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Preparation and characterization of magnetic polysulfone/thiourea microcapsules and their application for Cr(III)removal

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ABSTRACT

In this study, novel magnetic polysulfone microcapsules based on N-Benzoyl-N′-(4-methylphenyl) thiourea (TTU) were prepared with the phase inversion method. Characterization of the microcapsules was performed by using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and thermogravimetric analysis (TGA) techniques. The investigation of the adsorption properties of prepared microcapsules for the Cr(III) ion in the aqueous solution were evaluated. The parameters affecting the adsorption such as pH, contact time, amount of adsorbents (microcapsules), temperature and concentration were examined. Langmuir and Freundlich adsorption isotherms were studied to investigate the suitability of adsorption mechanism. The adsorption behavior of Cr(III) ions was found to be appropriate for the Langmuir isotherm. Cr(III) ion adsorption is spontaneous and exothermic and the adsorption process is more suitable to pseudo second order kinetic model according to the thermodynamic and kinetic analysis of the experimental data. Besides, real wastewater sample was used in order to highlight the effects of background water chemistry. Tannery wastewater was used for the removal of Cr(III) ions. Cr(III) ions were effectively removed by 87.54%.

Keywords: Adsorption; Cr(III); Microcapsule; N-Benzoyl-N′- (4-methylphenyl) thiourea; Polysulfone

1. Introduction

Constructive researches on the fabrication of easily producible and widely applicable new materials with different physical and chemical properties become more critical with rapid advancements in materials science and technology. Recent studies showed that alternative solvent extraction techniques have been developed for the enhanced recovery of metal ions from aqueous solutions. Nowadays, large number of techniques such as supported liquid membranes, emulsion liquid membranes, solvent impregnated resins and microcapsules attracts more attention for an efficient separation process.

Application of microcapsules in separation process has critical advantages such as stability, large specific interfacial area, high adsorption capacity, high selectivity, easy isolation and minimum use of organic solvent [1–3]. In recent years, microcapsules have been extensively used in

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various fields, such as increasing the shelf life of products, enzyme immobilization, improving hazardous and toxic material handling properties, masking unpleasant tastes and odors, enabling controlled release of drugs, converting liquids to solids, and recovery of metal ion pollutants [4,5].

Water pollution caused by toxic metal ions from various industrial effluents has gained much attention worldwide. Chromium and its compounds are contaminants commonly found in wastewater produced by several industries, including dye, leather tanning, plating, cement, and photography industries [6–8]. Several methods such as coagulation and precipitation, adsorption, solvent extraction, membrane process and ion-exchange have been employed for the removal of toxic chromium ions from wastewater [9–14].

Recently, magnetic separation technologies (MSTs) have been gaining growing attention. Magnetite (Fe_3O_4) has been widely used as magnetic material because of their excellent magnetic properties, chemical stability and bio compatibility [15]. Yin et al. [16] reported the preparation of magnetic polysulfone microcapsules containing tributyl phosphate and Fe_3O_4 using the phase-inversion precipitation method. The removal of phenolic pollutants from an aqueous solution with prepared microcapsules was studied [16].

The microcapsules are prepared by coating polymers that contains an immobilized suitable extraction reagent. In a relatively simple form, a microcapsule is a small sphere with a uniform wall around it [17]. Many preparation techniques have been proposed for microcapsules, including solvent evaporation, interfacial polycondensation, interfacial cross-linking, in-situ polymerization, coacervation, meltable dispersion, and phase- inversion precipitation etc. [18–20]. Phase-inversion precipitation and magnetic separation processes are preferred due to its easy phase separation and time saving properties [21].

Thiourea and their derivatives can be used in agriculture and medical field as insecticides, herbicides, plant growth regulators, antiviruses, antitumors and anticancers [22,23]. Thiourea compounds are also known as an efficient chelating agent due to its strong interactions with heavy metal ions [24,25].

In this study, polysulfone (PSF) microcapsules containing both N-Benzoyl-N’-(4-methylphenyl) thiourea as extractant and magnetic nanoparticles (Fe_3O_4) which help the isolation process were developed for the first time by using a phase inversion method (Fig. 1). The prepared microcapsules were named PSF/TTU. Developed micro capsules were applied for the removal of Cr(III) ions from aqueous solution by means of batch adsorption technique. Consequently, magnetic PSF/TTU microcapsules are regarded as a promising biosorbent for removing Cr(III) due to the strong metal chelating capability and good magnetic separation performance. Characterization of microcapsules was also investigated.

