption isotherms were performed using 0.2 g adsorbent in various metal ion concentrations in a range of 10–400 mg/L at different temperatures (25, 35 and 45 °C). The interfering effect of Ca and Mg ions on Pb(II) adsorption were also investigated by contacting 30 mL of solution (containing 50 mg/L of each ions) with 0.2 g of modified nano titania in a shaker at 25 °C and pH=6 for 90 min. Adsorption process was quantified by calculating the adsorption percentage (%Ad) and the adsorption capacity ( $q_e$ , mg/g) by equation (1) and equation (2), respectively:

$$\%Ad = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) \times \frac{v}{m} \quad (2)$$

in which

$C_0$ : initial Pb(II) ions concentration in mg/L

$C_e$ : equilibrium Pb(II) ions concentration in mg/L

$v$ : aqueous solution volume in mL

$m$ : adsorbent mass in mg.

The average absolute value of relative error, AARE, was used to compare the predicted results with the experimental data. A smaller AARE value indicates a better curve fitting. This is defined as follows:

$$AARE = \frac{1}{NDP} \sum_{i=1}^{NDP} \frac{|\text{Predicted value} - \text{Experimental value}|}{\text{Experimental value}} \quad (3)$$

in which, NDP is the number of data points.

#### Desorption experiments

In order to evaluate the regeneration capacity of amino phosphate functionalized nano titania, desorption experiments were performed using HNO<sub>3</sub> (0.01, 0.05 and 0.1 mol/L) as the desorbing agent. Adsorption experiments were done by the procedure described previously (30 mL, 50 mg L<sup>-1</sup>, 25 °C, optimum pH

and adsorbent dose, 90 min). Afterward, modified nano titania was centrifuged, agitated with HNO<sub>3</sub>, washed several times with distilled water, dried at 40 °C and reused for next adsorption. The adsorption–desorption processes were repeated for five cycles.

## RESULT AND DISCUSSION

### Bonding mode

OPA could be coordinated to the surface possibly in various monodentate, bidentate or even tridentate manner, bridging or chelating fashion. High-field NMR investigation of <sup>17</sup>O-enriched phosphonic acid chemisorbed on nano titania surface showed, that the chemical shift of the P–O–Ti sites were consistent with bridging modes [31, 32]. Chelating binding mode (two oxygen atoms binding to the same titanium centre) can be most probably excluded due to the resulting highly strained and energetically unfavourable four-membered Ti–O–P–O cycle [33]. Connor et al. showed, that phosphates bind to titania mainly bidentate in neutral and acidic aqueous solution [34]. The reaction mixture of OPA and nano titania was acidic (pH ca. 3.5), which was consistent with the finding of Corner et al. However, it is not easy for OPA to lose its second proton in such an acidic pH. Accordingly, the interaction of OPA with nano titania surface in a form of bridging bidentate through P=O and P–OH is more favorable. It is believed, in view of the coverage observed, that a realistic picture involves double and probably single, but not triple coordination [30].

### Adsorption experiments

#### Effect of surface modification

The results of comparative tests performed for Pb(II) adsorption on the untreated nano titania and the treated one showed that surface modification led to the 35% increase of adsorption percentage. Apparently, surface modification exhibited an important role in adsorption behavior. The enhanced adsorption could be due to the ability of free amine groups (–NH<sub>2</sub>) to form complexes with Pb(II).

#### Effect of pH

The initial pH value is one of the main parameters affecting the adsorption due to pH dependency of the various complexation reactions or electrostatic interactions at the surface [35]. pH values higher than 6

may lead to the precipitation of Pb(II) in hydroxide forms and lower the available Pb(II) content in aqueous phase leading to incorrect results. Thus, the pH effect on the adsorption was examined by varying the initial pH values of the solutions in the range of 2–6 (Fig. 4). The adsorption was increased with increasing pH due to competitive adsorption of  $H_3O^+$  and Pb(II) ions for the same active adsorption sites on the surface of adsorbent. Increasing pH and thereby decreasing  $H_3O^+$  concentration in solution makes the surface less positive and consequently electrostatic attraction between the Pb(II) ions and the surface starker. The amine functional groups could probably take part in metal uptake process through complexation which is pH-dependent and led to the adsorption yield enhancement. The trend of pH effect on the adsorption efficiency and the proposed reasons were confirmed by the results of zeta potential measurement of the adsorbent in the pH range of 2–6 (Fig. 1). Accordingly, increasing pH resulted in more negative zeta potential and surface charge leading probably to enhance adsorption efficiency of Pb(II) cations onto the surface at higher pHs. The nature of the active sites and sorbent may also change with pH [36]. Total removal was achieved at pH value of 6.0 which was used for all subsequent experiments.

