Novel tyrosine-containing inorganic–organic hybrid adsorbent in removal of heavy metal ions

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In this study, tyrosine-containing inorganic–organic hybrid bioadsorbent was synthesized, characterized, and used in the removal of heavy metal ions from aqueous solution. The preparation of adsorbent was conducted by hydrolysis of mixture between Ti-tyrosinate and poly-3-glycidyloxypropyltrimethoxysilane (poly-GPTS). This new hybrid adsorbent (hydrolyzed-[poly-GPTS/Ti-Tyr]) was characterized by several techniques. Adsorptions of Pb^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions by new adsorbent have been performed with batch method. As a result of the large number of highly electronegative oxygen and nitrogen atoms, the maximum capacity for adsorbed metal ions was high in hydrolyzed-[poly-GPTS/Ti-Tyr]. Different parameters such as solution pH, contact time, adsorbent amount, initial metal ion concentration and adsorption isotherms were studied. The adsorption thermodynamics and kinetics also were determined with equilibrium data. The maximum adsorption capacities of Pb^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} were found 240.5, 196.7, 182.4, 126.3 mg g^{-1}, respectively. The adsorption equilibrium data were fitted well with Langmuir isotherm. The thermodynamic studies indicated that the adsorption was spontaneous and exothermic. The adsorption kinetic parameters were best suited to pseudo-second-order model. The synthesized adsorbent promises to be an effective adsorbent for the removal of heavy metal ions from aqueous solutions.

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Introduction

There are many environmental problems caused by chemical substances with rapid development of industries. These problems such as heavy metal contamination and dye contamination are effective in the aquatic media of earth. The water pollutions produced by humans are frequently loaded with toxic metals such as copper, nickel, zinc, and lead [1]. There are many studies on the removal of toxic metals from aqueous solution by various methods such as ion exchange, neutralization, reverse osmosis, precipitation, solvent extraction and adsorption [2-4]. Compared to other methods, adsorption method could be an economical choice because it is easy-to-handle and highly efficient in removing heavy ions from aqueous solutions especially at medium to low ion concentrations [2,3]. There are a number of adsorbents used for the removal of heavy metals from aqueous solution such as activated carbon, modified clays, biosorbent, polymeric resins, zeolites, and hybrid materials [4-6]. In recent years, researchers have examined the inorganic–organic hybrid materials as adsorbents. Especially metal alkoxide compounds were used in the synthesis of adsorbents. Addition of water to metal alkoxide complexes led to hydrolysis of alkoxys groups and condensation reactions resulting in inorganic networks without organic groups [7].

Adsorption of heavy metals on inorganic–organic compounds was studied intensively in the literature because of the specific chemical reactivity and flexibility of the organic functional groups, their attractive mechanical properties, and thermally stable inorganic backbone. Properties of hybrid materials depended on chemical composition, structure and physical properties. Da’na and Sayari studied heavy metals adsorption with SBA-15 functionalized with 3-aminopropyltrimethoxysilane which exhibited that ionic strength did not affect the adsorption process and showed a high efficiency for all metal ions in dilute solutions [8]. Hybrid inorganic–organic adsorbents based on alumina and 4-aminonitriptyrene were synthesized and characterized for the removal and preconcentration of heavy metals from waters studied by Mahmoud et al. [9]. In 2007, Li et al. prepared the silica-supported porous sorbent by organic-inorganic hybridization combined with sucrose and polyethylene glycol imprinting for removal of heavy metals from wastewater. They chose copper ion as a model ion to evaluate the effectiveness of this new biosorbent [10]. Cross-linked organic–inorganic hybrid beads formed with sol–gel derivized poly(vinyl alcohol)–3-(2-aminoethylamino)propyl trimethoxysilane were used for the removal of Pb^{2+} from aqueous solution and 67.56 mg g^{-1} adsorption capacity was found at pH 5.5. Parakash et al. mentioned that this result was much higher compared to other adsorbents reported in literature [11]. Jin et al. synthesized a nano-adsorbent poly(acrylic acid–acrylonitrile)/attapulgite and a novel amphiphilic hybrid material for adsorption of heavy metals and organic molecules in aqueous solution.
[12,13]. Novel zwitterionic inorganic–organic hybrids were synthesized with a new route and used for Cu\(^{2+}\) removal [14]. The competitive removal of metal ions by PAMAM-SBA-15 (polyamidoamine-silica based adsorbent-15) and EDTA-PAMAM-SBA-15 inorganic–organic materials was performed by Jang et al. [15]. They determined the pH, time, maximum adsorption amounts and removal efficiency factors to indicate the higher adsorption capacities of the inorganic–organic materials [15].