2. Materials and methods

PSF, $FeCl_2·4H_2O$, $FeCl_3·6H_2O$, N,N-dimethylformamide (DMF), ethanol, sodium dodecyl sulfate (SDS), $Cr(NO_3)_3·9H_2O$, $Cd(NO_3)_2·4H_2O$, $Cu(NO_3)_2·3H_2O$, NH_3, HCl and NaOH were obtained from Sigma-Aldrich and

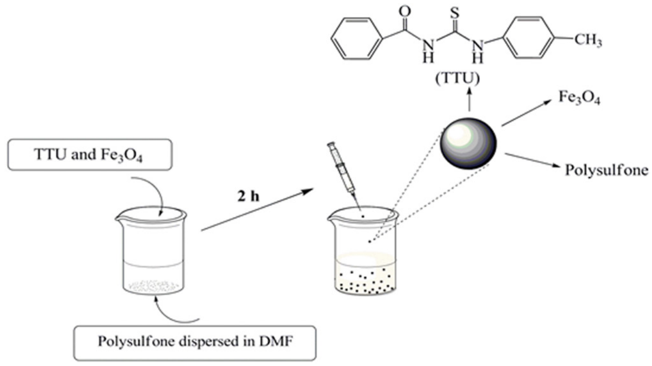

Fig. 1. Schematic procedure of magnetic PSF/TTU microcapsule production.

Merck. All reagents were of analytical purity grade. All aqueous solutions were prepared with deionized water. TTU was synthesized according to the method described in literature [26].

2.1. Preparation of PSF/TTU microcapsules

First of all, Fe_3O_4 magnetic nanoparticles were prepared via the co-precipitation method according to the method described in literature [27]. For that, 0.8 M $FeCl_3·6H_2O$ and 0.4 M $FeCl_2·4H_2O$ solutions were mixed and added to 250 mL of NH_3 solution. This solution was stirred with magnetic stirrer at 1000 rpm. After stirring for another 1 h, this solution was cooled down to room temperature. The precipitated Fe_3O_4 nano particles were filtered, washed with several times with methanol and dried under vacuum at room temperature.

PSF/TTU microcapsules were prepared with phase-inversion method described by Yin et al. [16]. PSF (1.2 g) was dissolved in DMF (16 mL) to prepare dispersed phase, then desired amount of TTU and Fe_3O_4 (0.05 g) magnetic particles were added into the dispersed phase and shaken for 2 h at room temperature. To prepare continuous phase, 0.5 wt.% sodium dodecyl sulfate (SDS) solution was mixed with ethanol/distilled water (1/1 volume ratio).After the preparation of two phases, the dispersed phase was injected into the continuous phase using a syringe with a needle (i.d. 300 μm). After that, PSF microcapsules containing the TTU extractant were obtained and separated from this solution using a magnet. Schematic procedure of PSF/TTU microcapsule production was shown in Fig. 1. They were washed several times with deionized water.DMF was allowed to remove completely in deionized water. Finally, the PSF/TTU microcapsules were air-dried at room temperature and kept in desiccators. Blank microcapsules were also prepared under the same conditions. The macroscopic morphologies of the microcapsules were viewed by a digital camera. It is seen in Fig. 2 that the PSF/TTU micro capsules in the solution could be easily isolated using a conventional magnet.

2.2. Characterization

Scanning electron microscope (SEM) and thermogravimetric analysis (TGA) was used to characterize the microcapsules. TGA of PSF/TTU microcapsules were performed with Perkin Elmer Diamond thermogravimetric analyzer at temperature range of 25–900ºC in nitrogen atmosphere. The diameter and surface morphology of the microcapsule samples were examined by SEM (Vega TescanII LSU, Czech Republic). The elemental analyses of microcapsules were performed by use of the SEM-EDX system (FEI Quanta FEG 250). The concentration of the Cr(III) was determined by ICP-OES (Perkin Elmer OPTIMA 5300 DV).