Very low adsorption was observed at  $pH < 3$  by the nanostructured  $TiO_2$  while the maximum amount of Pb(II) ions sorption was observed at pH 6 due to decreasing competition between  $H_3O^+$  and Pb(II) ions [37]. Zhao *et al.* showed also the adsorption of Pb(II) using  $TiO_2$ /MWCNTs was increased by pH increasing up to pH 6 first and then changes negligibly [38]. The optimized pH for Pb(II) removal by Polypyrrole/MWCNT composite was reported also 6 in an study by Sahmetlioglu *et al.* [39]. The quantitative adsorption of Pb(II) (more than 95%) by titania coated silica was observed in the pH range 5–6 [40].

#### Effect of adsorbent dose

Increasing the adsorbent mass in the range of 0.05–0.2 g led to increasing adsorption efficiency from 79% to total removal due to an increase in the number of adsorption sites (Fig. 2). Using more than 0.2 g adsorbent showed no effect on the adsorption percentage any more, therefore, 0.2 g of the adsorbent dose was selected as the appropriate amount for further adsorption experiments. The Maximum uptake of about 90% was attained after using 0.2 g of adsorbent (nanostructured  $TiO_2$ ) in another study reported

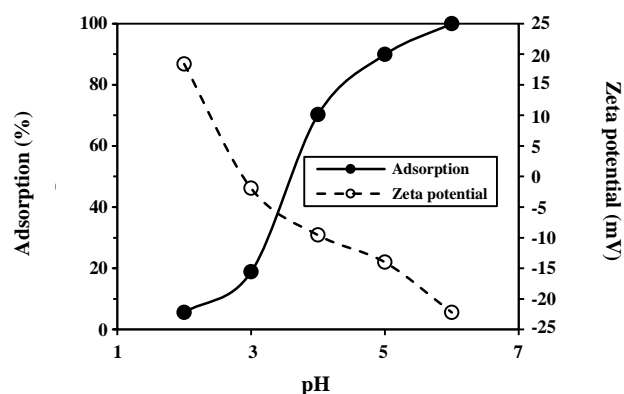


Fig. 1: Effect of pH on Pb(II) adsorption by OPA-nano titania.

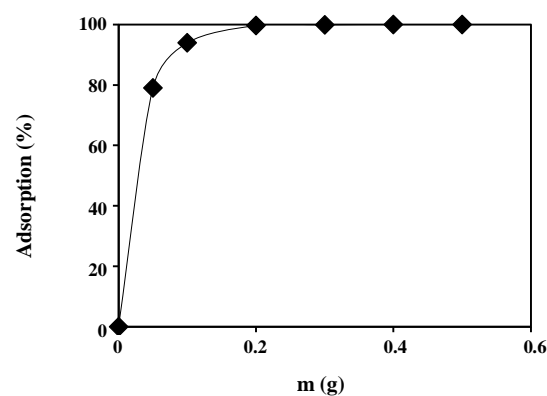


Fig. 2: Effect of adsorbent dose on Pb(II) adsorption by OPA-nano titania.

by Shokati *et al.* [37]. A maximum sorption capacity of 32.49 mg/g was obtained for Pb(II) removal by titania coated silica was obtained at an initial metal concentration in the range 50–250 mg/L, and adsorbent dose of 1 g/L, and the phase contact time 240 min [40].

