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Potential of L-tyrosine and L-tryptophan modified silica nanoparticles as adsorbents for Pb(II) ions: kinetics and thermodynamic investigation

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ABSTRACT

The search for novel adsorbents to lower the concentration of toxic species in polluted waters is ongoing globally. Organic ligands such as L-tyrosine (Tyr) and L-tryptophan (Trp) are constituted by electron-donors (i.e., oxygen and nitrogen atoms), and these ligands can greatly enhance the sorption capabilities of nanoparticles for toxic metallic ions. The effect of parameters influencing adsorption efficiency of Pb(II) by two adsorbents bearing Tyr (Tyr-SiO_2) and Trp (Trp-SiO_2) groups, including aqueous phase pH, amount of adsorbent, stirring time and initial concentration of the metal ions were assessed and discussed. Under optimum experimental conditions (0.2 g of the adsorbents, solution pH 5 and 1,000 rpm stirring rate), Tyr-SiO_2 showed a capacity of 7.60 mg/g after 10 min. Under the same conditions, the capacity presented by Trp-SiO_2 was 6.92 mg/g after 60 min. It was found that the adsorbed Pb(II) ions can be recovered by acid backwashing of the loaded nanoparticles Tyr-SiO_2 and Trp-SiO_2 with 5 mL of nitric acid 0.1 mol/L or hydrochloric acid 1 mol/L. The calculated thermodynamic parameters indicated that the adsorption process based on Tyr-SiO_2 adsorbents was endothermic and controlled by entropy changes, while process based on Trp-SiO_2 adsorbent was exothermic and controlled by changes in enthalpy. The adsorption of Pb(II) ions onto the studied adsorbents was well described by Langmuir model. Pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models were examined during the investigation of the kinetics of adsorption of Pb(II) ions by Trp-SiO_2. This investigation indicated that the process is well described by pseudo-second-order kinetics. Although both the studied adsorbents showed good adsorptive capacity with respect to that reported for some other adsorbents, a higher adsorptive capacity, more rapid kinetics, and the ability to remove Pb(II) ions at lower pH values, were the superiority of Tyr-SiO_2 in comparison with Trp-SiO_2.

Keywords: Lead ions; Decontamination; Water solutions; Adsorption; Modified silica nanoparticles; Amino acids; Kinetics; Thermodynamics

1. Introduction

Pollution created by heavy metals is a serious environmental issue of global concern due to the rapid industrial progress [1–3]. Among heavy metals, lead has an eminent place due to its industrial applications [4] on one hand, and environmental aspects as a toxic chemical species [5,6], on the other hand. Production and consumption of lead are increasing worldwide, and on the weight basis, it is the fifth most used metal in the world [7]. The industrial sources of lead released into the environment are mainly battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass printing, painting and dying industries. These extensive industrial activities are the main anthropogenic source of lead found

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in the environment. Lead enters and accumulates in the human body via the food chain. This may eventually become a threat to human health since Pb(II) ions form strong, stable complexes with some enzymes and biomolecules, rendering them dysfunctional. This is the basis of lead poisoning [8]. Thus, the elimination of Pb(II) ions from the human food chain, particularly from water sources forms the subject of many investigations [9–14].

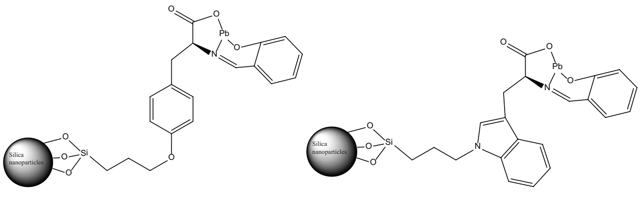
Some conventional methods for removal of heavy metals are chemical reverse osmosis, chemical precipitation, ion-exchange, liquid–liquid extraction, electrolytic and adsorption processes [15]. Although reverse osmosis is known as an effective method, it is a cost preventing process because the expensive membranes used in this technique required to be frequently replaced [16]. Chemical precipitation is another technique used for treatment of wastewater solutions containing high concentration of heavy metals [17]. This technique produces a large amount of sludge, and also suffers from inability to remove the trace amounts of pollutants in the samples. High cost and sophisticated procedure of ion-exchange techniques prohibit their application in removal of heavy metals from water and wastewater solutions [18]. The main disadvantages of liquid–liquid extraction (solvent extraction) methods are they need generally a large volume of expensive and toxic organic solvent [19]. In addition, effective solvent extraction needs to selective extractants, which are also cost-prohibitive. Electrocoagulation is not effective for removing metallic ions already in very dilute solutions [20,21].

Adsorption is one of the important techniques for removal of toxic species from water samples as it has been found to be simple and effective. This technique bears additional advantages of applicability at very low concentrations, low capital cost, ease of operation, suitable for using batch and continuous processes, possibility of regeneration and reuse the applied adsorbents and relatively little sludge generation [22–27].

Natural and synthetic adsorbents have been used in a great number of investigations relating to the decontamination of aqueous solutions. Among the synthetic materials, nanomaterials have been shown to be potential adsorbents and play a substantial role in adsorption of a variety of toxic species [28–33]. Silica nanoparticles bearing ligating functionalities were used for decontamination of water solutions from heavy metals [34–40].

Schiff base ligands bearing nitrogen/oxygen donor atoms have been shown to exhibit ionophoric properties, especially toward heavy metal ions; an ionophore is a chemical species that chemically binds ions reversibly [41]. These properties have been investigated by their application in a variety of analytical methods including solid phase extraction–concentration of trace amounts of metal ions [42,43], liquid–liquid extraction [44], cloud point extraction procedures [45,46] and transport of metal ions through liquid membranes [47].

