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Role of silica mid-layer in thermal and chemical stability of hierarchical Fe_3O_4 -SiO₂-TiO₂ nanoparticles for improvement of lead adsorption: Kinetics, thermodynamic and deep XPS investigation



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ABSTRACT

A core-shell of Fe_3O_4 -TiO₂ (FT) and a core-multishell of Fe_3O_4 -SiO₂-TiO₂ (FST) were synthesized to remove Pb (II) from water. Removal kinetics and isotherm fitted better with Pseudo-second order and Freundlich models, respectively. Activation energies for FST (55.54 kJ mol⁻¹) and FT (78.775 kJ mol⁻¹) suggested chemical adsorption and also easier adsorption on FST. The thermodynamic parameters disclosed that the adsorption of Pb (II) on nanoparticles was endothermic (Δ H^{*}: 38.27 and 65.43 kJ mol⁻¹) and spontaneous. XPS was done to determine the role of SiO₂ by its influence on chemical stability, surface properties and functional groups as well as to explore adsorption mechanism while XRD proved thermal instability for FT. The results suggested that ion exchange between hydroxyl groups and Pb species was accounted for by the adsorption and led to PbTiO₃ and PbO formation. However creation of Fe₂TiO₅/Fe₂O₃ interface on FT was responsible for its higher e/h recombination and lower adsorption capability.

1. Introduction

With the rapid development of chemical industries such as mining and battery manufacturing [1], the present of toxic metal ions in water has become a commonplace but concerning issue. Among various metal ions, it has been paid much attention to lead for its toxic properties and detrimental effects on animals and human beings [2]. It harms the human nervous system, mental decline [3], anemia, headache and diarrhea which are just a few examples [4]. This growing concern has led researchers to manipulate the properties of materials in order to find the one which can be easily synthesized and used for water refinement (see Scheme 1).

Various techniques for lead removal from water has been used so far including membrane filtration, chemical precipitation, adsorption, and so on [5]. However, most of the treatments are expensive and time-consuming. Herein, the combination of adsorption with simultaneous photocatalytic activity can be a promising way for water purification. Nano-TiO₂ has been widely attracted attentions for pollutants decontamination due to its excellent electronic and optical properties, thermal stability, and low-cost and chemically stable structure in acidic and alkaline solutions [6]. In addition to photocatalytic decomposition of pollutants, the above-mentioned features make it beneficial for dye-

sensitized solar cells [7] and photochemical water splitting [8], too. Although a beneficial and applicable material, TiO₂ in water purification confronts difficulty of nanoparticles recovery from medium. Therefore, catalyst immobilization over diverse inactive supports has been proposed including stainless steel substrates, quartz, and glass [9]. However, reduction of active surface area in these methods make a significant decrease in TiO2 photoactivity. Thus, a multi-functional system with high photoactivity and recyclability by magnetic targeting should be considered. This need can be met by heterostructure coreshell of TiO₂ with a magnetic material [10]. Among the many magnetic photocatalysts that have been synthesized so far, the ferrimagnetic Fe₃O₄ is chosen as magnetic core in magnetically recyclable photocatalysts for its known high magnetization [6]. Though, it is demonstrated that direct contact between magnetic Fe₃O₄ and TiO₂ photocatalyst increases electron-hole (e/h) recombination based on photodissolution phenomena, and this can reduce total photocatalytic efficiency of material [10]. The occurrence of this phenomena should be prevented by introduction of a passive layer. poly(sodium 4-styrene sulfonate) polyanion (PPS) and poly(diallyldimethylammonium) (PDD) in y-Fe₂O₃@PPS-/PDD@TiO₂ [11], and SiO₂ in y-Fe₂O₃@SiO₂@TiO₂ [12] are some different passive layers that have ever been used. However, the use of porous SiO₂ in the structure benefits some advantages.

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Scheme 1. Illustration of synthesis and adsorption processes.

As the first positive effect, it blocks electron injection from TiO_2 higherenergy conduction band to Fe_3O_4 lower-energy one, as well as hole transfer from TiO_2 lower-energy valance band to Fe_3O_4 higher-energy one at the interface. The other effect is to establish a large surface-tovolume ratio as a result of porous surface and raise catalytic reactions [12]. As an anti-sintering agent, SiO_2 can also improve the chemical stability of Fe_3O_4 against oxidation [13]. Albeit, the thickness of SiO_2 porous layer should be considered as a key factor because charge carriers can still transfer if the thickness is less than 5 nm [6].