#### Effect of contact time

The amount of Pb(II) adsorbed per unit mass of the adsorbent increased quickly with time (Fig. 3). More than 90% of the total metal ions absorption occurred within the first 20 min, due to the great number of vacant active sites on the adsorbent surface, and slowly reached the saturation at about 90 min, which was less than the time needed for complete removal of Pb(II) on the nanostructured  $TiO_2$  (4 h) [37]. So the equilibrium time was set at 90 min for the further experiments. The adsorption capacity for Pb(II) in other studies using titania coated silica and  $TiO_2$ /MWCNTs

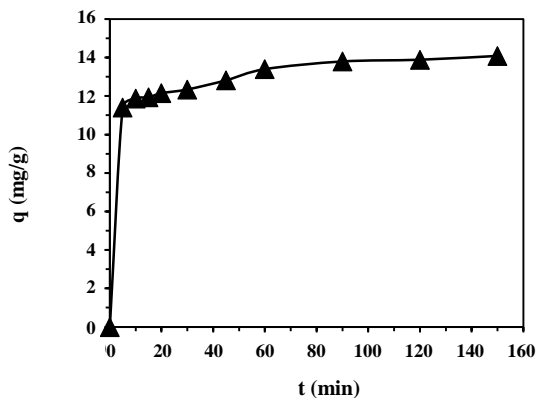


Fig. 3: Effect of time on Pb(II) adsorption by OPA-nano titania.

achieved plateau (more than 95%) after 240 min [40] and 60 min [38], respectively.

#### Effect of initial concentration and temperature

The measured amounts of adsorbed Pb(II) ions per unit mass of adsorbent were higher at high initial concentrations (investigated in the range of 10-400 mg/L), which could be attributed to higher accessibility of Pb(II) ions leading to increase the probability of surface adsorption (Fig. 4). The measured adsorption capacity at 25 °C was enhanced from 2.41 mg/g ( $C_0=10$  mg/L) to 40.21 mg/g ( $C_0=400$  mg/L) due to an increase in the initial concentration providing a larger driving force to overcome the total mass transfer resistance of the Pb(II) between the liquid and solid phases and more collision between adsorbates and surface of adsorbent [41]. The adsorption capacity of titania coated silica for Pb(II) sorption was increased by increasing temperature (20, 40, 60 °C) and initial concentration of Pb(II) starting from 50 mg/L and gained its maximum amount of 32.49 mg/g at 250 mg/L [40]. Biosorption capacity of *S. cerevisiae* biomass for Pb(II) adsorption was reported to be 89.6 mg/g, which relatively occurs slowly and equilibrium was reached within 4 days [42]. The polypyrrole/MWCNT nanocomposite was synthesized by *Sahmetlioglu et al.* and used for solid extraction of Pb(II) in trace amounts in water sample. Its adsorption capacity was determined 25 mg/g with a reusability more than 150 times, while retaining its sorption characteristics [39].

The observed improvement of the adsorption capacities with increasing temperature could be due to

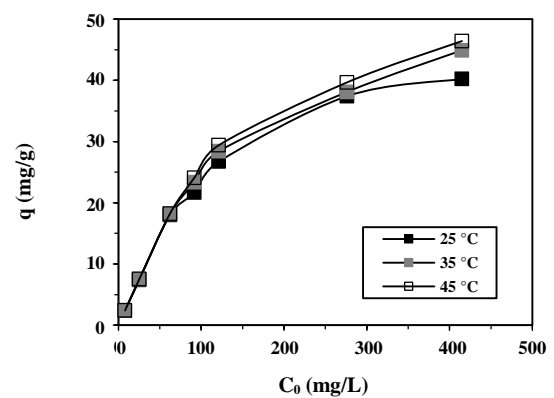


Fig. 4: Effect of initial concentration and temperature on Pb(II) adsorption by OPA-nano titania.

increased mobility of Pb(II) ions and their tendency to be adsorbed from the aqueous solution. The adsorption of Pb(II) ions onto OPA-nano titania was found to be an endothermic process.

#### Adsorption kinetic

In order to investigate the adsorption kinetics, providing important information about the mechanism and the rate limiting step, three kinetic models including pseudo-first-order, pseudo-second-order and intra-particle diffusion models were applied to the experimental data. According to the pseudo-first-order kinetic model, the adsorption rate is proportional to the number of free sites [43, 44]. The rate constant of adsorption can be determined using equation (4):

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (4)$$

where  $q_e$  and  $q_t$  (mg/g) are the adsorption capacities at equilibrium and at any time,  $t$  (min), respectively. Integration and applying boundary conditions also give:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo first-order rate constant for adsorption and can be obtained from equation (5) using the MATLAB software.