The aims of this work were to synthesize an appropriate new adsorbent for removal of heavy metal ions, investigate the adsorption capacity of synthesized adsorbent for Pb\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) metal ions, study the effects of pH, contact time, adsorbent amount and initial metal concentration and study adsorption kinetics, adsorption isotherm and thermodynamics. It is also important to note that tyrosine-containing inorganic–organic hybrid material is reported first time by this study.

**Materials and methods**

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**Reagents and equipment**

Titanium(IV) n-butoxide (98%, Merck), 3-glycidoxypropyltrimethoxysilane (GPTS, 97%, Alfa Aesar), l-tyrosine (100%, Merck), and butanol (99.5%, Merck) were used as received. The stock metal ion solutions (1000 mg L\(^{-1}\)) of Pb\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) were prepared from their nitrate salts (Merck). For pH adjustment 0.1 mol L\(^{-1}\) HCl and NaOH solutions were used. All the used chemicals were of analytical grade.

\(^1\)H NMR measurement was carried out with a Bruker 300 MHz Ultra shieldTM spectrometer. Infrared spectra of complexes were recorded on a Shimadzu 8201/86601 PC spectrometer (FT-IR). The elemental analyses were carried out with a LECO CHNS-932 elemental analyzer. Molecular mass measurement of compound was performed on AB SCIEX MALDI TOF/TOF 5800. Thermogravimetric measurement was carried out in a Protherm furnace with a heating and cooling rate of 10 °C min\(^{-1}\) under air. In addition, scanning electron microscopy (SEM) analysis was carried out using a scanning electron microscope (Model JEOL JSM 6060) to study the surface texture and morphology of the adsorbent. A PerkinElmer model Flame AAnalyser 800 Atomic Absorption Spectrometer (FAAS) was used for metal quantity analysis. The pH measurements were performed by Hanna pH 211 model pH-meter and several model magnetic stirrers were used for adsorption process. The average values of the three same experiment results were evaluated.

**Preparation of organic–inorganic hybrid material**

The new organic–inorganic hybrid material was synthesized in two steps. In the first step, the preparation of titanium-tyrosinate compound was performed. In the second step, the hydrolysis of mixture of titanium-tyrosinate compound with poly-GPTS was performed to form hydroxylated poly-GPTS/Ti(Tyr) compound.

**Preparation of [Ti\(_4\)O\(_n\)Bu\(_4\)]\(_2\)O**

\[
\text{Ti(O\(_n\)Bu\(_4\)) + 2L-tyrosine} \rightarrow \frac{1}{2} \text{[Ti\(_4\)O\(_n\)Bu\(_4\)]}_2\text{O}
\]