While most works focus on adsorption of different pollutants and recoverability of nanoparticles, little has been reported on the exact mechanism of adsorption (chemical or physical) and the effect of insulator (SiO₂) on structural change and type of adsorption. In addition, the heavy metal used in the present study (lead) exists in various forms at different pH. The species of Pb(II) at pH < 6 is mainly Pb(II), while at pH > 6. In addition to Pb(II), different lead hydroxyl complexes are formed including $Pb(OH)^+$, $Pb_4(OH)_4^{4+}$ and $Pb_3(OH)_4^{2+}$ [3]. So the adsorption mechanism of lead at different conditions with various structures would not be the same. Here, we report the simultaneous adsorption and photocatalytic degradation of Pb(II) by FST and FT nanoparticles. The whole synthesis and characterization processes of a hierarchical, core-multi-shell Fe_3O_4 -SiO₂-TiO₂ heterostructure have been reported in our previous work [14]. In fact, water remediation includes two parts: adsorption removal of pollutants and catalytic reduction of pollutants [15], which photocatalytic adsorption process by the nano-system in the present study can meet both simultaneously. The adsorption method alone cannot completely omit pollutants, and the problem of secondary pollution remains, which requires further treatment [15]. By studying adsorption kinetic, isotherm and thermodynamic, surveys on the details of the first part have been fulfilled. Deep investigation on XPS has been done to obtain sufficient evidence for the proposed mechanism of the second part. These findings would facilitate the design and physical analysis of nanostructured system for relevant applications.

2. Experimental

2.1. Material

Iron (II) chloride tetrahydrate, $FeCl_2 \cdot 4H_2O$ and Iron (III) chloride 6hydrate, $FeCl_3 \cdot 6H_2O$ were used as initial salts for synthesis of Fe_3O_4 nanoparticles. Ethanol (96%, Merck), hydrochloric acid (HCl, 37%, Merck) and ammonia (NH₄OH, $^>$ 99%, Merck) were also used in producing magnetite nanoparticles. Hydrochloric acid was used to raise ionic strength of the solution while presence of ammonia prevents synthesis of undesirable productions such as akaganeite, by sudden change in pH.

Tetraethyl orthosilicate (TEOS, C8H20O4Si) and titanium butoxide (TBOT, C16H36O4Ti) were purchased from Merck as two precursors to be hydrolyzed in two sol–gel processes.

Bacteriophage E. coli ATCC25922 was originally obtained from the ATCC as the pollutant model.

2.2. Synthesis of magnetic nanophotocatalysts (FST and FT)

To synthesize magnetite nanoparticles by co-precipitation synthesis route, a 300 mL aqueous solution containing FeCl₃·6H₂O and FeCl₂·4H₂O (2:1 mol ratio of Fe³⁺: Fe²⁺) was heated to 70 °C with the mixture being continuously stirred under nitrogen to remove oxygen. Then, 150 mL ammonia was added under vigorous stirring. The reaction was let to progress for an hour and then, 20 mL of 1 M acid citric was added. After 60 min, the precipitate was collected in the bottom of the vessel using a permanent magnet and washed five times with distilled water to remove excess NH4OH solution. Finally, it was freeze dried for 48 h. SiO₂ coating on magnetite nanoparticles was the next step which took place by Stober process [16]. To have this done, 0.1 g magnetite nanoparticles and 16 mL deionized water were mixed for 15 min using ultrasonic technique (Branson 3510, 60 Hz). Then 80 mL ethanol, 2 mL ammonia and 0.1 mL TEOS were added to the flask on a magnetic stirrer. Fe₃O₄-SiO₂ (FS) nanoparticles were gathered magnetically after 2 h, washed and dried in the oven. As the last step, TiO₂

layer was deposited on FS nanoparticles by sol–gel. This process was accomplished by hydrolysis of TBOT in the presence of FS seeds, ethanol and deionized water for 180 min, resulting in a core–shell structure. Nanoparticles with 2 shells (SiO₂ and TiO₂) obtained here are called FST. In order to compare the role of SiO₂ on photocatalytic property, Fe_3O_4 -TiO₂ (FT) nanoparticles with the same conditions, but omission of Stober process, was obtained. Both samples were heat treated at 450 °C for 3 h with a rate of 8 °C/min to transform amorphous TiO₂ to anatase. The important parameters that are effective in obtaining optimal coverage have been studied in detail in our previous work [14].

2.3. Batch adsorption experiments

For adsorption studies, initial concentrations of 2, 5, 8 and 10 ppm were considered. To do so, a 20 ppm stock was prepared by dissolving Pb(NO₃)₂ in Deionized water (DI). Hereafter, mentioned initial concentrations of Pb(II) were provided by dilution of 20 ppm stock. Temperature and adsorbent concentration were constant in all tests and were set at 37 °C and 600 mg L⁻¹, respectively.

In addition, three tests were run to evaluate activation energy and thermodynamic adsorption parameters of Pb(II) with initial concentration of 10 ppm at 32, 37 and 42 $^{\circ}$ C.

The adsorption of Pb(II) on FST and FT was carried out by the batch technique. The mixtures of nanoparticles suspensions in DI were dispersed ultrasonically at 60 Hz for 15 min to obtain a completely homogenous colloid. Then, the desired concentration of Pb(II) solution was added and put on shaker at 160 rpm. After determined time intervals, suspension was sampled and placed under magnetic field to separate nanoparticles, and the remained concentration of Pb(II) in supernatant was analyzed by ICP-OES.

