

Removal of hexavalent chromium using modified pistachio shell

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Abstract. Pistachio shell (*Pistacia vera*) (PS), a low-cost material, has been utilized for the removal of the Cr(VI) ions after treatment with citric acid. Batch experimental steps were applied to obtain Cr(VI) ion adsorption details for the equilibrium between Cr(VI) and modified pistachio shell (MPS). The influences of contact time, pH, adsorbent dose and initial chromium concentration on the adsorption performance of MPS was investigated in detail. The results displayed that adsorption of Cr(VI) by MPS reached to equilibrium after 2 h and after that a little change of Cr(VI) removal efficiency was observed. The sorption percent is higher at lower pH and lower chromium concentration. Two possible mechanisms for reduction of Cr(VI) to Cr(III) can be suggested in Cr(VI) removal. In the first mechanism, Cr(VI) is reduced to Cr(III) by surface electron-donor groups of the adsorbent and the reduced Cr(III) forms complexes with adsorbent or remains in the solution. This Cr(III) is not adsorbed by adsorbent at pH 1.8. But in second mechanism, the adsorption-coupled reduction of Cr(VI) to Cr(III) occurred on the adsorbent sites. The equilibrium sorption capacity of Cr(VI) ion after 2 h was 64.35 mg/g for MPS.

Keywords: sorption; isotherm; Cr(VI); pistachio shell

1. Introduction

Rapid industrial growth has caused water pollution over the world and heavy metals have become an important economic and environmental issue for the water pollution (Köhler *et al.* 2007). Increasing urbanization worldwide had substantially ravaged our aquatic environment through the discharge of industrial and domestic wastes. These wastewaters are frequently laden with toxic heavy metals in which significant amounts are deposited into the natural aquatic ecosystems (Chen and Lim 2002). Among these toxic metals, chromium (Cr) is one of important pollutants in surface water and groundwater. The industrial use of chromium has increased, because of the extensive use of chromium in chromium plating, tanning of leather, photography, metal finishing and textile manufacture, etc. Among its several oxidation states, trivalent and hexavalent species of chromium are principal ones found in industrial effluents (Wang *et al.* 2009, Zouboulis *et al.* 1995, Park *et al.* 2006). Chromium can be beneficial and toxic to living organism depending on its oxidation state and concentrations. Cr(VI) is more toxic than Cr(III) and it is better absorbed than Cr(III) for both

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acute and chronic exposures.

The traditional physical–chemical methods for the removal of heavy metals from effluents which include neutralization/precipitation, ion exchange, chelation, reverse osmosis, oxidation are highly expensive and not quite effective at lower concentrations of metal ions (Volesky 1990, Zinkus 1998). A variety of low cost natural biomaterials for the heavy metal elimination from diluted solutions has the potential to remove inorganic pollution (Blázquez 2009).

Ecofriendly and economical agricultural waste materials being highly efficient due to their unique chemical composition, availability in abundance, renewable natural agricultural by-products, low in cost and more efficient are seem to be an alternative adsorbent for chromium ion removal. These cellulosic materials are used in the removal of chromium ions from dilute aqueous solutions either in their natural or modified form. Agricultural waste materials are mainly composed of three groups of polymers; lignin, hemicellulose and cellulose as the main constituents and their matrix comprise a variety of functional groups. For example, the lignin fraction consists of non-sugar type molecules. Other components contain a variety of functional groups such as extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons and ash. Cellulosic agricultural waste materials can be an abundant source for significant chromium adsorption.

Certain types of natural adsorbents, in the categories of microbial biomass and plant wastes have been successfully used as adsorbing agents in wastewater treatment. In recent years, a vast number of publications related to safe and economical methods for the elimination of heavy metals from contaminated water has been dedicated by using adsorption techniques with different low cost materials (Chong and Volesky 1995). It has been reported that various natural adsorbents were tried for Cr(VI) removal such as green algae (Gupta *et al.* 2001), Turkish Brown coals (Arslan and Pehlivan 2007), wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal (Dakiky *et al.* 2002), bark (Aoyama and Tsuda 2001), citric acid modified soybean straw (Zhu *et al.* 2008), soybean hull (Marshall *et al.* 2001, Marshall and Wartella 2003), olive stones (Fiol *et al.* 2003), walnut hull (Wang *et al.* 2010). Citric acid modified wood for copper, lead (Low *et al.* 2004), peanut hulls for Co(II) and Ni(II) (Hashem *et al.* 2005) and Pinus halepensis sawdust for cadmium (Semerjian 2010) were tried in the adsorption experiments.

In this study, adsorption of chromium onto the MPS as an alternate adsorbent was investigated. Batch removal of Cr(VI) experiments were performed for kinetic studies. The studies on the adsorption of Cr(VI) were conducted by varying various physico–chemical parameters such as pH, time, adsorbent amount, and concentration level (Wang 2009). The Langmuir and Freundlich isotherms were applied to analyze the experimental data obtained from the equilibrium.