Tyrosine (5.88 × 10\(^{-3}\) mol, 1.06 g) was used as a source of titanium n-butoxide (2.94 × 10\(^{-3}\) mol, 1.01 g) in 15 mL n-butoanol. The reaction mixture was stirred for 3 h at room temperature. Then, the volatile parts were removed from white solid product by vacuum evaporator at 30 °C. The yellow product was washed with hexane (20 mL)/butanol (20 mL) and dried under reduced pressure (1.6 × 10\(^{-3}\) mbar). Elemental analysis (C\(_{44}H\(_{80}\)N\(_{15}\)Ti\(_2\), (Tyr)\(_4\)Ti\(_2\)(OC\(_4\)H\(_9\))\(_2\)O, Mw = 978.68 g mol\(^{-1}\)): Calc: C, 54.0; H, 5.97; N, 5.72%. Found: C, 53.72; H, 6.19; N, 5.79%. MS(MALDI-TOF/TOF), m/z: 968.0867 Da. Calc. for Ti\(_2\)C\(_{44}H\(_{80}\)N\(_{15}\)Ti\(_2\), (Tyr)\(_4\)Ti\(_2\)(OC\(_4\)H\(_9\))\(_2\)O, Mw = 978.29 Da. \(^1\)H NMR (DMSO) δ: 0.87 (t, CH\(_3\), O\(_{Bu}\)), 1.26 (m, CH\(_2\), O\(_{Bu}\)), 1.37 (m, CH\(_2\), O\(_{Bu}\)), 2.74 (dd, CH\(_2\), Tyr), 3.03 (dd, CH\(_2\), Tyr), 3.86 (t, OCH\(_2\), O\(_{Bu}\)), 4.4 (br, CH, Tyr). 6.67 (d, CH, Ph), 7.05 (d, CH, Ph), 9.34 (s, OH–C\(_6\)H\(_4\)). FTIR (KBr pellet, cm\(^{-1}\)): 3423 (OH), 3205 (NH), 2928, 2960, 2932, 1609, 1591, 1512, 1454, 1360, 1331, 1245, 1102, 1042, 840, 799, 648, 575, 530.

**Preparation of adsorbent, hydroxylated-Ti(Tyr)/PGPTS**

Poly-GPTS was prepared as previously described in literature [16]. Briefly, GPTS was polymerized by catalyst potassium t-butoxide under nitrogen atmosphere. The compounds poly-GPTS and Ti\(_2\)(Tyr)\(_4\)(O\(_n\)Bu\(_4\))O were mixed in 1:1 mol ratio in 50 mL of butanol and stirred for a few minutes. Then the mixture was hydrolyzed by 0.1 mol L\(^{-1}\) HCl (≈0.37 g). 4.0 mol of water per mole of Ti\(_2\)(O\(_n\)Bu\(_4\))O and 3.0 mol of water per mole of GPTS were added drop wise to the solution and stirred (≈900 rpm) at room temperature for 24 h. After 24 h stirring, the volatile parts of mixture were removed under reduced pressure at 50 °C and a beige solid was obtained (92%). The synthesis of Si–Ti–Tyr adsorbent can be summarized as in Scheme 1. The TGA of the hydroxylated product showed a weight loss of 20% up to 900 °C. FT-IR (KBr pellet): 3445 (OH), 3205 (NH\(_2\)), 2956, 2928, 1606, 1587, 1508, 1451, 1360, 1329, 1241, 1108 (Si–O–Si), 1096 (Si–O–Ti), 1042, 840, 800, 648, 572, 528 cm\(^{-1}\).

**Batch adsorption studies**

Stock metal ion solutions (1000 mg L\(^{-1}\)) of Pb\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) were prepared in deionized water and diluted with deionized water to desired concentration. The synthesized inorganic–organic hybrid material was used after grinding to powder form. Batch process was carried out by agitating 2.5 mg of adsorbent in 25 mL of metal
solution at 140 rpm for desired time interval. After desired time, the adsorbent was filtered through Whatman (110 mm Φ, 6 µm pore size) filter paper. Heavy metal ion concentrations in the filtrate solution samples were determined by FAAS. Controlled experiments were performed without the addition of adsorbent and no adsorption was observed on filter paper and glassware.

The adsorption capacity (q) is expressed as follows:

\[ q = \frac{C_o - C_e}{m} \times V \]  

and removal percentage (%R) is expressed as follows:

\[ %R = \frac{C_o - C_e}{C_o} \times 100 \]  

where q is the adsorption capacity of the adsorbent (mg g\(^{-1}\)), \( m \) is the weight of adsorbent [g], \( V \) is the volume of solution (L), %R, removal percentage and \( C_o \) (mg L\(^{-1}\)) and \( C_e \) (mg L\(^{-1}\)) are initial and equilibrium concentrations of adsorbate in solution, respectively.

The effects of the initial pH were studied between 2.0 and 7.0 for the Pb\(^{2+}\), Fe\(^{3+}\) and Cu\(^{2+}\) ions, 2.0–10.0 for Cr\(^{3+}\) and 2.0–10.0 for Zn\(^{2+}\) ions. pH values were adjusted with 0.1 mol L\(^{-1}\) NaOH and 0.1 mol L\(^{-1}\) HCl solution before adding adsorbent. The adsorption experiments were also performed to determine the effect of contact time in the range of 5–80 min, the effect of initial adsorption amount between 1.0 and 15 mg, and the effect of solution temperature at the range between 20° and 55° C. These parameters were studied by varying one of the experiment conditions while keeping all the other conditions constant.