The complete process of nanoparticles preparation and adsorption experiments are depicted in a flow chart in schematic 1.

2.4. Characterization

XRD: The crystal phase identification of nanoparticles before and after heat treatment was carried out by X–ray diffraction (XRD Explorer, GNR, Italy) with Dectris detector (fast stript) using a CuK_{α 1,2} radiation set (at 40 KV and 30 mA at room temperature with a 2 θ range of 20-80°). The step size and integration time were 0.01° and 2 s, respectively.

BET: The pore size and surface area was done by N_2 adsorption-desorption isotherms using Braunauer-Emmett-Teller (BET) analysis (Autosorb1-C-Quntachrome).

ICP: The concentration of remained heavy metal ions in solution after removal were determined using an inductively coupled plasmaoptical emission spectrometer (ICP-OES, 76004555spectroarcos, Germany).

XPS: The X-Ray photoelectron spectra (XPS) were characterized by spectrometer using Mg K_{α} X-ray source as incident radiation. The charging effect is removed by activation the flood gun at measurement time. The line C 1s at BE 285 eV is used to calibrate the XPS spectra. XPS lines of Pb 4*f*, O 1*s*, Si 2*p*, Ti 2*p* and Fe 2*p* were recorded. Spectral deconvolution was accomplished using CASAxps software.

3. Results and discussion

3.1. Adsorption kinetics

Fig. 1 shows the adsorption capacity of Pb(II) on FST and FT under varying time interval, initial concentration and type of adsorbent. The two-step adsorption process is shown by multi-linearity of these graphs, representing external mass transfer (step of rapid adsorption) and intraparticle diffusion (step of slow adsorption). The initial linear step is due to heavy metal diffusion through solution to the nanoparticles. It takes



Fig. 1. Adsorption capacity of Pb(II) on FST and FT versus time with varying initial concentrations of 2, 5, 8 and 10 ppm.

 \approx 15 min and almost 90% of contaminants are adsorbed in this level. The second step is slower and under the control of intra-particle diffusion. In this part, the ions that have reached the surface of nanoparticles diffuse the pores and internal structure of particles and it takes almost an hour to achieve equilibrium [3].

To determine the feasibility of a removal process, the rate-controlling step and removal mechanism of Pb(II) by FST and FT nanoparticles, two kinetic models of pseudo-first order and pseudo-second order were applied in this study. Based on pseudo-first order equation (Eq. (1)) [17], plotting $\ln(q_e \cdot q_i)$ versus *t* shows the validity of model, whereas the evaluation of pseudo-second order model was done by plotting t/q_t versus *t* (Eq. (2)) [18]. The mentioned equations are described as follow, for pseudo-first order and pseudo-second order models, repectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

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

where q_e and q_t (mg g^{-1}) are the amount of Pb(II) adsorption per adsorbent mass unit at equilibrium and t, respectively. Moreover, k_1 and k_2 are pseudo-first order and pseudo-second order rate constants, respectively.

As shown in Fig. 2A,B, the removal kinetics of Pb(II) by FST and FT does not obey pseudo-first order equation and fits better with pseudo-second order one. The calculated parameters of two kinetic models are listed in Table 1.

According to Table 1, the correlation coefficients obtained by pseudo-first order model are not mostly acceptable. So the best agreement was observed between the data and the pseudo-second order kinetic model. This model is used to explain chemical adsorption, specifically adsorption of metal ions on different adsorbents [19]. According to pseudo-second order model, the results demonstrated that the adsorption is irreversible and the rate of whole removal process was dominated by chemical adsorption, i.e., sharing pairs of electrons between adsorbate and adsorbent (nanoparticles) [3]. In this step, adsorbate can be a heavy metal ion (Pb(II)) or a combination of metal ions with oxygen and hydrogen (Pb(OH)⁺) [3].

An increase in initial concentration of contaminant results in a decrease in their mobility and permeability to reach the exterior surface of nanoparticles and makes mass transfer difficult. So as Fig. 3A depicts, when initial concentration of Pb(II) enhances, rate constant for both samples declines. Also it can be said that rate constant of FST is higher than that of FT, representing FST's desirable surface for ion adsorption. Fig. 3B illustrates that for all initial ion concentrations, q_e of FST



Fig. 2. (A) Pseudo-first order and (B) Pseudo-second order kinetic model for removal of Pb(II) with initial concentrations of 2, 5, 8 and 10 ppm.

overtakes that of FT.

A look at N₂ adsorption-desorption isotherms of FST and FT (Fig. 4) clears one of the reasons of higher lead uptake by the presence of SiO₂ shell. According to Fig. 4, both samples exhibited type IVa isotherm (based on IUPAC report) which are given by mesoporous materials [20]. Based on BET analysis data (Table 2), the specific surface area of FST nanoparticles was calculated to be 138.7 $m^2 g^{-1}$, which was higher than that of FT (79.94 $m^2 g^{-1}$). The high surface area for FST nanoparticles is established as a result of porous underlying SiO₂ layer. Therefore, the difference of the specific surface areas of samples can significantly influence their performance in pollution management, i.e., FST nanoparticles possess more favorable adsorption sites and therefore it is reasonable to show greater rate constant and equilibrium adsorption capacity. Although the size of the pores in the two samples is almost the same, greater pore volume on FST nanoparticles' surface can increase adsorption rate in intra-particle diffusion step and prepare more favorable adsorption sites for Pb(II).