The similarities in binding sites of amino acids and Schiff base molecules motivate us the study of the application of L-tyrosine and L-tryptophan amino acids modified nanosilica particles named (*S*)-2-((2-hydroxybenzylidene)amino)-3-(4-hydroxyphenyl)propanoic acid (Tyr-SiO_2) and (*S*)-2-((2-hydroxybenzylidene)amino)-3-(1*H*-indol-3-yl)propanoic acid (Trp-SiO_2) as adsorbents for decontamination of water solutions from Pb(II) ions. The surfaces of nanoparticles of silica have been modified by "Tyr" and "Trp" ligands. Structures of chelated complexes formed by Pb(II) ions with "Tyr" and "Trp" as complexants are conceptualized in Fig. 1. It is most likely that nitrogen and oxygen atoms are the donors of electrons with the result that covalent bonds are formed with lead ions. The 3-dimensional geometry of these chelates have yet to be instrumentally determined, but coordination numbers of 3–12 of Pb(II) have been reported in other types of complexes, with a variety of geometries such as octahedral, a few types of tetrahedral pyramids and a trigonal-capped hexagonal pyramid [48]. Therefore, the coordination number of the Pb(II) cation is not necessarily 6, as Fig. 1 suggests. Water molecules may or may not act as monodentate ligands to Pb(II).



Pb(II)/Tyr-SiO_2 Pb(II)/Trp-SiO_2

Fig. 1. Complexation of Pb(II) ions by the binding sites of the studied adsorbents.

The parameters affecting the adsorption properties of the studied adsorbents such as aqueous phase pH, amount of adsorbent, stirring time and initial concentration of the metal ions, were investigated and discussed. Experimental equilibrium data were evaluated using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. Pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion equations were tested to determine the kinetics of the adsorption process.

2. Materials and methods

2.1. Materials

Methanol, toluene, 3-(chloropropyl)-trimethoxysilane, 2-hydroxybenzaldehyde, L-tyrosine, L-tryptophan, hydrochloric acid, sodium hydroxide, nitric acid and sulfuric acid (Merck, Darmstadt, Germany) were used as received. Unmodified "silica" nanoparticles (APS 20–30 nm) were purchased from Iranian Nanomaterial Pioneers (Mashhad, Iran). Stock solution of Pb(II) ions (1,000 mg/L) was prepared using corresponding nitrate salts (Merck). The stock solutions were standardized complexometrically [49]. Working solutions were prepared by suitable dilution of the stock solution with deionized water.

2.2. Apparatus

Proton NMR (^{1}H NMR) measurements were performed using an FT-Bruker spectrometer (AVC 250 MHz) and the data were referenced relative to residual protonated solvents (7.26 ppm for $CDCl_3$). Fourier transform infrared (FTIR) spectra were recorded on a Thermo-Nicolet-iS10 FTIR spectrometer. The pH adjustments were performed using a Metrohm digital pH meter (model 780) equipped with a combined glass electrode. An Ika magnetic stirrer (MR 3001 K) was used for dispersing the adsorbent particles in the aqueous solutions. The temperature of the experiment vessels was controlled using a Julabo MP5 thermostat water circulator. Flame atomic absorption spectroscopy (FAAS; Varian 220AA) was used for metal ion determinations in water solutions. A furnace (Exiton, model Atash-1200-Iran) was applied for activation of the silica nanoparticle surfaces before modification. The separation of adsorbents from aqueous solution was assisted by a high speed centrifuge (Sigma, 3-30K). The SEM photograph was taken by a Philips XL30 scanning microscope. Deionized water with a resistivity of ≥18.2 MΩ was produced by an M-UV-3$^+$ Zolalan water purification system (Iran).

2.3. Preparation and characterization of modified silica nanoparticles

Modification of silica nanoparticles was carried out according to a procedure reported elsewhere [50]. Condensation of 2-hydroxybenzaldehyde with L-tyrosine and L-tryptophan in the presence of sodium hydroxide in toluene produced Schiff bases derived from L-tyrosine and L-tryptophan, (*S*)-2-((2-hydroxybenzylidene)amino)-3-(4-hydroxyphenyl) propanoic acid (Tyr-SiO_2) and (*S*)-2-((2-hydroxybenzylidene) amino)-3-(1*H*-indol-3-yl)propanoic acid (Trp-SiO_2), respectively. The prepared Schiff base ligands were characterized by ^1H NMR and FTIR spectroscopies. Refluxing the nanosized silicas with 3-(chloropropyl)-trimethoxysilane (CPTM) in toluene resulted CPTM/SiO_2. Then, the synthesized Schiff base ligands and CPTM/SiO_2 were refluxed in dichloromethane. The resulted products were the adsorbents Tyr-SiO_2 and Trp-SiO_2. Elemental analysis indicated that the amount of imine grafted on Tyr-SiO_2 and Trp-SiO_2 was 1.07×10^{-3} and 0.44×10^{-3} mol imine per gram of nanosilica, respectively. Fig. 2 shows the SEM of the adsorbent Tyr-SiO_2. The image shows that nanoparticles have a spherical morphology. Spectroscopic data of the products are given in supplementary data.

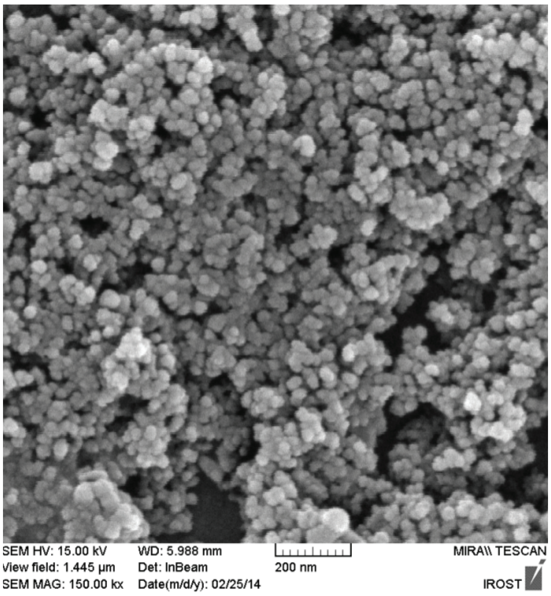


Fig. 2. SEM of the adsorbent Tyr-SiO_2.