2.3. Adsorption studies

The adsorption studies were performed with batch technique in an aqueous solution for Cr(III) ion. Adsorption experiments were also studied with similar ions such as Zn(II), Ni(II), Co(II), Pb(II). The experimental results showed that adsorption properties of Cr(III) ions was better than other ions. Therefore, Cr(III) ion was selected. The microcapsules (50 mg) were added into 10 mL of metal solution which has initial concentration of 50 mg/L for Cr(III). $Cr(NO_3)_3 \cdot 9H_2O$ (Merck) was used to prepare the metal ion solution. The samples were mechanically stirred for 5 h at 298 ± 1 K and the solid portion was separated by using a conventional magnet. The experimental parameters studied are the amount of adsorbent (30–90 mg), effect on pH (2–5), temperature (298–333 K), contact time (0.5–48 h) and ion concentration (50–250 mg/L). Original pH of 50 mg/L Cr(III) solution was 5. The desired pH values were obtained by adding 0.1 mol/L solutions of HCl. After finishing adsorption experiment, the adsorbent was isolated and metal concentration of the solution was determined by ICP-OES.

3. Results and discussion

In this study, first of all, the characterization of prepared microcapsules was performed by SEM, EDX and TGA. The adsorption of Cr(III) ions from aqueous solutions on to the PSF/TTU magnetic microcapsules was studied as a function of contact time, initial ion concentration, adsorbent concentration, temperature and pH.

Fig. 2. Photograph of PSF/TTU microcapsules attracted by a magnet.

3.1. Characterization

SEM images of microcapsule surfaces were presented in Figs. 3–5. The SEM image of blank microcapsules (Fig. 3) indicates a homogeneous surface. But, introduction of TTU

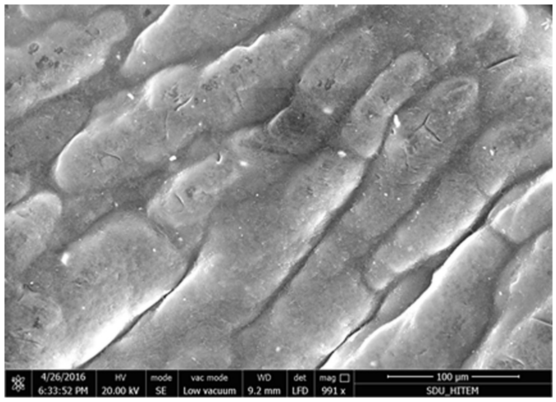

Fig. 3. SEM image of original PSF microcapsule.

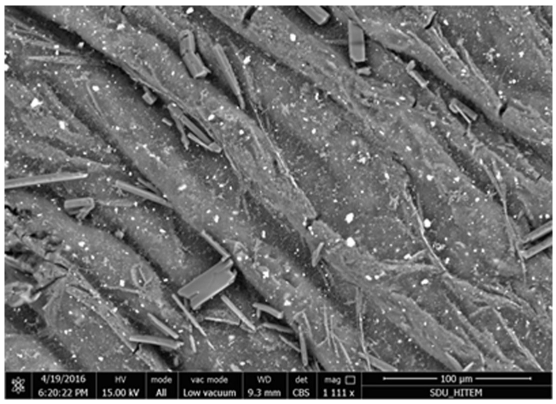

Fig. 4. SEM image of PSF/TTU microcapsule.

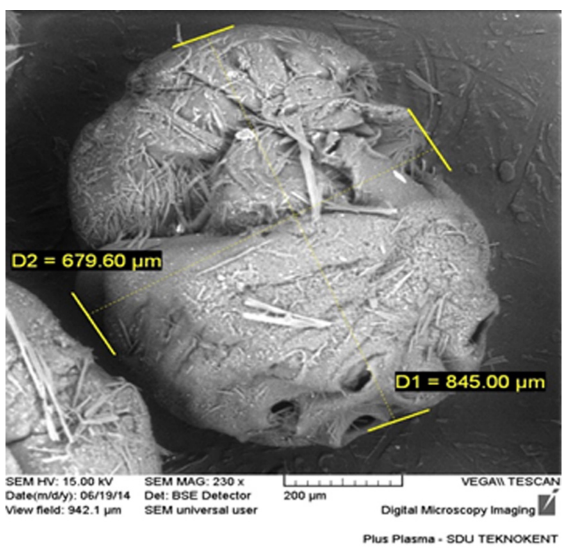

Fig. 5. SEM image of PSF/TTU microcapsule.

ligand onto the PSF microcapsules changed the surface structure (Fig. 4). As shown in SEM images, the immobilization of TTU onto magnetic PSF microcapsules was successfully performed. The micro size of the prepared PSF/TTU microcapsules was confirmed in Fig. 5. The average diameter of the microcapsules was also determined as 0.760 (±0.135) mm.