Thermal instability of FT nanoparticles is another reason for their lower efficiency. Fig. 5b shows obviously that after heat treatment, Fe₃O₄ in FT structure is partially oxidized to Fe₂O₃ as well as formation of new Fe-Ti-O component, named Pseudobrookit at 41.5° and 49.38°. The presence of these components have negative effect on photocatalytic property of FT since TiO₂ has better photoactivity [21]. However, SiO₂ mid-layer in FST nanostructure proved no change in compositions of Fe₃O₄ core or TiO₂ coating after heat treatment (Fig. 5d).

Removal process of heavy metals can be divided into two stages which are the main mechanism of heavy metal removal by metal-oxide nanoparticles: 1. Electrostatic attraction (including mass transfer and intra-particle diffusion), and 2. Forming bond on the nanoparticles surface via chemical bonding [22]. The surface of nanoparticles contained hydroxyl groups and physically adsorbed water molecules [3]. Presence of hydroxyl groups on the surface resulted in negatively charged nanoparticles. Zeta potentials of FST and FT nanoparticles in aqueous solution are illustrated in Fig. 6. Based on this figure, more hydroxyl groups on FST can be observed at pH = 7, implying more negative surfaces. Since Pb(II) ions existed predominantly at pH = 7 beside Pb(OH)⁺ (among other probable species, e.g. Pb₄(OH)₄⁴⁺ and Pb₃(OH)₄²⁺, Pb(OH)₃, Pb(OH)₂) [23], the electrostatic attraction between negatively charged nanoparticles and positively charged species is spontaneous and can be considered as the initial driving force to bind the cations onto the surface; of course the tendency of ions to FST is greater than FT. After the first stage, lead ions reach the nanoparticle surface and different bond formation occurs.

3.2. Activation energy

In general, any chemical interaction is possible if kinetic energy is sufficient. Herein, collision between Pb(II) ions and nanoparticles with enough energy and in right direction results in breaking bonds on the surface and formation of new bond. So the process of adsorption of lead ion on nanoparticles needs activation energy to be started, which can be calculated by Arrhenius equation [24]:

$$k = Ae^{-E_a/RT} \to \ln k = \ln A - \frac{E_a}{RT}$$
(3)

where E_a is the activation energy for the reaction, *k* is the rate constant, *T* is the absolute temperature (K), *A* is the pre-exponential factor and *R* is the universal gas constant. The activation energy in the range of 5–40 kJ mol⁻¹ and 40–800 kJ mol⁻¹ represents physical and chemical adsorption, respectively [25]. Fig. 7 depicts the logarithm of pseudo-second order constant versus reciprocal batch temperature. Based on this figure, activation energy for FST and FT was calculated to be 55.54 kJ mol⁻¹ ($R^2 = 0.99$) and 78.77 kJ mol⁻¹ ($R^2 = 0.96$),

Table 1

Kinetic parameters	of Pb(II)	adsorption	on FST	and 1	FT nanopartio	cles.
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Kinetic Model				q _e , experimental	Initial Pb(II) concentration	Material Code		
Pseudo-second order Pseudo-first order								
$q_e (mg g^{-1})$	\mathbb{R}^2	$K_2 (g mg^{-1} min^{-1})$	q _e (mg g ⁻¹)	\mathbb{R}^2	$K_1 (min^{-1})$			
14.6	0.99	0.03	11.9	0.94	0.08	14.27	10	FST
10.36	0.98	0.03	9.43	0.96	0.07	10.21	8	
7.82	0.99	0.12	4.17	0.69	0.04	8.11	5	
3.31	0.99	8.3	1.13	0.34	0.03	3.51	2	
11.87	0.99	0.01	3.22	0.11	0.03	12.94	10	FT
8.48	0.97	0.02	8.25	0.96	0.06	8.36	8	
7.09	0.98	0.05	5.12	0.83	0.04	7.3	5	
3.247	0.99	1.09	3.48	_	0	3.483	2	



Fig. 3. (A) Rate constant of pseudo-second order kinetic model. (B) Equilibrium adsorption capacity.



Fig. 4. N2 adsorption-desorption isotherms of FST and FT nanoparticles.

Table 2

Parameters extracted from BET analysis.

Pore volume (cc g^{-1})	Pore size (°A)	Surface area (m ² g ^{-1})	Material
0.09568	47.87	79.94	FT
0.1613	46.53	138.7	FST

respectively. The resulting E_a indicate the chemical adsorption which also confirms the matching of data to the pseudo-second order kinetic model.