2.4. Adsorption experiments

The adsorption experiments were carried out in stoppered plastic vessels using appropriate amount of adsorbent in 20 mL of a sample containing Pb(II) ions (20 mg/L) at pH 5. The adsorption equilibrium for Tyr-SiO_2 and Trp-SiO_2 was attained after 5 and 60 min, magnetically stirring the mixtures at 25°C, respectively. After separation of the phases by centrifugation (20,000 rpm), the cation concentration remaining in the aqueous phase was measured by FAAS. The percentage of ion uptake was calculated using Eq. (1):

$$\text{Uptake } \% = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

Here, C_0 and C_e are the initial and equilibrium concentration of Pb(II) ions (mg/L), respectively. In order to carry out the desorption experiments, 20 mL of aqueous solution containing 20 mg/L of Pb(II) ions adjusted at pH 5 was mixed with 0.2 g of the adsorbent and the mixture was magnetically stirred for 60 min. Then, the loaded adsorbents were separated and were washed twice by 5 mL of distilled water. After drying the adsorbents in an oven at 110°C, the stripping was realized by contacting the loaded Tyr-SiO_2 with 5 mL of nitric or hydrochloric acid 0.1 mol/L and the loaded Trp-SiO_2 with 5 mL of nitric acid 1 mol/L for desorption of Pb(II) ions, for 60 min. After separation of the phases, the aqueous solution was introduced to FAAS for metal determinations. The desorption efficiency was calculated by Eq. (2):

$$\text{Desorption } \% = \frac{m_d}{m_a} \times 100 \tag{2}$$

where m_d and m_a (mg) are the desorbed and adsorbed mass of ions, respectively.

3. Results and discussion

3.1. Effect of pH on the adsorption processes

Since the ionization of hydroxyl groups of the ligands grafted onto the nanosilica matrix depends on the aqueous phase pH, this parameter can play a decisive role on the adsorption efficiency of the adsorbents. The data in Fig. 3 confirm this role. A significant increase in adsorption of Pb(II) ions was observed by increasing the aqueous phase pH. An increase in the aqueous phase pH to 5.5 reduces the competition of H^+ ions and metal cations for adsorption sites. It is noteworthy that the investigation of adsorption at pH higher than 5.5 was not possible because of the precipitation of Pb(II) ions. These findings suggest an ion-exchange mechanism for the adsorption of the studied ions onto the adsorbents. The higher extraction percentage of Pb(II) ions at lower pH values by Tyr-SiO_2 with respect to Trp-SiO_2 indicated the higher acidic nature of the hydroxyl group anchored on the former adsorbent with respect to that of the latter. In addition, the higher adsorption efficiency of Tyr-SiO_2 can be attributed to the higher degree of the complexing groups grafted on this adsorbent with respect to Trp-SiO_2 (see section 2.3).

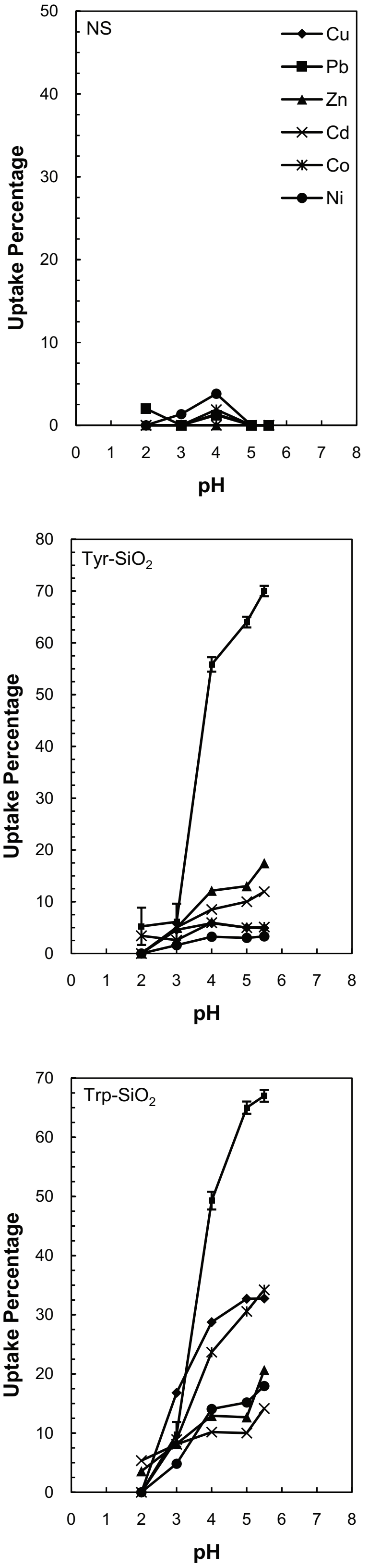


Fig. 3. Effect of pH on competitive adsorption of metal ions onto NS, Tyr-SiO_2 and Trp-SiO_2. Experimental condition: 20 mg/L initial concentration of metal ions; 0.05 g adsorbent; 60 min stirring time; 1,000 rpm; 25°C.

A comparison of the results obtained by using unmodified nanoparticles (NS) and modified nanoparticles (Tyr-SiO_2 and Trp-SiO_2; Fig. 3) revealed that modification remarkably increases Pb(II) uptake performance of the nanosilica particles.

In order to verify the selectivity of the studied adsorbents toward lead ions, the competitive adsorption of lead, copper, zinc, cadmium, cobalt and nickel ions onto NS, Tyr-SiO_2 and Trp-SiO_2 was performed. The results revealed a significant selectivity toward Pb(II) ions with respect to the examined ions, at higher pH values (Fig. 3). However, the selectivity toward Pb(II) ions presented by Tyr-SiO_2 adsorbent was more pronounced with respect to that of Trp-SiO_2.

The radius of the hydrated ion and the charge density (of which it is a function) to a large extent dictate the electrostatic forces of attraction and repulsion between adsorbent and adsorbate. The favorability of geometrical orientation of the ligand groups toward Pb(II) is very important, as opposed to steric hindrance of metal ion transfer to sites of complexation. These factors will affect any sorbent pairs.