The EDX analysis of PSF/TTU microcapsules was carried out by energy dispersive analysis of SEM-EDX. A spectrum of PSF/TTU microcapsule was showed in Fig. 6 from a selected area. The results show that carbon (67.19%), oxygen (15.78%), natrium (2.90%), sulfur (9.18%), and iron (4.94%) were the essential elements of the PSF/TTU microcapsules. The EDX analysis confirmed the presence of iron particles and sulfur functional group on the polysulfone matrix as shown in Table 1.

These images demonstrate that the prepared microcapsules are in micron level. The thermogravimetric curves reflect the thermal stability of anchored surface and also the confirmation of the amount of the compounds immobilized as shown in Fig. 7. The temperature was increased from room temperature to 900°C at a rate of 10°C/min in nitrogen atmosphere. The curves showed distinct mass losses of the organic groups (TTU) covalently bonded to inorganic phase (polysulfone). The PSF/TTU microcapsules lost weight in three regions of temperature spectrum.

The first weight-loss step for PSF/TTU microcapsules was occurred due to the physically adsorbed water in the microcapsules between 25°C and 100°C. The second weight loss of 29% approximately corresponds to the decomposition of TTU in the range of 100–470°C. The third phase of decomposition from 470°C to 800°C corresponds to the PSF. From the TGA, the encapsulation capacity of the microcapsules was calculated as 29%. Similar findings were reported for polysulfone microcapsules containing different ligands by previous studies [16,28].

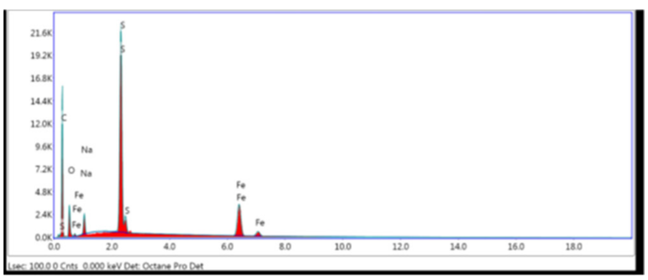

Fig. 6. SEM-EDX spectrum of prepared PSF/TTU microcapsules.

Table 1
Stoichiometric content of PSF/TTU microcapsules

Element	Weight, %	Atomic, %
CK	67.19	79.00
OK	15.78	13.93
NaK	2.90	1.78
SK	9.18	4.04
FeK	4.94	1.25

3.2. Effect of solution pH

The maximum adsorption of Cr(III) ion was obtained at pH 5. Fig. 8 shows the effect of pH on the adsorption of Cr(III) onto microcapsules. It was found that the adsorption of Cr(III) was increased with increasing solution pH up to 5. It should also be noted that an alkaline solution, with pH higher than 6.0, was not favorable for the adsorption. This phenomenon can be explained with the precipitation of $Cr(OH)_3$ onto the adsorbent surface [29]. Similar findings were also reported for the Cr(III) removal studies [30,31].

3.3. Effect of contact time and adsorption kinetics

Fig. 9 illustrates the adsorption of Cr(III) ion by time. It should mentioned that the adsorption capacity of Cr(III) ions increased with increased contact time. The removal of Cr(III) reached an equilibrium at the end of 600 min. Longer equilibrium time of PSF/TTU compared to other adsorbents was reported in the literature [16,32]. The adsorption kinetics was also studied in terms of pseudo-first order and pseudo-second order kinetic models [33,34].The kinetic parameters (q_e, q_t, k_1 and k_2) were calculated from curves and are listed in Table 2. The experimental data indicate that pseudo-second-order model