The pseudo-second-order kinetic model is based on the assumption that the adsorption rate is related to the square of the number of unoccupied sites [43, 45] and can be expressed as follows:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

Table 3: Kinetic parameters for Pb(II) adsorption by OPA-nano titania.

$q_{\text{exp}}$ (mg/g)	14.087		
Non-Linear pseudo first-order model			
$k_1$ ( $\text{min}^{-1}$ )	$q$ (mg/g)	$R^2$	AARE%
0.3846	12.99	0.9630	5.4874
Non-Linear pseudo second-order model			
$k_2$ (g/mg.min)	$q$ (mg/g)	$R^2$	AARE%
0.0391	14.091	0.9766	3.8127
Linear pseudo second-order model			
$k_2$ (g/mg.min)	$q$ (mg/g)	$R^2$	AARE%
0.0218	14.2857	0.9994	4.6245
Linear intra-particle diffusion model			
$k_{\text{id}}$ ( $\text{mg/g.min}^{0.5}$ )	$C$ (mg/g)	$R^2$	AARE%
0.2777	10.928	0.9684	4.9984

The pseudo-second-order equation and its linear form are given in Eq. (7) and Eq. (8), respectively:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (7)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where  $k_2$  (g/mg.min) is the pseudo second-order rate constant for adsorption. Chemical reaction may be considered as the rate-limiting step for pseudo-first-order and pseudo-second-order kinetic models.

According to the intra-particle diffusion kinetic model, diffusion phenomenon is the rate-controlling step [44, 45] and can be described by the Eq. (9):

$$q_t = k_{\text{id}} t^{0.5} + C \quad (9)$$

where  $k_{\text{id}}$  ( $\text{mg/g.min}^{0.5}$ ) is the intra-particle diffusion rate constant and  $C$  (mg/g) is the boundary layer thickness. The value of  $C$  is proportional to the boundary layer effect on the adsorption process and can be calculated from Eq. (9) by plotting  $q_t$  against  $t^{0.5}$ , if a single straight line passing through the origin ( $C=0$ ) is produced, then intra-particle diffusion only controls the adsorption process. If multi-linear portions are yielded, then two or more mechanisms like external diffusion, pore diffusion, surface diffusion, and adsorption onto the pore surface influence the adsorption process. The kinetic parameters of the described models were calculated for Pb(II) adsorption (Table 3).

The coefficient of correlation for the linear and non-linear pseudo-second-order kinetic models was higher than the pseudo-first-order and intra-particle diffusion kinetic models and also the obtained values of AARE% for the pseudo-second-order kinetic model were lower in comparison with two other kinetic models. Accordingly pseudo-second-order kinetic model successfully described the kinetics of Pb(II) ions adsorption onto the OPA-nano titani (Fig. 5).

#### Adsorption isotherms

The interactive behavior between the adsorbate and adsorbent is necessary in the design of new adsorption systems and can be described by the equilibrium adsorption isotherm. In this study, the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were used to fit the experimental data and analyzed at three different temperatures (25, 35 and 45 °C) by non-linear regression using the MATLAB software. The Langmuir isotherm model assumes that all adsorption sites are energetically identical and adsorption occurs on a homogenous surface by monolayer adsorption without any interaction between the adsorbed species [46, 47]. This model can be expressed by equation (10):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (10)$$

Where  $q_e$  (mg/g) is the amount of solute adsorbed per mass unit adsorbent and  $C_e$  (mg/L) is the equilibrium concentration of the metal ions.  $q_m$  (mg/g) and  $K_L$  (L/mg)