3.2. Time dependency of the adsorption process

Following the progress of the adsorption process with respect to time serves to: (i) understand the time scale for the system to attain equilibrium; (ii) determine the required kinetics, that is, time taken for the separation process to achieve its objective of removing a preset percentage of metal ions in aqueous solution. The adsorption of metal ions from aqueous solution (pH 5) using 0.05 g of adsorbent was studied by contacting the solid and liquid phases in the range 3–120 min (Fig. 4). It was confirmed that the equilibrium of

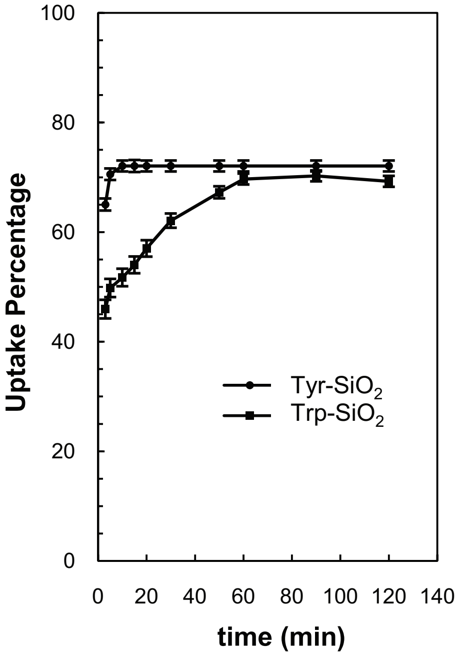


Fig. 4. Adsorption percentage of Pb(II) ions by Tyr-SiO_2 and Trp-SiO_2 as a function of stirring time. Experimental condition: 20 mg/L initial concentration of metal ions; 0.05 g adsorbent; pH 5 aqueous phase; 1,000 rpm; 25°C.

adsorption process for Pb(II) ions on the Tyr-SiO_2 adsorbent was very rapid and it can be attained after <5 magnetically stirring. However, this time was 60 min when Trp-SiO_2 was used. This investigation demonstrated that the kinetics of Pb(II) ions adsorption onto Tyr-SiO_2 is more rapid than Trp-SiO_2.

3.3. Adsorbent dose

The number of binding sites available for adsorption of an analyte depends directly on the amount of adsorbent, and therefore the adsorbent dose can affect the efficiency of the process. To determine the effect of this parameter, a series of experiments were carried out using 0.025–0.2 g of the adsorbents for removal of Pb(II) ions from aqueous phase, adjusted at pH 5 (Fig. 5). It was seen that an increase in the amount of adsorbents augments the removal percentage of Pb(II) ions. This can be attributed to the increase in the number of complexing groups available on the adsorbent surface. It was found that although the use of more than 0.1 g of Tyr-SiO_2 results quantitative removal of Pb(II) ions from the aqueous phase, the lower efficiency of Trp-SiO_2 results the removal of this ion up to 88% by using the same mass of the adsorbent. It means that by using the amounts more than 0.1 g of Trp-SiO_2 adsorbent, no significant increase in removal percentage was observed. The independency of the uptake amount of lead to the adsorbent dose beyond 0.1 g can be interpreted by a possible aggregation of higher dose of this adsorbent. Such observation has been also reported in other studies [51,52].

Also, this result can be shown by a simple calculation. 88% of Pb(II) ions removed means that X moles (1.7×10^{-6} mol) of Pb(II) ions removed by 0.1 g Trp-SiO_2 (initial concentration 20 mg/L). Therefore, number of moles of Pb(II) ions removed per unit mass of adsorbent is equal to $X/0.1$ (mol/g). So, 12% of the applied Pb(II) ions, that is, Y moles (2.3×10^{-7} mol) of them left in solution. We said that 0.1 g Trp-SiO_2 will not adsorb more than 88% of Pb(II) ions, and that the remaining 12% is removed (quantitatively) by an extra Z grams (0.05 g) of Trp-SiO_2. Therefore, the absorptive ability of Trp-SiO_2 is Y/Z (mol/g).

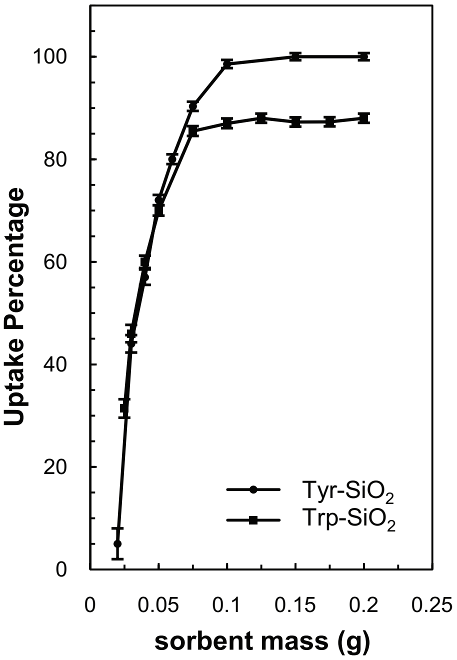


Fig. 5. Effect of the amount of Tyr-SiO_2 and Trp-SiO_2 nanoparticles on the adsorption of Pb(II) ions. Experimental condition: 20 mg/L initial concentration of metal ions; pH 5 aqueous phase; 60 min stirring time; 1,000 rpm; 25°C.

Since Y/Z (4.6×10^{-6} mol/g) is smaller than $X/0.1$ (1.7×10^{-5} mol/g), we may suggest that Trp-SiO_2 has aggregated to make a portion of its functional groups, so they will be unavailable for chelation.

3.4. Initial concentration of lead

An increase in the initial lead ion concentration in the aqueous solutions increases the adsorption percentage of the metal ions in the range 10–20 mg/L (Fig. 6(a)). A decrease in the relative complexing sites by increasing the initial concentration of lead ions beyond 50 mg/L, lowered the percentage of removal of the ions. This investigation allowed determination of the maximum amount of metal ions adsorbed (q_m) onto the adsorbents at pH 5 and at 25°C (Fig. 6(b)). The q_m values were found to be 7.60 and 6.92 mg/g for Tyr-SiO_2 and Trp-SiO_2 adsorbents, respectively. These values agree with the order of the amount of imines grafted onto modified nanosilica particles.

3.5. Desorption process

From economical and applied aspects, it is important to reuse an adsorbent after its application in an adsorption process. To this end, a series of adsorption and desorption experiments were performed, as discussed in section 2.4. The loaded adsorbents were stripped with 5 mL of nitric acid, hydrochloric acid and sulfuric acid solutions (0.1 mol/L), for 60 min. It was found that, hydrochloric or nitric acid solutions are able to strip quantitatively Pb(II) ions (95% and 100%, respectively) from Tyr-SiO_2. None of the examined acid solutions could strip quantitatively Pb(II) ions from Trp-SiO_2 surface. For a quantitative stripping of lead ions from loaded Trp-SiO_2, the stripped adsorbent from the first step by nitric acid solution (5 mL, 1 mol/L) was mixed with a second 5 mL solution of 1 mol/L nitric acid. Under such conditions, an amount of ~70% of the adsorbed metal ions was back-extracted into the aqueous phase. It is noteworthy that by increasing the acid concentration up to 2 mol/L, a significant improvement was not observed in the desorption efficiency of the loaded lead ions from the surface of the adsorbents. The separated nanoparticles were used repeatedly for the experiments described above. The results revealed the stability of the adsorbents and it were seen that the capacity of the adsorbents decreased lower than 5% after three adsorption–desorption cycles.