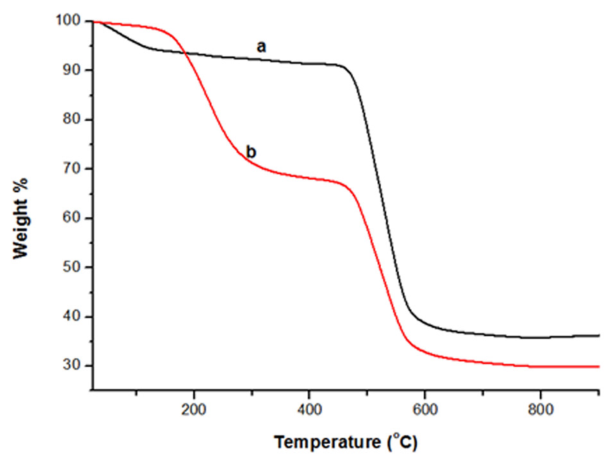

Fig. 7. Thermogravimetric diagrams of (a) PSF, (b) PSF/TTU microcapsule.

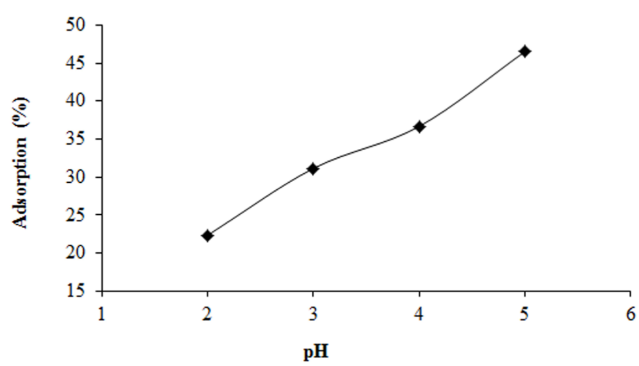

Fig. 8. The effect of pH on the adsorption of Cr(III) (Cr(III): 50 mg/L, adsorbent amount: 0.05 g, *t*: 5 h, temperature: 298 K).

was fitted better than the first-order model. As a result, mechanism of Cr(III) adsorption was found as pseudo-second-order rate equation for developed microcapsules. Fig. 10 also highlights the pseudo-second-order kinetic model for PSF/TTU microcapsules.

3.4. Effect of adsorbent amount

The effect of adsorbent amount's variation on the adsorption of Cr(III) by microcapsule is shown in Fig. 11. From the results, it is understood that the removal of Cr(III) increased with increased amount of microcapsule up to a certain level, and then leveled off.

This is consistent with the expectation that higher adsorbent dosages will result in lower adsorption capacity values. Optimum adsorbent dosage was found as 0.05 g of PSF/TTU for 50 mg/L Cr(III) solution (Fig. 11). This result can be attributed to the steric hindrance effect between more adsorbent sites [35].

3.5. Effect of temperature and thermodynamic parameters

The effect of temperature on the equilibrium constant (K) for the adsorption of Cr(III) ion onto microcapsules was investigated at this stage. The equilibrium constant for Cr(III) was low and adsorption decreased with increasing temperature for developed microcapsules (Fig. 12). This is due to the exothermic adsorption reactions of Cr(III) ion with microcapsule.

The maximum Cr(III) uptake was obtained at 298 K for PSF/TTU microcapsule. Thermodynamic parameters such as the standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated to explain

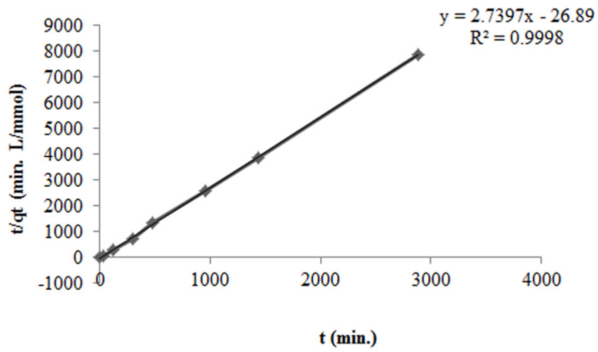

Fig. 10. The fitting of pseudo-second-order model for Cr(III) on PSF/TTU microcapsule (Cr(III): 50 mg/L, adsorbent amount: 0.05 g, pH: 5, temperature: 298 K).