3.3. Adsorption isotherm

To study the adsorption capacities of adsorbents, the adsorption isotherm of Pb(II) on FST and FT nanoparticles was evaluated. Therefore the experimental data was fitted to two models of Langmuir and Freundlich. The same adsorption sites on solid surface, monolayer adsorption and no interaction or steric barrier among adsorbed molecules on surface (even adjacent molecules) are the assumptions of Langmuir [23]. However, the Freundlich is an empirical relationship which assumes that the surface of solid adsorbent is heterogeneous and the surface sites of solid have a spectrum of different binding energies [23]. The Langmuir and Freundlich models are defining as Eqs. (4) [26] and 5 [27]:



Fig. 5. XRD patterns of: (a) FT before heat treatment, (b) FT after heat treatment, (c) FST before heat treatment, and (d) FST after heat treatment.



Fig. 6. Zeta potential of FST and FT nanoparticles at pH = 3 to 7, in aqueous solution.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max}K_L}$$
(4)



Fig. 7. Plots of ln K_2 vs. 1/T for Calculation of E_a according to Arrhenius equation, $C_{nanoparticles}$ = 600 mg $L^{-1},\ C_0$ Pb(II) = 10 ppm, T = 305, 310, 315 K.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where $q_e (\text{mg g}^{-1})$ and $C_e (\text{mg L}^{-1})$ are the amount of Pb(II) adsorption per adsorbent mass unit and Pb(II) concentration at solution after equilibrium, respectively. K_L (L mg⁻¹) and K_F (mg g⁻¹) are the Langmuir and Freundlich constants, respectively. q_{max} (mg g⁻¹) is the maximum adsorption capacity, and n indicates the tendency of adsorbate to the solid surface, so that for $0.1 < n^{-1} < 0.5$, $0.5 < n^{-1} < 1$ and $n^{-1} > 1$ adsorption would be easy, hard and impossible, respectively [28]. In addition, it can be said that the more heterogeneous the surface, the closer the slope is to zero [29].

Fig. 8A,B show the adsorption isotherms of Pb(II) on FT and FST nanoparticles based on Langmuir and Freundlich models. Also, the relevant parameters calculated from the two models are listed in Table 3.

The correlation coefficients obtained from Langmuir model point that this model is less suitable to describe adsorption of Pb(II) on nanoparticles, while Freundlich fits better with the data of adsorption process in equilibrium. The values obtained for n^{-1} shows the ease of heavy metal ion adsorption on nanoparticles and the non-uniform surface of the adsorbents. n^{-1} for FST (0.25) in comparison with that of FT (0.28) shows that the surface of FST nanoparticles is much more desirable for Pb(II) ions to be adsorbed. In addition, Freundlich constant explains relative adsorption capacity of Pb(II) ions on adsorbent. So it is obvious that FST nanoparticles have higher capacity and

Table 3

Parameters for isotherm models of Pb(II) adsorption on FT and FST nanoparticles (T = 310 K).

Isothe	rm Model		Material Code			
Freun	dlich		Langn	nuir		
R ²	n ⁻¹ (L ⁻¹ g)	K _F (mg g ⁻¹)	R ²	K _L (L mg ⁻¹)	q _{max} (mg g ⁻¹)	
0.96 0.97	0.25 0.28	10.69 7.33	0.89 0.87	15.59 2.967	12.1 11.23	FST FT



Fig. 9. Plots of lnK_d vs. 1/T for calculation of thermodynamic parameters, $C_{0,\ Pb}_{(II)}$ = 10 ppm.

tendency to Pb(II) ions.

3.4. Thermodynamic of adsorption

The thermodynamic parameters were estimated from the adsorption isotherms at three different temperatures. Herein, the parameters of entropy and enthalpy were obtained by the slope and intercept of the plots of lnK_d versus 1/T (Fig. 9) based on the following equations [30]:

$$\Delta G^{\circ} = -RT \ln K_d \tag{6}$$

$$\ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(7)



Fig. 8. (A) Langmuir and (B) Freundlich adsorption isotherms of Pb(II) adsorption on FT and FST at T = 310 K.

Table 4

Thermodynamic parameters of Pb(II) adsorption on FT and FST nanoparticles.

Parameters ΔG° (kJ mol ⁻¹)		ΔS° (J mol ⁻¹ .K ⁻¹)	ΔH° (kJ mol ⁻¹)	Adsorbents	
315 K	310 K	305 K	_		
-7.26 -3.72	-6.11 -3.05	-4.96 -2.39	230.78 133.31	65.43 38.27	FST FT

where *R* (8.314 J mol⁻¹ k⁻¹) is the gas constant, K_d represents the adsorption equilibrium constant, *T* is the absolute temperature in Kelvin. In addition, ΔG° , ΔH° and ΔS° are symbols of standard Gibbs free energy change, standard enthalpy change and standard entropy change of the adsorption, respectively. The thermodynamic values calculated from Eqs. (6) and (7) for different adsorbents are tabulated in Table 4.