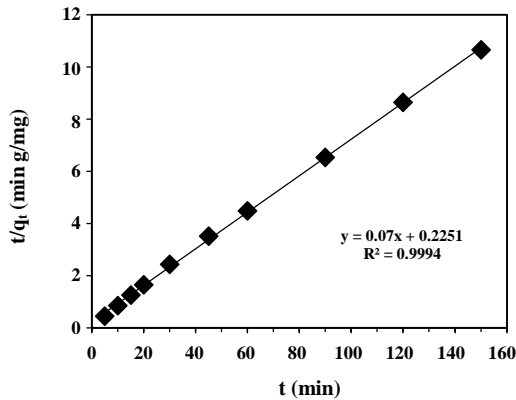


Fig. 5: Linear second order kinetic curve for Pb(II) adsorption by OPA-nano titania.

are the Langmuir constants related to monolayer capacity and energy of adsorption, respectively. The adsorption is considered to be (i) favorable when  $0 < R_L < 1$ , (ii) irreversible when  $R_L = 0$ , (iii) linear when  $R_L = 1$ , and (iv) unfavorable when  $R_L > 1$ . This dimensionless parameter is calculated using Equation (11):

$$R_L = \frac{1}{1 + K_L C_0} \quad (11)$$

Where  $C_0$  (mg/L) is the initial concentration of metal ions.

The Freundlich isotherm model is valid for multilayer adsorption process with a non-uniform distribution of heat of adsorption on heterogeneous surfaces [48, 49]. This empirical equation is given as Eq. (12):

$$q_e = K_F C_e^n \quad (12)$$

Where  $K_F$  ( $\text{mg/g} \times (\text{L/mg})^n$ ) is Freundlich constant related to the adsorption capacity. The parameter  $n$  is Freundlich constant representing the degree of dependence of the adsorption on the equilibrium concentration. The Dubinin–Radushkevich isotherm [49] is described by Eq. (13):

$$q_e = q_{DR} \exp(-K_{DR} \varepsilon^2) \quad (13)$$

The Polanyi potential ( $\varepsilon$ ) is defined by Equation (14):

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (14)$$

Where  $R$  (8.314 J/mol.K) and  $T$  (K) are the gas universal constant and the absolute temperature, respectively.

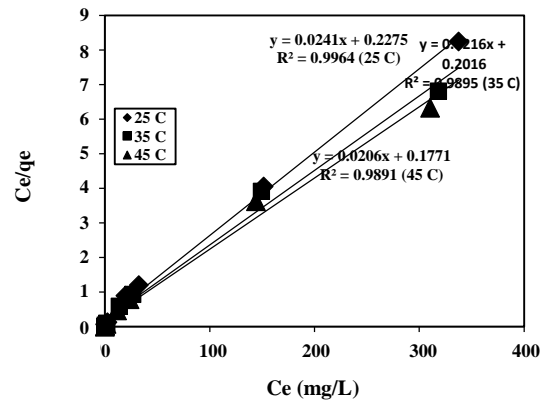


Fig. 6: Langmuir isotherm curve for Pb(II) adsorption by OPA-nano titania.

$E$  (kJ/mol) is one of the other parameters of (D–R) equation which defines the free energy change of transferring one mole of solute to the surface of the adsorbent from infinity in the solution:

$$E = \frac{1}{\sqrt{-2K_{DR}}} \quad (15)$$

The estimated parameters of the isotherm models were reported in Table 4. Higher correlation coefficients and lower average absolute values of relative error showed that Langmuir model described the experimental data better than Freundlich and Dubinin–Radushkevich models, which may be due to the fairly homogenous distribution of active sites on the nano adsorbent (Fig. 6). Energetically identical adsorption sites and occurring monolayer adsorption on a homogenous surface without any interaction between the adsorbed species are assumptions for Langmuir model [46, 47].

As can be noticed, the  $n$  value between 0 and 1 showed the favorable nature of adsorption for Pb(II) ions. Also the values of  $R_L$  were all between 0 and 1, indicating that the adsorption was favorable. The values of  $K_L$  increased as the temperature increased, showing the enhancement of adsorption at higher temperatures. The Langmuir maximum adsorption capacity increased from 41.49 to 48.54 mg/g with a rise in temperature from 25 to 45 °C. These results reflected the endothermic nature of the adsorption process.