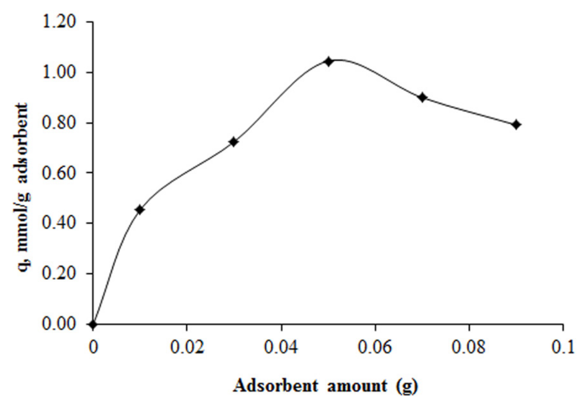

Fig. 11. The effect of adsorbent amount on the adsorption of Cr(III) (Cr(III): 50 mg/L, pH:5, *t*: 5 h, temperature: 298 K).

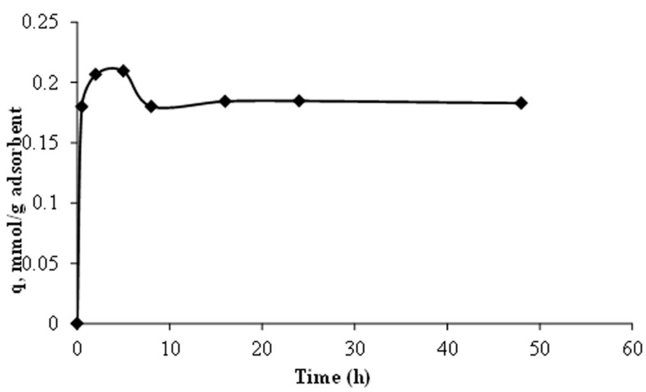

Fig. 9. The effect of time on the adsorption of Cr(III) (Cr(III): 50 mg/L, adsorbent amount: 0.05 g, pH: 5, temperature: 298 K).

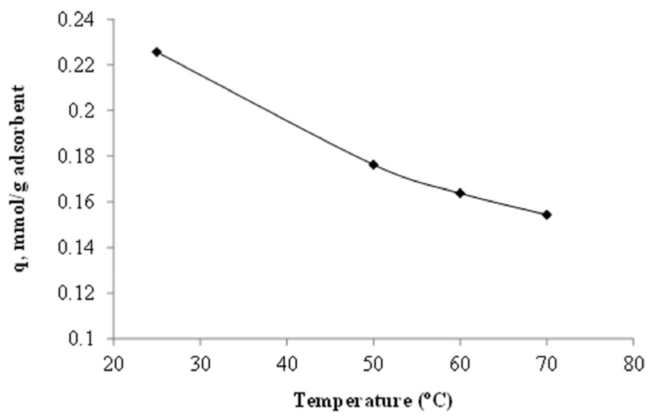

Fig. 12. The effect of temperature on the adsorption of Cr(III) (Cr(III): 50 mg/L, adsorbent amount: 0.05 g, pH: 5, *t*: 5 h).

Table 2
The rate constants of adsorption kinetic model for Cr(III) on PSF/TTU microcapsule

Pseudo-first-order				Pseudo-second-order		
q (experimental)	k_1	q_e (calculated)	R^2	k_2	q_e (calculated)	R^2
0.3794	2.3×10^{-5}	4.6377	0.1481	0.2791	0.3650	0.9998

q = mg/g , k_1= min^{-1}, q_e = mg/g, k_2 =g/mg·min, R^2 = correlation coefficient the nature of adsorption process [36,37]. The obtained parameters of the adsorption process are given in Table 3. As it can be seen from Table 3, negative ΔG° values confirm the feasibility of the process and spontaneous nature of the adsorption for the adsorbent. The negative values of ΔH° indicate the exothermic nature of the process while the negative ΔS° corresponds to a decrease in the degree of freedom of the adsorbed species.