3.6. Applicability of the process

A series of experiments were designed to elucidate the applicability of the proposed adsorbents for decontamination of water samples from lead ions. Three water samples (tap and well water samples from the University of Zanjan campus, and a sample of molten snow) were first digested by nitric

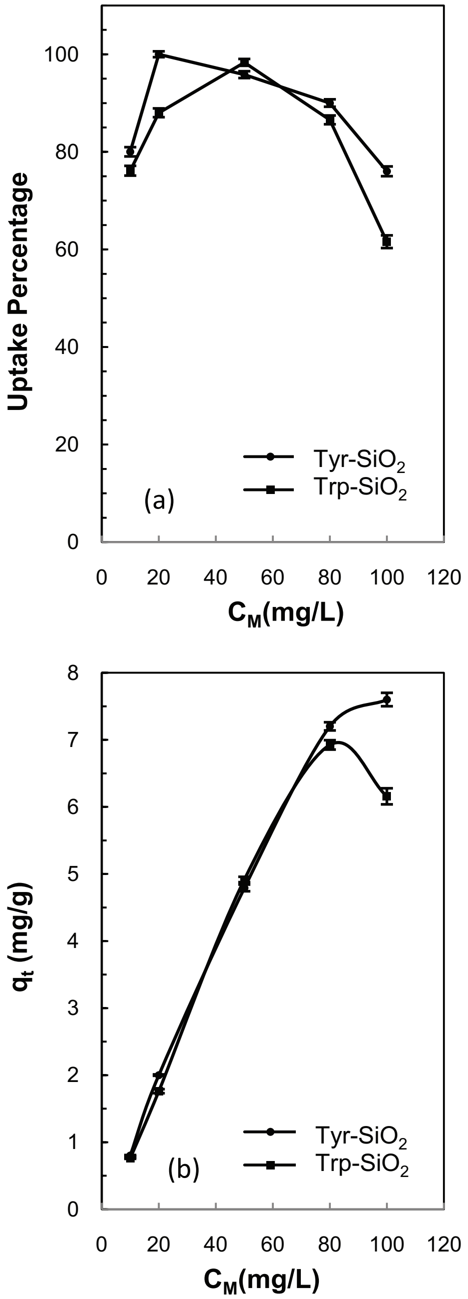


Fig. 6. Variation of Pb(II) uptake percentage (a) and adsorbents capacity (b) as a function of the initial Pb(II) ions concentration in aqueous solutions. Experimental condition: 0.2 g adsorbent; pH 5 aqueous phase; 60 min stirring time; 1,000 rpm; 25°C.

acid solution. The resulting solutions were spiked with Pb(II) ions (20 mg/L). A volume of 20 mL of samples adjusted at pH 5 was stirred with 0.2 g of one of the adsorbents at room temperature. After 60 min of magnetic stirring, the solid particles were separated from the aqueous phase by centrifugation. The concentration of Pb(II) ions remaining in the aqueous phase was determined by FAAS. These experiments were repeated three times. The results are given in Table 1. It was found that 100% of Pb(II) ions by Tyr-SiO_2 and ~86% of this ion by Trp-SiO_2 were removed under selected conditions.

Table 1
Applicability of the adsorbents for removal of Pb(II) ions from real samples[a]

Adsorbent	Well water	Tap water	Molten snow
Tyr-SiO_2	99.4 (±0.3)	99.8 (±0.3)	100.0 (±0.5)
Trp-SiO_2	85.6 (±0.4)	88.4 (±0.2)	86.8 (±0.3)

[a]Experimental conditions: aqueous phase, 20 mL of the samples injected by 20 mg/L of Pb(II) ions; pH 5; 0.2 g adsorbent dose; 60 min stirring time; 1,000 rpm; 25°C.

3.7. Thermodynamics of the process

To verify the influence of temperature on the studied adsorption processes and evaluating the corresponding thermodynamic functions, the removal of lead ions from aqueous solutions by the modified nanoparticles was examined in the range of 293–323 K. The thermodynamic distribution coefficient (K_0) was calculated using Eq. (3):

$$K_0 = \frac{a_s}{a_e} = \frac{\gamma_s}{\gamma_e}\frac{C_s}{C_e} \tag{3}$$

where a_s is the activity of adsorbed Pb(II), a_e is the activity of Pb(II) in solution at equilibrium, γ_s is the activity coefficient of adsorbed Pb(II), γ_e is the activity coefficient of Pb(II) in equilibrium solution, C_s is the Pb(II) concentration adsorbed on adsorbent (mmol/g) and C_e is the Pb(II) concentration in equilibrium solution (mmol/mL). The expression of K_0 can be simplified by assuming that the concentration in the solution approaches zero resulting in $C_s \rightarrow 0$ and $C_e \rightarrow 0$ and the activity coefficients approach unity at these very low concentrations [53]. Eq. (3) can be written as:

$$C_s \rightarrow 0,\; K_0 = \frac{a_s}{a_e} = \frac{C_s}{C_e} \tag{4}$$

It was found that the adsorption of Pb(II) ions onto Tyr-SiO_2 increases with temperature, whereas a decrease in lead adsorption by Trp-SiO_2 was observed by increasing temperature (Fig. 7).