In the present study, the positive enthalpy values for both samples revealed that the adsorption process was endothermic. Also, ΔG° value of adsorption of Pb(II) on FST is more negative in comparison with that of Pb(II) on FT, indicating that the adsorption on FST nanoparticles occurs more spontaneously, as negative ΔG° is a sign of spontaneous process.

3.5. XPS investigation

To identify the chemical lead species in the reaction products and investigate the adsorption mechanism by the presence of porous SiO₂,

Pb-free and Pb-loaded FST and FT nanostructures were prepared and analyzed by XPS. Samples are assigned as FST (before adsorption), FT (before adsorption), FSTPb (after adsorption), and FTPb (after adsorption). The full-range XPS spectra, before and after adsorption, are shown in Fig. 10. As shown in Fig. 10A, FST nanoparticles contain O 1s, Ti 2p, Fe 2p and Si 2p peaks while Si-related peaks were not observed for FT nanoparticles (Fig. 10B). After adsorption, Pb-related peaks are appeared in both samples (Fig. 10C, D), which demonstrates successful chemical adsorption of Pb on the surface of nanoparticles. Albeit, Pb 4f peak of FST possesses higher intensity than that of FT which is a sign of FST higher adsorption capacity. For more details, core-level XPS spectra of O 1 s, Ti 2p, Fe 2p, and Pb 4f are to be investigated.

O 1s: A high-resolution O 1s XPS spectrum of FST in Fig. 11A (before adsorption) is deconvoluted into 6 peaks. The peaks which are located at 532.97 and 533.85 eV are related to the oxygen atoms in bridging and terminal hydroxyl groups that were bound to titanium atoms (Ti-OH), while oxygen atoms in H₂O molecules (O–H) are proved by the peak at 534.64 eV [23,31]. Henderson et al. reported that different kinds of hydroxyl groups can be formed on TiO₂ nanostructures when exposed to water molecules [32]. These groups named terminal and bridging hydroxyl are due to the existence of Lewis acid or Lewis base sites. 5-coordinate Ti(IV) cations (as acidic sites) and 2-coordinate O(II) - anions (as basic sites) allow the O or H of water to bond. So after entering water, two types of hydroxyl groups can be created on the surface of nanoparticles. Moreover, the O 1 *s* spectrum at 530.63 eV assigned to the oxygen in the lattice (Ti-O) and KL₂₃L₂₃ Auger spectra at 975.6 eV (shown in full-spectrum Fig. 10A,C) which clearly evidence



Fig. 10. Full-scan XPS spectra of: (A) FST before Pb(II) adsorption, (B) FT before Pb(II) adsorption, (C) FST after Pb(II) adsorption, and (D) FT after Pb(II) adsorption.



Fig. 11. The O 1s XPS spectra of: (A) FST before Pb(II) adsorption, (B) FT before Pb(II) adsorption, (C) FST after Pb(II) adsorption, and (D) FT after Pb(II) adsorption.

the existence of TiO₂ [33]. Two peaks at 531.3 and 532.24 eV in Fig. 11A belong to the oxygen in Fe-O and Si-O, respectively. Silica deposition as the underlying layer for titania as well as magnetite in the core results in low Si-O and Fe-O intensities. It is obvious that the O 1s XPS spectra of sample changed after adsorption of Pb(II) (Fig. 11C). A change in total O 1s area from 5339.1 to 5760.43 indicates that the amount of oxygen in FST is increased after adsorption. However, very minor change in FWHM, from 2.536 to 2.519, reveals that oxygen increase is not due to a change in FST nanoparticles chemical composition, and it results from lead bond formation on the surface. In fact, the hydrogen ions in Ti-OH groups which are placed on the surface of nanoparticles may be exchanged with heavy metal ions species (Pb(II)) [34] and formed Ti-O-Pb⁺ [35]. So two H⁺ of hydroxyl group should be replaced by lead in order to have an inert composition [36]. In the case of Pb(OH)⁺, it needs just one H⁺. The terminal OH decreased while the bridging one increased. Pb-O peak has been clearly emerged at 529.67 eV [1]. According to successive decrease in electronegativity difference of Ti-O, Si (Fe)-O and Pb-O, the later possesses lower binding energy [29]. Pb-O is responsible for a shift in all components toward higher binding energies which was attributed to the bond formation between lead and oxygen atoms and influenced electrons surrounding the oxygen atoms.

An extra hill beside the main oxygen peak in FST (Fig. 11A,C) is due to the presence of SiO₂ in the structure and a large amount of OH groups on the surface [37]. So it is not observed in O 1*s* peaks of FT as illustrated in Fig. 11B,D. However, intense Fe-O peak in Fig. 11B (related to FT) proves the entrance of Fe ions to the surface after heat treatment. The peak of Ti-O in FT (%area = 51.86) is lower than that of FST (%area = 69.31) which as well indicates that some surface oxygen are involved in Fe compositions. Total area corresponding to bridging and terminal O (Me-OH; Me = Ti or Fe) in FT is 16.64% and in FST is 21.3%. Thus it is clear that more suitable sites are located on FST surface for ion exchange with lead species. It was previously proved by Zeta potential results. It has been claimed the surface OH groups increases with $\Delta \chi_{M-O}$. The term of $\Delta \chi_{M-O}$ describes the electronegativity difference between the oxygen and metal element directly bound to the oxygen atom. Since parts of the surface of FT nanoparticles are covered by Fe-O ($\Delta \chi_{Fe-O} = 1.61$) in addition to Ti-O bonds ($\Delta \chi_{Ti-O} = 1.9$), FT nanoparticles have less potential to adsorb hydroxyl groups [38].