The present results are similar to the results obtained by Sargın et al. [30] whom studied on the adsorption of some heavy metals from aqueous solutions by pollen-chitosan composite microcapsules. The thermodynamic analysis revealed the exothermic nature of the adsorption of the metal ions onto pollen–chitosan microcapsules. Especially, the negative ΔG°, ΔH°and ΔS° values were obtained for Cr(III) removal.

3.6. The effect of initial concentration

The effect of initial concentration on Cr(III) ion adsorption was studied with different initial Cr(III) concentrations by using optimum conditions. The effect of initial Cr(III) concentration is shown in Fig. 13 for PSF/TTU microcapsule. The results clearly highlighted that Cr(III) adsorption efficiency on PSF/TTU microcapsule was increased by increasing the initial Cr(III) concentration.

The experimental data was also applied to well-known Freundlich and Langmuir adsorption isotherms [38,39]. The parameters of these isotherms were calculated for Cr(III) adsorption by micro capsule and presented in Table 4. Comparison of the R^2 values confirmed that Langmuir isotherm represents an excellent fit to the experimental data compared to the Freundlich isotherm for micro capsules.

It can be concluded that, the number of adsorption sites on PSF/TTU was limited and metal ion adsorption can be occurred on a homogeneous surface. The Langmuir isotherm model assumes that adsorption occurs on a completely homogenous surface with uniform distribution of energy levels [40,41].

Comparison of the maximum Cr(III) adsorption capacities of PSF/TTU micro capsules in the present study with those reported for various adsorbents in literature is given in Table 5. The data show that the adsorption capacities of these adsorbents which were investigated in this study are higher than those reported in the relevant literature.

Table 3
The thermodynamic parameters for the adsorption of Cr(III) on PSF/TTU microcapsule

T(K)	1/T	lnK (kJ/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
298	0.0034	0.4393	–1.2330	–17.4286	–0.0544
308	0.0033	0.3739	–0.6895		
323	0.0031	–0.0994	0.1257		
333	0.0030	–0.2352	0.6692		
343	0.0029	–0.3395	1.2127		

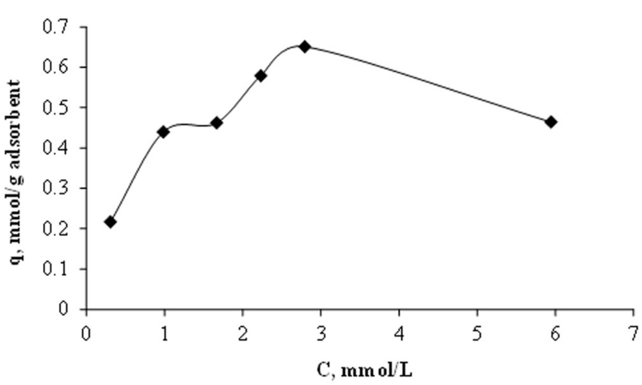

Fig. 13. The effect of initial concentration on the adsorption of Cr(III) (Adsorbent amount: 0.05 g, pH:5, *t*: 5 h, temperature: 298 K).

3.7. The effect of other metal ions on the removal of Cr(III)

The effects of other metal ions including Cd(II) and Cu(II), on the removal of Cr(III) by PSF/TTU microcap-

Table 4
The parameters of adsorption isotherms

Model	Parameters		
Langmuir	K_b	A_s	R^2
	183.009	0.4923	0.9569
Freundlich	K_f	1/n	R^2
	2.6104	0.3037	0.6397

K_f = adsorption capacity (mmol/g adsorbent), n = experimental constant, R^2 = correlation coefficient, A_s = adsorption capacity (mmol/g), K_b = adsorption energy constant (L/mmol).