**Adsorption isotherms**

Metal ions adsorption isotherms and effect of initial metal concentration were studied in the range of 20–100 mg L\(^{-1}\). The maximum adsorption capacities of adsorbent for removal of metal ions were determined with Eq. (1) and with the adsorption isotherm models. Many models have been published in the literature to describe the experimental data of adsorption isotherms [17]. The Langmuir and Freundlich isotherms are the two most commonly used models. In this study, adsorption data are fitted to Langmuir and Freundlich equations to find the relationship between the equilibrium concentration and the amount of metal ion. The Langmuir and Freundlich isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. Langmuir model proposed the following equation:

\[ \frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \]  

where \( C_e \) (mg L\(^{-1}\)) and \( q_e \) (mg g\(^{-1}\)) are the concentration and adsorption capacity at the equilibrium, respectively. \( Q_m \) (mg g\(^{-1}\)) and \( b_L \) (L mg\(^{-1}\)) are adsorption capacity and binding energy of adsorption of Langmuir, respectively.

The essential characteristics of the Langmuir adsorption can be expressed in terms of a dimensionless constant referred to as separation factor, \( R_L \), for predicting whether an adsorption system is favorable or unfavorable. This equation is defined as:

\[ R_L = \frac{1}{1 + b_L C_o} \]  

where \( C_o \) is the highest initial solute concentration, \( b_L \) is the Langmuir’s adsorption constant (1 mg\(^{-1}\)). The \( R_L \) value implies the adsorption to be unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favorable (\( 0 < R_L < 1 \)) or irreversible (\( R_L = 0 \)) [18]. Freundlich model proposed the following equation:

\[ \ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \]  

where \( K_F \) and \( n_F \) are Freundlich constants measuring the adsorption capacity and the adsorption intensity, respectively.

**Results and discussion**

**Characterization of organic–inorganic hybrid material**

The compound Ti\(_2\)(Tyr)\(_4\)(O\(^{Bu}\))\(_2\)O was prepared as explained in experimental section. In the characterization of this compound, a few techniques were used. \(^1\)H NMR spectrum of compound showed expected peaks at 0.87 ppm for CH\(_3\) of O\(^{Bu}\) and 6.67 ppm for CH of C\(_6\)H\(_4\) unit and so on. The absence of proton of carboxyl group indicated that tyrosine was coordinated to titanium from carboxylate oxygen atom. The mass spectrum of this new compound gave the molecular peak at \( m/z \): 968.88667 Da. FTIR measurement of compound also supported the suggested formulation of compound. The characteristic C \( = \)O peak of tyrosine-Ti compound appeared at 1609 cm\(^{-1}\) [19].

The new hybrid adsorbent (hydrolyzed-poly-GPTS/Ti (Tyr)) was prepared as explained in experimental section and characterized by spectroscopic methods. FT-IR studies support the condensation reactions between poly-GPTS and titanium tyrosine compounds in the presence of HCl\(_{aq}\). FTIR spectrum shows that tyrosine remains bonded to titanium after hydrolyzed reaction. The poly-GPTS shows characteristic bands at 1089 cm\(^{-1}\) for Si–OCH\(_3\) bonds. When poly-GPTS undergoes condensation with metal alkoxides, the peak at 1089 cm\(^{-1}\) disappears in the FT-IR spectrum. This disappearance supports the fact that the Si–OCH\(_3\) undergoes a condensation reaction. After condensation reaction, new peaks appeared at 1108 cm\(^{-1}\) for Si–O–Si and 1096 cm\(^{-1}\) for Si–O–Ti bonds, respectively [20]. The presence of the OH groups bounded to silicon and titanium atoms appeared at 3445 cm\(^{-1}\) in the FT-IR spectrum. Thermogravimetric analysis also supports the presence of organic groups (CH\(_2\)CH\(_2\)CH\(_2\))Si with 10% of C and H) after combustion reaction. In addition to above spectroscopic techniques, SEM was also used to characterize the surface of new hybrid adsorbent. From the SEM image in Fig. 1, it is clear to see the porous and irregular surface structure of the adsorbent. The adsorbent has heterogeneous porous and cavities which provide a large surface area for adsorption of heavy metals.