By considering the equation which relates the free-energy changes ($\Delta G°$) for the adsorption equilibrium to the distribution coefficients:

$$\Delta G^\circ = -RT\ln K_0 \tag{5}$$

and the Gibbs–Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

It is possible to determine $\Delta G°$, $\Delta H°$ and $\Delta S°$ using the plots of $\ln K_0$ vs. T^{-1} [54] and Eq. (7):

$$\ln K_0 = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{7}$$

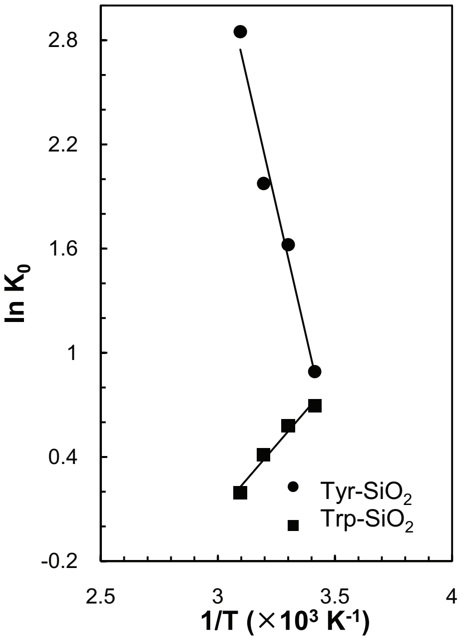


Fig. 7. Variation of lnK_d vs. T^{-1} for adsorption of Pb(II) ions onto Tyr-SiO$_2$ and Trp-SiO$_2$ adsorbents. Experimental condition: 20 mg/L initial concentration of metal ions; pH 5 aqueous phase; 0.075 g adsorbent; 60 min stirring time; 1,000 rpm; 25°C.

These equations were used for the evaluation of thermodynamic parameters ΔG°, ΔH° and ΔS° (Table 2). The evaluated thermodynamic parameters revealed that the Tyr-SiO$_2$ adsorption process is endothermic and controlled by entropy changes. An interpretation for the positive changes in enthalpy can be given by considering the dehydration of lead ions during adsorption process. This phenomenon requires an amount of energy which is superior to that from the heat released by the adsorption reaction. In contrast, the Trp-SiO$_2$ adsorption process was exothermic and controlled by changes in enthalpy.

3.8. Adsorption isotherms

The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms were examined for interpretation the experimental adsorption of Pb(II) ions by Tyr-SiO$_2$ and Trp-SiO$_2$.

The Langmuir isotherm considers monolayer coverage of the adsorption surface. This model is presented mathematically by Eq. (8):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{8}$$

in which C_e is the equilibrium concentration of metal ions in solution (mg/L), q_e is the amount of metal ions adsorbed per unit mass of adsorbent under equilibrium conditions (mg/g), q_m is the maximum adsorptive capacity (mg/g) and K_L is the Langmuir constant related to the adsorption energy (L/mg). A plot of C_e/q_e vs. C_e allows determination of q_m and K_L.

Table 2
Thermodynamic parameters for the adsorption of Pb(II) ions

Adsorbent	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)[a]		
			298	308	318
Tyr-SiO$_2$	48.9	0.17	–3.0	–4.8	–6.5
Trp-SiO$_2$	–13.0	–0.04	–1.6	–1.2	–0.8

[a]Standard deviation < ±0.6.

The dimensionless parameter R_L is named separation factor or equilibrium parameter indicates the probability of the occurrence of adsorption, and is determined by Eq. (9):

$$R_L = \frac{1}{1 + K_L C_0} \tag{9}$$

A process is unfavorable if $R_L > 1.0$ or $R_L < 0$; linear favorable if $R_L = 1$ and favorable if the value of R_L falls between 0 and 1. An irreversible process occurs when $R_L = 0$ [54,55].

The Freundlich isotherm is based on this suggestion that the uptake of a sorbate occurs on a heterogeneous surface by multilayer adsorption [56]. The mathematical expression for the Freundlich isotherm is shown by Eq. (10):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{10}$$

where K_F and n are Freundlich constants for adsorptive capacity and adsorption intensity, respectively. In this model, n is greater than unity and smaller value for $1/n$ indicates stronger interaction between adsorbent and solute.

A linear decrease in the heat of adsorption by progress in the adsorbent coverage is the fundamental assumption of the Temkin isotherm [57]. This isotherm is described by Eq. (11):

$$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b}\ln C_e \tag{11}$$

where R is the gas constant (0.0083 kJ/mol K), T is the absolute temperature (K), b is the Temkin constant related to heat of adsorption (kJ/mol) and K_T is the Temkin isotherm constant (L/g). Parameters K_T and b can be estimated by drawing the variation of q_e as a function of lnC_e.

The D–R isotherm does not assume homogeneous or constant adsorption potential for the surface [58]. The equation describing D–R is given by Eq. (12):

$$\ln q_e = \ln q_m - K_{\text{D–R}}\varepsilon^2 \tag{12}$$

Here, $K_{\text{D–R}}$ (mol^2/J^2) is a constant related to adsorption energy and ε is the Polanyi potential as defined by Eq. (13):

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{13}$$

Drawing a plot of the variation of lnq_e as a function of ε^2 allows evaluating the parameters $K_{\text{D–R}}$ and q_m. The parameter E is the mean energy (kJ/mol) required to bring a mole of adsorbate from infinity to the surface of the adsorbent [59]. It can be calculated by Eq. (14):

$$E = \frac{1}{\sqrt{2K_{\text{D-R}}}} \tag{14}$$

The value of $E < 8$ kJ/mol indicates a physical nature for the adsorption process. An ion-exchange mechanism can be considered E is >8 and <16 kJ/mol [54].

The parameters evaluating based on the application of the examined isotherm models are given in Table 3. A comparison of R^2 values correspond to the tested isotherms confirms that the adsorption of Pb(II) ions onto both adsorbents obeyed the Langmuir model. Although this model describes the adsorption of Pb(II) ions by Tyr-SiO_2 closely, the adsorptive process is also well represented by the Freundlich and Temkin isotherms. The results obtained based on the application of the Langmuir model showed a good agreement between the calculated and experimental values of q_m ($q_{m,\text{exp}}$ and $q_{m,\text{cal}}$). The R_L values calculated by the Langmuir isotherm indicate that the processes were favorable.

Table 3 shows that the values for 1/n derived from the Freundlich model for Tyr-SiO_2 and Trp-SiO_2 were 0.28 and 0.24, respectively. These values confirmed that the metal ions were favorably adsorbed by both the modified adsorbents. It was also concluded that, the interaction between the adsorbed ion and the adsorbents for Trp-SiO_2 is stronger than Tyr-SiO_2.