#### Thermodynamic studies of the adsorption

Thermodynamic parameters for the adsorption such as Gibbs free energy change ( $\Delta G^\circ$ , kJ/mol), enthalpy change



Table 4: The isotherm parameters for Pb(II) adsorption by OPA-nano titania

T (°C)	Langmuir isotherm				
	q <sub>m</sub> (m/g)	K <sub>L</sub> (L/mg)	R <sub>L</sub>	R <sup>2</sup>	%AARE
25	41.49	0.1059	0.020-0.540	0.996	34.777
35	46.30	0.1071	0.019-0.529	0.990	41.435
45	48.54	0.1163	0.018-0.517	0.989	42.280
Freundlich isotherm					
	K <sub>F</sub> (mg <sup>1-n</sup> L <sup>n</sup> g <sup>-1</sup> )	n		R <sup>2</sup>	%AARE
25	11.04	0.2341		0.951	34.251
35	12.95	0.2236		0.982	48.351
45	14	0.2177		0.985	49.832
Dubinin–Radushkevich isotherm					
	q <sub>DR</sub> (mmol g <sup>-1</sup> )	K <sub>DR</sub> (mol <sup>2</sup> kJ <sup>-2</sup> )	E (kJ mol <sup>-1</sup> )	R <sup>2</sup>	%AARE
25	0.1868	0.0101	7.043	0.921	31.069
35	0.2072	0.0096	7.219	0.913	43.978
45	0.2171	0.0087	7.566	0.916	44.908

Table 5: Thermodynamic parameters for Pb(II) adsorption by OPA-nano titania.

ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	ΔG° (kJ/mol)		
		298 K	308 K	318 K
3.658	0.095	-24.756	-25.709	-26.662

(ΔH°, kJ/mol) and entropy change (ΔS°, kJ/mol.K) were determined using the following Van't Hoff thermodynamic equations [50]:

$$\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (16)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

Where K<sub>L</sub> (mol/L) is the Langmuir constant.

The results are shown in Table 5. The positive values of ΔH° confirmed the endothermic nature of adsorption processes of for Pb(II) ions on the adsorbent. In addition, the calculated positive values of ΔS° indicated the increasing randomness at solid-liquid interface during the adsorption of Pb(II) ions on the OPA-nano titania surface. The Gibbs free energy change is the basic criterion of spontaneity. The increasing negative values of ΔG° suggested the adsorption to be a feasible and spontaneous

process, which led to better adsorption at higher temperatures.

#### Effect of interfering cations on the adsorption of Pb(II)

The influence of Ca and Mg cations, which are found commonly in aqueous solutions, was investigated on the adsorption of Pb(II) ions in mono and multi-metal reaction systems in a range of 50-150 mg/L. No significant change was observed in the adsorption percentage of Pb(II) ions in the presence of Ca and Mg cations (Fig. 7).

#### Desorption and regeneration studies

Desorption, a phenomenon whereby the adsorbate is released from the adsorbent surface, is important to evaluate the economic justification for regeneration of the adsorbent especially in industrial application to remove heavy metal. According to the results corresponding to the desorption experiments, 0.1 mol/L HNO<sub>3</sub> was more

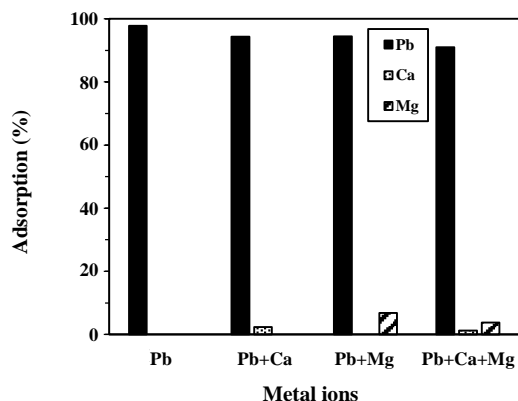


Fig. 7: Effect of interfering ions (Ca and Mg ions) on Pb(II) adsorption by OPA-nano titania.

effective than 0.01 and 0.05 mol/L  $\text{HNO}_3$ . It seemed that increase of  $\text{H}_3\text{O}^+$  concentration led to more competition for the active sites where the metal ions hosted on the adsorbent. Adsorption capacity of OPA-nano titania for Pb(II) ions decreased from 13.96 to 12.06 mg/g after five cycles of adsorption-desorption (regeneration with 0.1 mol/L  $\text{HNO}_3$ ). No significant loss in adsorption performance was observed after frequent use, indicating modified nano titania as a promising adsorbent for Pb(II) removal (Fig. 8).