Table 5
Comparison of adsorption capacity of PSF/TTU microcapsules for Cr(III) with various adsorbents

Adsorbent	pH	Maximum adsorption capacity (mg/g)	Reference
Kaolin	4.34	1.81	[42]
Ballclay	3.25	3.58	[42]
Sawdust	4.0	5.52	[43]
Reed mat	4.5–5.5	7.18	[44]
Tunisian clay	2.13	7.65	[37]
Modified peanut husk	4.0	7.67	[43]
Chitosan	3.0	7.74	[45]
Coir pith	3.3	11.60	[46]
Chelex-100	4.5	15.08	[47]
Lignin	5.0	17.97	[48]
Lewatit S 100	3.5	20.27	[47]
Celtek clay	6.0	21.55	[49]
PSF /TTU microcapsules	5.0	25.59	In current study

sule were also investigated. Cd(II) and Cu(II) ions were selected since they have a strong affinity to make complexes with TTU ligand. The adsorption experiments were carried out in the presence of 50 mg/L salt solutions of cadmium nitrate, copper nitrate and chromium nitrate at pH 5.0. The results indicated that Cr(III) was preferably removed by PSF/TTU microcapsule against Cd(II) and Cu(II) ions. The adsorption percentage of Cr(III)in the presence of 50 mg/L Cd and Cu ions was 62.44%. Similar findings were reported in related studies [50].

3.8. The performance of PSF/TTU on waste water

The potential of PSF/TTU microcapsule was tested by the tannery wastewater samples collected from Special Zone for Tannery Industries (DOSB) located in Isparta, Turkey. The pre-selected optimum conditions of pH 5, temp 25 °C, adsorbent dosage: 0.1 g and the contact time 300 min were used and the results obtained on residual Cr(III) level. The Cr(III) concentration of tannery wastewater sample was determined as 0.682 mg/L. The removal of Cr(III) from tannery wastewater sample was obtained as 87.54%. Despite complex background water chemistry and presence of various ions in the wastewater sample, the Cr(III) adsorption capacity of developed micro capsule was impressive.

3.9. The re-usability of PSF/TTU adsorbent

Reusability of developed microcapsules for Cr(III) adsorption was tested under optimum conditions. After the adsorption experiments, the loaded PSF/TTU microcapsules were respectively treated with 1.0 mol/L HCI and distilled water for the regeneration. Treated PSF/TTU microcapsules were kept in desiccators. The adsorption process was repeated by using the same adsorbent in four runs of 30 day duration. Fig. 14 shows that Cr(III) adsorption capacity of the PSF/TTU adsorbent decreased from 59.86% to 34.56% after 4 months. Results of the adsorption tests indicated that PSF/TTU microcapsules can be employed as a kind of recyclable adsorbents for the removal of Cr(III) ion.

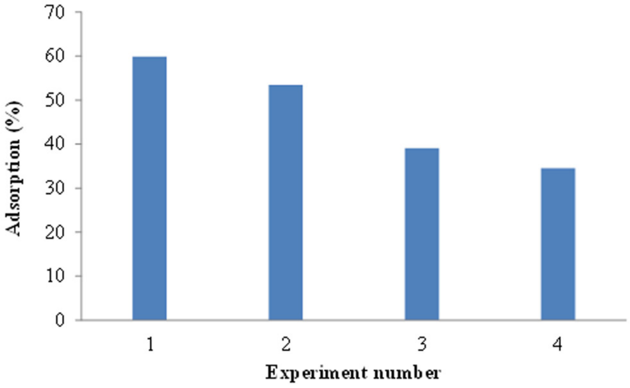

Fig. 14. Cr(III) adsorption percentage for conducted experiments.

4. Conclusions

A novel adsorption material PSF/TTU was developed and characterized by using TGA, SEM and SEM-EDX. As it can be seen from all results, PSF/TTU microcapsules that immobilized with TTU are more selective than blank microcapsules to Cr(III) ions. Cr(III) adsorption properties of this novel adsorbent (PSF/TTU) were investigated by using various parameters. The maximum removal of Cr(III) was observed at an optimum pH of 5.0. Adsorption study indicated that the obtained experimental data is fit better with the Langmuir type adsorption isotherm. The Langmuir adsorption capacity of PSF/TTU microcapsules was 0.4923 mmol/g. The adsorption kinetic data well fit with the pseudo-second-order model. The adsorption thermodynamic parameters were also calculated and determined for PSF/TTU. The equilibrium constant for Cr(III) was low and adsorption decreased with increasing temperature for PSF/TTU microcapsule. On the basis of all results, it can be concluded that developed novel PSF/TTU microcapsule has a strong potential for the efficient removal of Cr(III) from aqueous solutions. Development of a novel, economical and efficient adsorbent for the removal of Cr(III) from industrial effluents can be regarded as the main importance of the study.

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