**Effect of pH on adsorption**

The removal of heavy metal ions from aqueous solutions by adsorption is highly dependent on the pH of solution. The variation of pH can affect the surface charge of the adsorbent, the degree of ionization and the speciation of the adsorbate. A series of experiments were preformed at different pH values to obtain optimum pH values of adsorption of Pb\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) metal ions and the results are presented in Fig. 2. 20.0, 2.0, 7.0 and 7.0 mg L\(^{-1}\) initial
concentration of Pb\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\) were prepared respectively. After, the pH of the solution mixture (adsorbent + metal ion solution) was measured and there were no clear difference in the pH changes. Therefore, the adsorbent was not affected from the pH changes. However, the adsorption mechanism was affected from the pH changes.

All four metal ions have low adsorption capacity at low pH ranges. In acidic media, active sites of the adsorbent were protonated and the metal ions adsorption was reduced as mentioned in literature [4,11]. With increasing the pH values, the adsorption capacity values of adsorbents increased for all metal ions. As the pH increases, the adsorption surface becomes less positive and the electrostatic attraction between the metal ions and adsorbent surface increased, as expected [2]. After pH 6.0, Pb\(^{2+}\) ion precipitates as lead hydroxide. Thus, the optimum pH value for Pb\(^{2+}\) ion on this adsorbent was determined with experiments to be 5.5 at low and high concentration. For other three metal ions, adsorption studies were performed over pH range of 2.0–10.0, yet there was no metal precipitation because of the low metal ion concentration values. The maximum adsorption capacity values were observed at pH 10.0 for Ni\(^{2+}\) (at low and high concentration values) 8.0 for Cu\(^{2+}\), and Zn\(^{2+}\) ions. But with increasing the initial metal ions concentrations of Cu\(^{2+}\) and Zn\(^{2+}\) ions in the range of 20–100 mg L\(^{-1}\), the precipitation was seen after pH 6.5 values because of the formation of oxide of these metal ions. So the optimum pH values for Cu\(^{2+}\) and Zn\(^{2+}\) ions were determined to be 6.5 at high concentration and 8.0 for low concentration (7.0 and 2.0 mg L\(^{-1}\), respectively).

Effect of contact time on adsorption

The effect of contact time on the adsorption is shown in Fig. 3. From Fig. 3, it can be seen that the amount of adsorption capacity increases with increasing the time to 10 min for Ni\(^{2+}\) and Cu\(^{2+}\), 20 min for Zn\(^{2+}\) and Pb\(^{2+}\) ions. There were no significant changes until 80 min. The removal of the metal ions was observed in a very short time about 10 min and 20 min (Fig. 3). Effect of contact time for each metal ion on adsorbent was different. As expected, during the initial stages there was a high concentration gradient between metal solution and adsorbent; thus rapid adsorption occurred on adsorbent having a high number of vacant sites. This observation was consistent with literature data [21]. Therefore, the adsorption studies for these metal ions were established at 10 and 20 min for Ni\(^{2+}\), Cu\(^{2+}\) and for Zn\(^{2+}\), Pb\(^{2+}\) ions, respectively.

Effect of adsorbent amount on adsorption

The effect of adsorbent amount on metal ions adsorption was studied by changing the adsorbent amount from 0.1 to 15 mg at room temperature, while keeping the other conditions constant such as pH and contact time for each metal ion. The results are shown in Fig. 4a. As seen from the figure, when the amount of adsorbent increases, the adsorption capacity decreases for all four metal ions. Unsaturation of adsorption sites, the particle interaction like aggregation [22,23] and less active site at high adsorbent dose [11] may be the reasons of the decreasing in adsorption capacity. The removal percentages of the metal ions were with maximum values at 2.5 mg adsorbent amount (Fig. 4b), so this value was chosen for other experiments.