3.9. Kinetic investigations

Pseudo-first-order, pseudo-second-order, simple Elovich and intra-particle diffusion kinetic models are known as conventional models applied for investigation of adsorption processes kinetics [54,60,61]. The pseudo-first-order kinetics model assumes that adsorption is controlled by the diffusion step and its adsorption is proportional to the difference in adsorptive capacity at equilibrium and at any time t (q_e and q_t, respectively, in mg/g). This model is mathematically described by Eq. (15):

Table 3
Parameters evaluated by using various isotherms on the experimental data

Isotherm type	Parameter	Tyr-SiO_2	Trp-SiO_2
	$q_{m,\text{exp}}$ (mg/g)	7.6	6.9
Langmuir	K_L (L/mg)	0.68	0.64
	$q_{m,\text{cal}}$ (mg/g)	7.25	7.09
	R_L	0.07	0.07
	R^2	0.999	0.999
Freundlich	K_F ((mg/g)/(mg/L)$^{1/n}$)	3.44	3.59
	n	3.51	4.25
	1/n	0.28	0.24
	R^2	0.990	0.967
Temkin isotherm	K_T (L/g)	11.85	13.91
	b (kJ/mol)	1.81	1.95
	R^2	0.998	0.975
D–R isotherm	$K_{\text{D–R}}$ (mol²/kJ²)	0.84	0.59
	$q_{m,\text{cal}}$ (mg/g)	6.59	6.25
	E (kJ/mol)	15.8	15.8
	R^2	0.945	0.986

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,\text{ads}}}{2.303} t \tag{15}$$

where $k_{1,\text{ads}}$ is the pseudo-first-order rate constant.

The pseudo-second-order model describes the relationship between the mass of adsorbate per unit mass of adsorbent vs. time (Eq. (16)):

$$\frac{t}{q_t} = \frac{1}{k_{2,\text{ads}} q_e^2} + \frac{t}{q_e} \tag{16}$$

in this equation $k_{2,\text{ads}}$ denotes the pseudo-second-order rate constant. Initial rate of adsorption (mg/g min) can be calculated by using Eq. (17):

$$h_0 = k_2 q_e^2 \tag{17}$$

The Elovich equation establishes if the process is controlled by diffusion or chemical reaction, and is shown by the following equation:

$$q_t = a + 2.303b \ \log t \tag{18}$$

where a is the desorption constant (mg/g) and it is a function of both particle structural–chemical characteristics and the solute diffusion coefficient, and b is the initial adsorption rate (mg/g min). These quantities can be obtained by plotting q_t vs. log$t$.

Intra-particle diffusion in the solid phase is the rate-controlling step and the mathematical equation describing adsorption is the Weber and Morris equation [62] (Eq. (19)):

$$q_t = k_{\text{int}} \sqrt{t} + C \tag{19}$$

In this equation k_{int} is the intra-particle diffusion equation constant (mg/g min$^{0.5}$) and C is a constant. The plot of q_t vs. $t^{0.5}$ should be a straight line when diffusion controls the adsorption rate and should cross the origin if intra-particle diffusion is the rate-determining step.

It is noteworthy that the rapid kinetics of the adsorption process of Pb(II) ions onto Tyr-SiO_2 prohibited investigation of the kinetic models by the experimental method used in this work. Table 4 contains the kinetic parameters for the investigated models on the adsorption of Pb(II) ions onto Trp-SiO_2. The pseudo-second-order kinetic model provided an impressive and comparable correlation for the adsorption of ions. It is noted that although R^2 obtained by using pseudo-first-order

Table 4
Parameters evaluated by using different kinetic models on the experimental data

Kinetic model	Parameter	Value
	$q_{e,\exp}$ (mg/g)	5.62
Pseudo-first-order equation	$q_{e,\mathrm{cal}}$ (mg/g)	2.29
	k_1 (1/min)	0.04
	R^2	0.986
Pseudo-second-order equation	$q_{e,\mathrm{cal}}$ (mg/g)	5.78
	k_2 (g/mg min)	0.05
	h (mg/g min)	1.65
	R^2	0.998
Elovich equation	a (mg/g)	2.14
	b (mg/g min)	0.83
	R^2	0.989
Intra-particle diffusion equation	k_3 (mg/g min$^{0.5}$)	0.31
	C	3.18
	R^2	0.992

model for metal adsorption is around that found by the pseudo-second-order kinetic model, the value of q_e evaluated by the pseudo-first-order model was too far from that was found experimentally. The comparison of the evaluated adsorptive capacity based on the pseudo-second-order equation (q_e) and that found experimentally ($q_{\exp}$) also confirms the validity of the proposed model. It suggests that the rate-determining step for adsorption is a chemical adsorption process, and this process involves valence forces from sharing of electrons by the metal ions and adsorbent [63–65]. The adsorbent Trp-SiO_2 has chelating functional groups on its surface that probably behave as chelating exchanger, therefore a complexation reaction is expected for the adsorption process [66].

From the above arguments, one may be able to infer that the adsorption of Pb(II) ions onto Trp-SiO_2 follows pseudo-second-order kinetics. This may also imply that the mechanism for adsorption involves chemical bonding between Pb(II) ions and the adsorbent. A further confirmation for such mechanism can be deduced by considering the evaluated R^2 value (≥0.9) based on the Elovich plot [61].

3.10. Comparison of the adsorbent capacity

The adsorptive capacity of the investigated adsorbents toward Pb(II) ions was comparable with those reported based on some other adsorbents (Table 5). The results showed the superior adsorptive capacity of both the studied adsorbents toward Pb(II) ions with respect to some of the adsorbents such as *p*-dimethylaminobenzaldehyde-modified nanometer SiO_2 (SiO_2-DMABD), sodium dodecyl sulfate-coated poly(vinyl) chloride modified with bis(2-hydroxyacetophenone)-1,4-butanediimine (SDS-PVC-BHABDI), SBA-15 modified with γ-aminopropyltriethoxysilane (SBA-15-APTS), silica gel/nanometer titanium dioxide, Amberlite XAD-7/xylenol orange and activated carbon/4,6-dihydroxy-2-mercaptopyrimidine. However, chestnut shell showed a comparable adsorbent capacity with that presented by Tyr-SiO_2 and Trp-SiO_2 adsorbents.