After lead adsorption on FT (Fig. 11D), a Pb-O peak at 528.67 eV is appeared which its belonged area (0.33%) reveals that FT nanoparticles have lower capacity for Pb(II) adsorption. Moreover, the specific peak at 532.58 eV is ascribed to Fe-O-Ti in Fe₂TiO₅ [39].

The O 1s total area of FT nanoparticles had an impressive increase after lead adsorption (from 4522.84 to 5742.14), which along with peak broadening (FWHM = 1.794 to 3.555) is a sign of not only Pb-O bond formation but also chemical composition change in FT nanostructure. It can be interpreted that FT nanoparticles, unlike FST, are chemically unstable.

Ti 2p: A high-resolution Ti 2p XPS spectra of FT and FST (before and after adsorption) are shown in Fig. 12. The Ti 2p spectrum for FST (Fig. 12A) exhibits two contributions, Ti $2p_{3/2}$ and Ti $2p_{1/2}$ (resulted from the spin–orbit splitting), at 459.1 eV and 464.8 eV respectively. The results represented that Ti was in Ti(IV) state which belongs to pure anatase TiO₂ [33,40]. Moreover, a peak which is corresponded to Ti in Ti-O-Si bond is seen at 461.09 eV and proves chemical bonding between TiO₂ and SiO₂ layers. In Fig. 12C, it can be seen that after Pb adsorption on FST, a small peak at 462.21 eV is emerged which is related to Ti-O-Pb bond formation. In consequence, PbTiO₃ forms on FST surface via chemical bond and results in a slight shift in Ti 2p double peaks toward higher binding energies, suggesting no specific effects on the electron density surrounding the titanium atom. In addition, a decrease in Ti(IV) %area after adsorption is another result of PbTiO₃ formation. Approximate stability in FWHM and area before and after lead adsorption on



Fig. 12. The Ti 2p XPS spectra of: (A) FST before Pb(II) adsorption, (B) FT before Pb(II) adsorption, (C) FST after Pb(II) adsorption, and (D) FT after Pb(II) adsorption.

FST is an evidence of FST nanoparticles chemical stability.

For FT, in addition to Ti(IV) in anatase TiO₂ structure (purple peaks), a second Ti(IV) can be seen in Fig. 12B which is attributed to Fe₂TiO₅ (dark blue peaks) [39,41]. There is no evidence of trivalent Ti (Ti(III)), which usually appears at 457 eV [39]. After adsorption, the amount of TiO₂ is decreased drastically (Fig. 12D), Ti-O-Pb and Ti(III) are created at 461.63 and 456.7 eV, respectively. Creation of Ti(III) is implying Ti₂O₃ formation [42] and chemical instability of FT nanoparticles. Also FT XPS spectrum after Pb adsorption illustrated a drastic decrease in Ti 2*p* area (3369.9 to 829.63) in comparison to the one before Pb adsorption.

Fe 2p: Fig. 13A shows the core-level XPS spectra of Fe 2p corresponding to Fe₃O₄. The main peaks of Fe(III) $2p_{3/2}$ and Fe(III) $2p_{1/2}$ are located at 711.89 and 725.53 eV, which are considered as specific Fe₃O₄ spectrum [6]. Moreover, by fitting Fe 2*p* double peak, another peaks yield at 710.94 and 723.33 eV, which belong to Fe(II) $2p_{3/2}$ and Fe(II) $2p_{1/2}$ [6]. A peak at 719.51 is also attributed to Fe₃O₄ and called Fe(III) satellite [43]. Albeit there is also an Fe(II) satellite in Fe₃O₄ structure which can rarely be seen in nanostructures [43]. After adsorption, no impressive change is observed (Fig. 13C) because Fe atoms are located in the core of structure and adsorption of Pb cannot affect them. Fe(III)/Fe(II) ratio for FST before and after adsorption is about 2, which is in good agreement with stoichiometry of Fe_3O_4 [6]. However, for FT nanoparticles, Fe(II) satellite can be seen beside Fe(III) satellite in Fig. 13B. It may be due to Fe atoms transfer to the surface and ease of detection by XPS. In this figure, extra Fe(III) double peaks (light blue) are appeared at 714.75 and 726.76 eV, which are belonged to Fe₂TiO₅ [39]. Fe(III)/Fe(II) ratio for FT is 3.8 which its deviation from stoichiometry of Fe_3O_4 is a sign of α - Fe_2O_3 formation (thermal instability). After Pb adsorption, Fe(II) peaks are reduced drastically (Fig. 13D), indicating that magnetite in core is turned to hematite (chemical instability). Fe(III) satellite peak is intense and in good consistent with

that of Fe₂TiO₅ [39,44,45].