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**Fig. 2.** Effect of pH at 20.0 mg L\(^{-1}\) Pb\(^{2+}\), 7.0 mg L\(^{-1}\) Ni\(^{2+}\), 7.0 mg L\(^{-1}\) Cu\(^{2+}\) and 2.0 mg L\(^{-1}\) Zn\(^{2+}\) ions (25 °C, contact time: 20 min, adsorbent amount 2.5 mg).

**Fig. 3.** Effect of contact time on adsorption of Pb\(^{2+}\) (pH: 5.5, 20.0 mg L\(^{-1}\); Ni\(^{2+}\) (pH: 10.0, 7.0 mg L\(^{-1}\)), Cu\(^{2+}\) (pH: 8.0, 7.0 mg L\(^{-1}\)); Zn\(^{2+}\) (pH: 8.0, 2 mg L\(^{-1}\)) 25 °C with 2.5 mg adsorbent.

**Fig. 4.** Effect of adsorbent amount Pb\(^{2+}\) (pH: 5.5, 20.0 mg L\(^{-1}\), 20 min); Cu\(^{2+}\) (pH: 8.0, 7.0 mg L\(^{-1}\), 10 min); Ni\(^{2+}\) (pH: 10.0, 7.0 mg L\(^{-1}\), 10 min); Zn\(^{2+}\) (pH: 8.0, 2 mg L\(^{-1}\), 20 min) 25 °C. (a) Adsorption capacity and (b) removal percentage.
Effect of initial concentration and adsorption isotherms

The effect of initial metal ions concentrations on adsorption capacity is shown in Fig. 5. Adsorption isotherms were performed in the range of 20–100 mg L\(^{-1}\) of metal ion concentration. Adsorption processes were performed for metal ions (Pb\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), and Cu\(^{2+}\)) in 20 min at known pH with 2.5 mg adsorbent amount. The adsorption capacities increase with increasing initial concentration of the metal ions (Fig. 5). This case indicates that initial concentration depends on the adsorption process. The adsorption capacity increased in the order of Zn\(^{2+}\) < Cu\(^{2+}\) < Ni\(^{2+}\) < Pb\(^{2+}\). This result can be attributed to the ionic size and electropositivity of metal ions [24,25].

Two popular adsorption isotherms were applied to adsorption process. The data in Fig. 5 were analyzed with Freundlich and Langmuir equations (Eqs. (3)–(5)). The adsorption isotherms are shown in Fig. 6. The values calculated from the isotherm equations are presented in Table 1.

The results obtained from the equations indicated that the equilibrium data fitted to Langmuir adsorption isotherms better than Freundlich adsorption isotherms. The regression coefficient shown in Table 1 was an evidence of this result. Langmuir isotherms are valid for monolayer adsorption because of a surface of a finite number of identical sites. On the other hand, Freundlich isotherms are an indication of surface heterogeneity of the adsorbent [2].

The calculated \(q_a\) from Table 1 was found to be 270.3 mg g\(^{-1}\) for Pb\(^{2+}\) and decreased slightly in the order of Ni\(^{2+}\) > Cu\(^{2+}\) > Zn\(^{2+}\). Adsorption capacity results of the adsorbent for Pb\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), and Cu\(^{2+}\) show similar results with calculated results from Eq. (1), 240.5, 196.7, 182.4, and 126.3 mg g\(^{-1}\) respectively. These results show that the new tyrosine-containing hybrid adsorbent has high adsorbent capacities [24]. As a result of the large number of highly electronegative oxygen and nitrogen atoms, the maximum capacity of adsorbed metal ions was high in hydrolyzed-[poly-GPTS/Ti-Tyr]. In other words, the Si–Ti-Tyr adsorbent contains many oxygen and nitrogen atoms which provide adsorption sites to bind metal ions. The adsorption capacity results of some other similar adsorbents in the literature are summarized in Table 2.

The \(R^2\) values of metal ion solutions (100 mg L\(^{-1}\), \(C_0\)) were calculated from the Langmuir adsorption isotherms equation (Eq. (4)). The results were found between 0 and 1, by Pb\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\) and Cu\(^{2+}\) 0.038, 0.027, 0.033 and 0.044 respectively. So the adsorption of metal ions on adsorbent is favorable and Langmuir adsorption isotherms are applicable to the adsorption process.