#### Comparison of methods

Various methods for heavy metals removal (Table 1), the importance of surface modification to enhance the adsorptive properties of an adsorbent, and also characteristics of some modifiers (Table 2) has been briefly mentioned before. Some factors including affordability of nano titania core, simple surface modification procedure, chemical attachment of OPA to the surface via Ti-O-P bonds, the presence of free  $-\text{NH}_2$  groups on the surface to take part in a probable complexation with Pb(II) ions [30] make OPA-nano titania a trustworthy choice as an adsorbent for Pb(II) ions. The surface modification alone, without any optimization of the conditions, resulted in a 35% increase in lead absorption in the present study. The maximum adsorption capacity of Pb(II) ions onto the OPA-nano titania and some other adsorbents including natural, synthesized, modified, and biopolymer adsorbents are listed in Table 6. The adsorption capacity of the synthesized nano titania for lead removal was reported 7.41 mg/g [37]. The observed adsorption capacity of OPA-nano titania under optimized

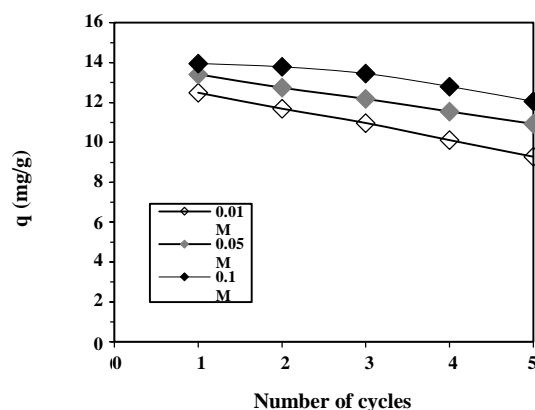


Fig. 6: Langmuir isotherm curve for Pb(II) adsorption by OPA-nano titania.

adsorption condition was 46.41 mg/g. Depending on total cost, lead initial concentration, adsorbent dosage and required time to gain the maximum adsorption capacity, the appropriate adsorbent can be different. For example, the reported equilibrium time for Pb(II) adsorption using Nd-TiO<sub>2</sub> / bentonite nanocomposite was only 5 min. However, it should be noted that the initial concentration of lead was only 5 mg/L [51]. Ferric activated sludge-based adsorbent was utilized to remove Pb(II) with initial concentration 50 mg/L. Although the adsorbent showed the adsorption capacity of 42.96 mg/g, the equilibrium time was high (24 h) [52]. Among the adsorbents introduced in Table 4, tea waste shows the highest adsorption capacity for the removal of Pb(II) with an initial concentration of 200 mg/L in 90 min. However, nearly high amounts of adsorbent is needed (12.5 g/L) [53]. The removal of Pb(II) ions with an initial concentration of 400 mg/L was performed using fair amount of OPA-nano titania (4 g/L) in 90 min. The adsorption capacity was calculated 46.41 mg/g. The presence of Ca and Mg cations with a concentration up to 150 mg/L showed no significant change in the adsorption percentage of Pb(II) ions. In addition, no considerable loss in adsorption performance was observed after frequent use of adsorbent (5 cycles). By comparison, it can be seen that lead removal from aqueous solutions was performed using OPA modified nano titania effectively.

#### CONCLUSIONS

Nano titania (p-25) was surface modified using o-phosphoethanolamine. It has been confirmed that OPA