Table 5
Comparison of the adsorptive capacity of the studied adsorbents with that of some reported adsorbents

Adsorbent	Adsorptive capacity (mg/g)	Reference
SiO_2-DMABD[a]	6	[67]
SDS-PVC-BHABDI[b]	2.2	[68]
SBA-15-APTS[c]	1.1	[69]
Silica gel/nanometer titanium dioxide	3.16	[70]
Amberlite XAD-7/xylenol orange	3.14	[71]
Activated carbon/4, 6-dihydroxy-2-mercaptopyrimidine	0.45	[72]
Chestnut shell	8.5	[73]
Tyr-SiO_2	7.60	This work
Trp-SiO_2	6.92	This work

[a] *p*-Dimethylaminobenzaldehyde-modified nanometer SiO_2.
[b] Sodium dodecyl sulfate-coated poly(vinyl)chloride modified with bis(2-hydroxyacetophenone)-1,4-butanediimine.
[c] γ-Aminopropyltriethoxysilane (APTS).

4. Conclusions

Nanosilica particles modified with Schiff base ligands derived from L-tyrosine (Tyr-SiO_2) and L-tryptophan (Trp-SiO_2) were potential adsorbents for very rapid and selective removal of lead ions from aqueous solutions. The higher adsorptive capacity of Tyr-SiO_2 (7.60 mg/g) with respect to Trp-SiO_2 (6.92 mg/g) was attributed to the amount of imines grafted onto modified nanosilica particles. Adsorption/desorption of the lead ions onto the adsorbents allow their use repeatedly for removal of these ions from aqueous solutions. Hydrochloric or nitric acid solutions (5 mL, 0.1 mol/L) were able to strip quantitatively (95% and 100%, respectively) Pb(II) ions from Tyr-SiO_2. Application of two 5 mL volumes of nitric acid 1 mol/L allowed to strip 70% of the adsorbed Pb(II) ions from loaded Trp-SiO_2. The calculated thermodynamic parameters indicated that the adsorption process based on Tyr-SiO_2 adsorbent was endothermic and controlled by entropy changes. In contrast, the adsorption of Pb(II) ions onto Trp-SiO_2 was exothermic and controlled by enthalpy changes. The adsorption of Pb(II) ions onto both adsorbents obeyed the Langmuir model. The results obtained based on the application of this model showed, a good agreement between the calculated and experimental values of q_m ($q_{m,\exp}$ and $q_{m,\mathrm{cal}}$). The R_L values calculated by the Langmuir isotherm indicate that the processes are favorable. The values for $1/n$ derived from the Freundlich model for Tyr-SiO_2 (0.28) and Trp-SiO_2 (0.24) adsorbents confirmed that the metal ions were favorably adsorbed by both the modified adsorbents. It is also concluded that, the interaction between the adsorbed ion and the adsorbents for Trp-SiO_2 is stronger than Tyr-SiO_2. The adsorption kinetic for Trp-SiO_2 was described well by pseudo-second-order model, suggesting the chemisorption as the rate-limiting mechanism of the process. This result also confirmed by considering the evaluated R^2 value (≥0.9) based on the Elovich plot and the values of E (15.8 kJ/mol) obtained from the D–R isotherm model.

Symbols

NS — Nanosilica
Tyr-SiO$_2$ — Silica nanoparticle modified with (*S*)-2-((2-hydroxybenzylidene)amino)-3-(4-hydroxyphenyl)propanoic acid
Trp-SiO$_2$ — Silica nanoparticle modified with (*S*)-2-((2-hydroxybenzylidene)amino)-3-(1*H*-indol-3-yl)propanoic acid

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Supplementary data

Spectroscopic data of the products

(*S*)-2-((2-Hydroxybenzylidene)amino)-3-(1*H*-indol-3-yl) propanoic acid (Trp-SiO_2): FTIR (KBr, cm^{-1}): 3,555 (w) (O–H), 3,403 (w) (N–H), 2,963 (w), 2,930 (w), 1,671 (vs) (C=N), 1,526 (s), 1,455 (s), 1,357 (m), 1,239 (w), 1,170 (m), 1,117 (m), 895 (m), 758 (m), 653 (m), 578 (w), 470 (w). ^{1}H NMR: 250 MHz, DMSO-d_6: δ = 2.99 (1H, d, CH_2), 3.15 (1H, d, J CH_2), 6.2–7.5 (9H, CH_{Ar}), 8.04 (1H, s, CH=N), 9.9 (1H, br s, –COOH), 10.73 (1H, br s, OH) ppm. Trp-SiO_2 adsorbent: FTIR (KBr, cm^{-1}): 3,423 (br, w), 2,924 (w), 2,854 (w), 1,638 (s), 1,528 (w), 1,081 (vbr, vs), 811 (m), 738 (m), 474 (s). (*S*)-2-((2-Hydroxybenzylidene) amino)-3-(4-hydroxyphenyl)propanoic acid (Tyr-SiO_2): FTIR (KBr, cm^{-1}): 3,204 (w) (O–H), 2,960 (w), 2,930 (w), 1,670 (vs) (C=N), 1,609 (s), 1,514 (m), 1,417 (m), 1,330 (s), 1,244 (s), 1,099 (m), 841 (s), 739 (m), 650 (s), 575 (s), 529 (s), 493 (w), 434 (w). ^{1}H NMR: 500 MHz, DMSO-d_6: δ = 2.77 (1H, dd, J = 9.0 Hz, J = 13.5 Hz, CH_2, H-2), 3.13 (1H, dd, CH), 3.74 (1H, dd, CH_2, H-2), 6.56 (2H, d, CH_{Ar}), 6.63 (1H, d, CH_{Ar}), 6.69 (1H, d, CH_{Ar}), 6.90 (2H, d, CH_{Ar}), 7.16–7.20 (2H, m, CH_{Ar}), 8.04 (1H, s, CH=N, H-7), 14.29 (1H, br s, –COOH), 9.14 (1H, br s, OH) ppm. Tyr-SiO_2 adsorbent: FTIR (KBr, cm^{-1}): 3,453 (br, w), 3,206 (w), 2,960 (w), 2,854 (w), 1,618 (s), 1,514 (m), 1,084 (vbr, vs), 804 (s), 649 (w), 575 (w), 468 (s).