**Adsorption thermodynamics**

The effect of temperature on metal ions adsorption was examined with Van’t Hoff’s equation. The thermodynamic parameters of equation including the Gibbs free energy change \(\Delta G^\circ\), the enthalpy change \(\Delta H^\circ\), and the entropy change \(\Delta S^\circ\) were determined using the following equations respectively:

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

\[
K_c = \frac{q_e}{C_e}
\]

\[
\ln K_c = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{RT}\right)
\]

\[
\Delta G^\circ = -RT \ln K_c
\]

\(C_c\) and \(q_c\) have same meaning as noted previously. \(K_c\) is the thermodynamic equilibrium constant. \(R\) is the universal gas constant 8.314 J mol\(^{-1}\) K\(^{-1}\) and \(T\) is the absolute temperature of solution. A plot of \(\ln K_c\) against 1 T\(^{-1}\) gives a gradient (Fig. 7). The values of \(\Delta S^\circ\) and \(\Delta H^\circ\) were calculated form the intercept and slope of the plot.

The thermodynamic results of metal ions at different temperatures were given in Table 3. Negative values of \(\Delta G^\circ\) show the feasibility and spontaneous nature of adsorption process. The \(K_c\) values are related to the affinity of the binding of metal ions on adsorbent [22,26] as seen from Table 3, the highest value of \(K_c\) for four metal ions is at 25 °C. Therefore, all the other experiments were performed at this temperature.
The ions. Comparison log first and commonly contribute Negative negative low cating

Table 1
The isotherms for adsorption of metal ions.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$R^2$</th>
<th>$Q_e$ (mg g$^{-1}$)</th>
<th>$h_i$ (1 mg$^{-1}$)</th>
<th>$R^2$</th>
<th>$K_i$ (mg g$^{-1}$)</th>
<th>$n_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>0.991</td>
<td>270.3</td>
<td>0.251</td>
<td>0.792</td>
<td>177.1</td>
<td>13.11</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.992</td>
<td>204.1</td>
<td>0.355</td>
<td>0.413</td>
<td>165.9</td>
<td>31.25</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.993</td>
<td>188.7</td>
<td>0.294</td>
<td>0.603</td>
<td>142.2</td>
<td>19.72</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.993</td>
<td>131.6</td>
<td>0.215</td>
<td>0.934</td>
<td>47.7</td>
<td>40.78</td>
</tr>
</tbody>
</table>

Table 2
Comparison of maximum adsorption capacities of similar adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_{0m}$ (mg g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(A-O)/AT</td>
<td>109</td>
<td>[12]</td>
</tr>
<tr>
<td>ASDO</td>
<td>131.6</td>
<td>[13]</td>
</tr>
<tr>
<td>G3-PAMAM-SPA-15</td>
<td>5.3</td>
<td>[15]</td>
</tr>
<tr>
<td>EDTA-G3</td>
<td>6.0</td>
<td>[15]</td>
</tr>
<tr>
<td>PAMAM-SPA-15</td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td>Poly-GPTS-Ti</td>
<td>199.0</td>
<td>[24]</td>
</tr>
<tr>
<td>Si/Al-pr-N = salicyl aldehyde</td>
<td>91</td>
<td>[21]</td>
</tr>
<tr>
<td>Poly-GPTS/Ti(Tyr)</td>
<td>240.5</td>
<td>[21]</td>
</tr>
</tbody>
</table>

Fig. 7. Thermodynamic equilibrium constant $K_e$ versus $1/T$ plot for adsorption of metal ions.

The $\Delta G^\circ$ values increased with increasing the temperature indicating the adsorption process were rapid and more spontaneous at low temperature like in Chu et al. at 2004 results [17]. All processes for four metal ions were exothermic. The $\Delta H^\circ$ for Pb$^{2+}$ was $-30.48$ kJ mol$^{-1}$, for Ni$^{2+}$ was $-30.46$ kJ mol$^{-1}$, for Cu$^{2+}$ was $-20.14$ kJ mol$^{-1}$, and for Zn$^{2+}$ was $-14.68$ kJ mol$^{-1}$. The enthalpy changes of adsorption indicated the exothermic nature of adsorption process. The negative $\Delta S^\circ$ and $\Delta G^\circ$ values are required for negative $\Delta H^\circ$ results. Negative entropy shows the adsorbed metal ions on the adsorbent in the solution. So in the solution media there are no more free ions that contribute to chaos in the entropy.