**Table 6: Adsorption capacity for Pb(II) adsorption by OPA-nano titania and some other investigated adsorbents.**

Adsorbent	Optimum condition				
	q (mg/g)	IC <sup>1</sup> (mg/L)	AD <sup>2</sup> (g/L)	pH	t (min)
Cocopeat [54]	3.92	30	10	4	30
Nano titania [55]	7.41	25	3	6	4 h
Fish scale [56]	11.49	60	0.2	6	30
Bin husk [56]	12.64	80	0.2	7	60
Ferrihydrites [7]	13.75	50	5	6	180
AC/IO <sup>3</sup> magnetic composite [57]	19.37	50	5	6	60
Nd-TiO <sub>2</sub> / bentonite nanocomposite [51]	27.39	5	3	7	15
Titania-coated silica modified by SA <sup>4</sup> [40]	32.49	100	2.5	5	240
Ferric activated sludge-based adsorbent [52]	42.96	50	0.06	6	24 h
Orange peel [58]	43.5	20	2	6	150
This study	46.41	400	4	6	90
Formaldehyde treated Nizimuddinia zanardini [59]	51.83	~ 104	2	5.5	180
Bentonite [60]	52.63	100	0.5	3.4	10
Tea waste [53]	65	200	12.5	5-6	90

1) Initial concentration; 2) Adsorbent dose; 3) Activated carbon/Iron Oxide; 4) Sodium Alginate

molecules bonded covalently to the nano titania surface mainly through phosphate groups in a bidentate bridging mode, while the amine groups remained free. The modified nano titania was utilized to remove Pb(II) from aqueous solutions. The enhanced adsorption of Pb(II) onto treated nano titania comparing with untreated one could be due to the ability of  $-NH_2$  on the nano titania surface to coordinate to Pb(II). The effects of important parameters were investigated. The results indicated that the adsorption was strongly dependent on pH and the optimum pH was 6.0. The kinetic and equilibrium data were described by the pseudo second order and Langmuir models. In addition, from the equilibrium parameter ( $R_L$ ) values, it was concluded that modified nano titania was useful for Pb(II) adsorption from aqueous solutions. Thermodynamic parameters showed that the adsorption process was spontaneous and endothermic in nature. The presence of cations commonly present in aqueous solutions such as Ca and Mg ions had no significant effect on the adsorption of Pb(II).  $HNO_3$  ( $0.1 \text{ mol L}^{-1}$ ) was considered as an efficient agent for desorption studies and the results revealed no appreciable loss in efficiency over the studied five adsorption-desorption cycles. Due to high adsorption

percentage (total removal), and low cost it is concluded that the use of amino phosphate modified nano titania as an appropriate adsorbent is promising for the removal Pb(II) from contaminated sites.

### Nomenclatures

% Ad	Adsorption percentage
$C_0$	Initial ion concentration, mg/L
$C_e$	Equilibrium ion concentration, mg/L
v	Aqueous solution volume, mL
m	Adsorbent mass, mg
AARE	Average absolute value of relative error
NDP	Number of data points
$q_e$	Adsorption capacity at equilibrium, mg/g
$k_1$	Pseudo first-order rate constant, $\text{min}^{-1}$
$q_t$	Adsorption capacity at any time, mg/g
$k_2$	Pseudo second-order rate constant, $\text{g/mg}\cdot\text{min}$
$k_{fd}$	Intra-particle diffusion rate constant, $\text{mg}\cdot\text{g}\cdot\text{min}^{0.5}$
C	Boundary layer thickness, mg/g
$K_L$	Langmuir constant related to the energy of adsorption, L/mg
$q_m$	Langmuir constant related to the monolayer capacity, mg/g

$R_L$	Dimensionless parameter related to $K_L$ and $C_0$
$K_F$	Freundlich constant related to the adsorption capacity ( $\text{mg/g} \times (\text{L/mg})^n$ )
$n$	Freundlich constant representing the degree of the dependence of the adsorption on the equilibrium concentration
$q_{DR}$	Dubinin Radushkevich constant related to the capacity, $\text{mg/g}$
$R$	8.314 J/mol.K
$T$	Temperature, K
$\epsilon$	Polanyi potential
$E$	Parameter of Dubinin Radushkevich equation related to free energy change, $\text{kJ/mol}$
$\Delta G^\circ$	Gibbs free energy change, $\text{kJ/mol}$
$\Delta S^\circ$	Entropy change, $\text{kJ/mol.K}$
$\Delta H^\circ$	Enthalpy change, $\text{kJ/mol}$

### Supplementary

Supplementary Materials Available: SEM and HRTEM images, XRD pattern, and ATR-FTIR spectrum (3 pages). Ordering information is given on any current masthead page.

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