Pb 4*f*: A high-resolution double Pb 4*f* XPS peaks for FST after Pb adsorption is illustrated in Fig. 14A. Deconvolution of these peaks was carried out to disclose Pb oxidation state. There are two peaks of Pb 4*f* for FST after adsorption, suggesting that two different Pb-O may exist at the surface of nanoparticles. An initial analysis revealed intense signals corresponding to Pb 4*f*_{7/2} and 4*f*_{5/2} photoelectrons at 139.51 and 144.19 eV, respectively. According to the energies found, the signal was assigned to PbTiO₃. This peak is in good agreement with the value of 139.1 eV reported in other reports [2]. According to the energies found at 138.45 and 141.21 eV, another compound could be fitted. The signal belongs to PbO, in agreement with the value of 138.6 eV which was reported previously [46].

The same compounds (PbTiO₃ and PbO) were found in FT after Pb adsorption XPS spectrum (Fig. 14B), too. However, the intensity of both Pb 4*f* peaks for FST are stronger than the ones for FT, which indicates that the amount of adsorbed Pb(II) on FST is much more. Moreover, there can be seen a third compound in FT, with binding energy of 145.43 eV [2].

It was demonstrated that after heat treatment and entering FT nanoparticles to the water, magnetite core changed to hematite as a result of oxidation and pseudobrookite formed on the surface as a result of Fe ion transfer to TiO₂ lattice (by XRD and XPS). So without SiO₂ midlayer in nanostructure, thermal and chemical instability leads it to a final structure with α -Fe₂O₃ in the core and combination of TiO₂ and Fe₂TiO₃ as the shell. Pure anatase TiO₂ in FST limits the fast e/h recombination, compared to Fe₂O₃/Fe₂TiO₅ in FT due to both: 1. the high absorption coefficient of TiO₂ compared to Fe₂O₃ [47].



Fig. 13. The Fe 2p XPS spectra of: (A) FST before Pb(II) adsorption, (B) FT before Pb(II) adsorption, (C) FST after Pb(II) adsorption, and (D) FT after Pb(II) adsorption.



Fig. 14. The Pb 4f XPS spectra of: (A) FST and (B) FT, after Pb(II) adsorption.

4. Conclusion

In this study, kinetic behavior of both FST and FT was fitted with pseudo-second order model; however, for all initial Pb concentrations, FST showed higher rate constant. Moreover, higher activation energy of FT (78.77 kJ mol⁻¹) in comparison to the one of FST (55.54 kJ mol⁻¹) was due to slower chemical adsorption on FT nanoparticles. Thermodynamic study on samples proved spontaneous adsorption, with more negative ΔG° for FST. Also, ΔG° of FST and FT became more negative by increasing temperature, which indicated endothermic process.

Thermal instability of FT nanoparticles was demonstrated by XRD while their chemical instability after Pb adsorption was seen in O 1s, Ti

2p and Fe 2p spectra. The analysis of Pb ions adsorbed on FT and FST using XPS demonstrated that chemical adsorption occurred via ion exchange between H⁺ (in terminal-OH) and Pb(II). XPS O 1s and Pb 4f spectra indicated that polytype Pb-O bonds (PbTiO₃ and PbO) formed due to the interactions between Pb cations and hydroxyl groups. Moreover, Pb-O-Fe bonds were seen in Pb 4f plot of FT, suggesting the presence of Fe on surface.

Three important factors can be mentioned for higher removal capacity and stability of Fe_3O_4 -SiO₂-TiO₂ nanoparticles as the result of porous SiO₂ mid-layer:

1. SiO₂ as an insulator and anti-sintering agent keeps nanostructure intact against thermal and chemical instability; so during different

processes no chemical and structural changes occur. On the other hand, in Fe₃O₄-TiO₂ nanoparticles, conversion of magnetite in the core to hematite results from oxidation as well as formation of Fe₂TiO₅ on the surface which is due to Fe ions penetration to TiO₂ lattice. Fe₂TiO₅/Fe₂O₃ interface act as the place of e/h recombination, thus adsorption property of FT nanoparticle reduces.

- 2. More negative surface of FST nanoparticles is the consequence of more electronegativity difference between oxygen and the metalic atom which is bonded to it (Ti). The more the electronegativity difference, the more potential to adsorb OH groups and the more negative surface. Thus, FST nanoparticles show higher electrostatic attraction to Pb(II) and Pb(OH)⁺ cations.
- 3. The other effect is to establish a large surface-to-volume ratio as a result of porous surface under TiO_2 deposition and raise catalytic surface reactions.

The above-mentioned factors make FST nanoparticles a definitely proper nano-system for heavy metal removal with higher adsorption kinetics and isotherm, more spontaneous process (for more negative standard Gibbs free energy change), and lower activation energy to begin chemical bond formation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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