Adsorption kinetics

The kinetic models of adsorptions were determined with two most commonly used and known rate equations: pseudo-first order kinetic and pseudo-second order reaction kinetic models. The linear pseudo-first order (Eq. (10)) and pseudo-second order (Eq. (11)) kinetic are described by the following equations.

$$
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
$$

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

where $k_1$ (1 min$^{-1}$) and $k_2$ (g mg min$^{-1}$) are the rate constants of pseudo-first order and pseudo-second order respectively. $q_e$ (mg g$^{-1}$) is the amount of metal ion adsorbed at equilibrium and $q_t$ (mg g$^{-1}$) is the amount of metal ion adsorbed at any time $t$ [27,28]. The plot of $\log(q_e - q_t)$ versus $t$ is drawn to determine the $k_1$ and the plot of $t/q_t$ versus $t$ is drawn to determine $k_2$. The value of correlation coefficient is carried out by the plots correlations. Table 4 shows the computed results obtained from plots.

It is obvious that the $R^2$ values of pseudo-second order kinetic models are higher than pseudo-first order kinetic models. Therefore, the adsorption shows the pseudo-second order kinetic model and the calculated of $q_e$ from plots and experimental $q_e$ are similar to each
other. The values given in contact time section were used for the kinetic calculations.

Desorption

Adsorbed metal ions could be desorbed from adsorbent at low pH value or large amounts of H⁺ ions. 0.1 M HNO₃ was used for regeneration and three cycles were performed to desorb four metal ions. For desorption the parameters such as 2.5 mg adsorbent in 25 mL metal ion solution, optimum pH value, equilibrium contact time, metal ion concentrations 20.0 mg L⁻¹ for Pb²⁺ ion, 7.0 mg L⁻¹ for Cu²⁺ ion, 7.0 mg L⁻¹ for Ni²⁺ ion, 2.0 mg L⁻¹ for Zn²⁺ ion, and room temperature (25 °C) were chosen. The adsorption capacities for the first cycle were calculated to be 240.5, 196.7, 182.4, and 126.3 mg g⁻¹ for Pb²⁺, Ni²⁺, Cu²⁺, and Zn²⁺, respectively.

After being washed with 0.1 M HNO₃, the washed adsorbent was applied to the exact same adsorption test to check its reusability. The obtained adsorption capacities were 118.5, 98.4, 90.7, and 59.7 mg g⁻¹ for second cycle and 116.7, 99.5, 89.9, and 60.8 mg g⁻¹ for third cycle for Pb²⁺, Ni²⁺, Cu²⁺, and Zn²⁺, respectively. The percentage removal also decreased from 98, 96, 94, and 78% values to 46, 45, 42, and 38% values for second cycle and 43, 41, 38, and 32% for third cycle for Pb²⁺, Ni²⁺, Cu²⁺, and Zn²⁺, respectively. The same desorption experiments were carried out with 0.1 M HCl to compare the results with 0.1 M HNO₃. Similar results were obtained with 0.1 M HCl.

Conclusions

This tyrosine-containing hybrid adsorbent was used firstly in this paper to remove metal ions from aqueous solution. The maximum adsorption capacities and removal percentages of metal ions were found to be 240.5, 196.7, 182.4, and 126.3 mg g⁻¹ and 98, 96, 94, and 78% for Pb²⁺, Ni²⁺, Cu²⁺, and Zn²⁺, respectively.

The adsorption equilibrium data fitted well with Langmuir isotherm. The adsorption process was spontaneous, exothermic, and followed a pseudo-second-order kinetic model. Meanwhile, a very small amount of tyrosine-containing poly-GPTS/Ti(Tyr)OH achieved high removal percentage values in a very short time. It is a promising alternative adsorbent for those metal ions to remove from individual aqueous solutions.

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References