2. Materials and methods

2.1 Materials

PS was ground in ball mill and the resulting crumbs were sieved to obtain size of 150 μm . Before the use, PS was rinsed thoroughly with de-ionized water and dried in air oven at 100°C for 24 h. All the chemicals and reagents used were of analytical grade (Merck-Sigma-Aldrich) and used without further purification. pH adjustment was done with various concentrations of NaOH and HCl, as required. A stock solution (1000 mgL⁻¹) of Cr(VI) was prepared by dissolving dried K₂Cr₂O₇ in double distilled water. Required concentrations of chromium were fixed up from the original

solution.

2.2 Experimental methods

2.2.1 Apparatus

Shells were grinded with Retsch RM 100 model grinding machine. The final pH value of the mixtures was measured with Orion 900S2 Model pH meter. A thermo stated shaker of GFL 3033 model and IKAMAG-RO15 model magnetic stirrer were used for adsorption experiments. An UV-Visible Spectrophotometer (Shimadzu UV-1700) (λ :540 nm) was used with the 1,5 diphenyl carbazide method in the analysis of Cr(VI) ion in the solution phase. Thermo gravimetric analysis were carried out using TA Instruments Q5000IR in a dynamic air atmosphere 25 mL/min. Samples were measured in open Pt pan, mass of the sample was typically 5 mg, heat rate 10°C.

2.2.2 Batch adsorption

The initial pH of the Cr(VI) solutions was adjusted in the range from 1.5 to 7 by using 0.1 M HCl and NaOH solution. 0.1 g of MPS (dry weight) was equilibrated with 40 mL aqueous solution of Cr(VI) ions at varying concentrations and initial pH values. The concentration isotherm curves and equilibrium sorption capacities were determined in batch experiments by shaking at prefixed times in sealed test tubes containing 0.1 g of adsorbent and 40.0 mL of 2×10^{-3} M Cr(VI) solution. MPS in the solution phase was separated by filtration through a membrane filter (0.45 μ m). The filtrate was analyzed for the chromium concentration remaining in the solution. The kinetic data of adsorbed amount of Cr(VI) at time t , q_t (in $\text{mg}\cdot\text{g}^{-1}$ of adsorbent), were obtained by the mass balance (Eq. (1))

$$q_t = [(C_o - C_t) V] / m \quad (1)$$

Time dependent experiments were carried out by shaking the adsorption mixture at various time intervals up to 240 min and analyzing the Cr(VI) ion content at the end of the contact time.

2.3. Sorbent preparation

2.3.1 Modification of PS with citric acid (CA)

First, 10 g of reagent citric (anhydrous) acid was dissolved in 50 ml distilled water. This solution was added to 10 g PS (1:1 w/w-CA/PS) and allowed to soak 24 hour at 60°C and excess water was removed. Then, the dry sample was reacted for 2 hours by elevating oven temperature at 120°C (optimum temperature). The oven temperature and reaction time were raised to the desired level (110–130°C) for 2 to 24 hours and the mixtures were allowed for the reaction (Table 1). The acid-modified PSs were then cleaned by rinsing with distilled water and filtered.

2.3.2 Carboxyl determination

0.25 g dry sample was slurred in pure water and 0.1 M NaOH was added and stirred for 24 h. The mixture was back-titrated with 0.1 M HCl until the phenolphthalein end point. Conversion factors were determined using citric acid as standards. Untreated PS was used for the comparison according to the carboxyl content.

Table 1 Effect of citric acid (CA) amount, temperature and reaction time on citric acid (CA) and PS reaction

Adsorbent	CA/Adsorbent (w/w)	Reaction time (h)	Temp. (°C)	Reaction efficiency (%)	COOH (mmol/g)
PS ^a	-	-	-	-	3.2
MPS ^b	0.5/1	24	120	84.205	5.7
MPS ^b	1/1	2	120	77.348	7.4
MPS ^b	1/1	4	120	80.947	7.2
MPS ^b	1/1	6	120	85.990	7.0
MPS ^b	1/1	12	120	88.449	6.9
MPS ^b	1/1	24	110	87.391	6.5
MPS ^b	1/1	24	120	91.034	6.8
MPS ^b	1/1	24	130	95.517	7.0

^aUntreated PS, ^bPS(10 g); CA(10 g); after initial dehydration

2.4 Characterization of adsorbent

2.4.1 FTIR analysis

FTIR analysis for PS and MPS were given in Fig. 1. FTIR records of the PS are richer in the content of OH groups which have broad bands around 3353 cm^{-1} ; in case of MPS, the intensity is significantly lower, and the OH groups are less stable at elevated temperatures. Next difference is around 2886 cm^{-1} where PS contains higher content of aliphatic groups corresponding to C-H, symmetrical stretching vibration with typical splitting and small shoulder at 2940 cm^{-1} originating probably from fatty acids; 1716 cm^{-1} in PS corresponds to the C=O stretching vibrations, in case of modified PS is shifted to 1731 cm^{-1} ; 1631 cm^{-1} C=C stretching vibration originated probably from

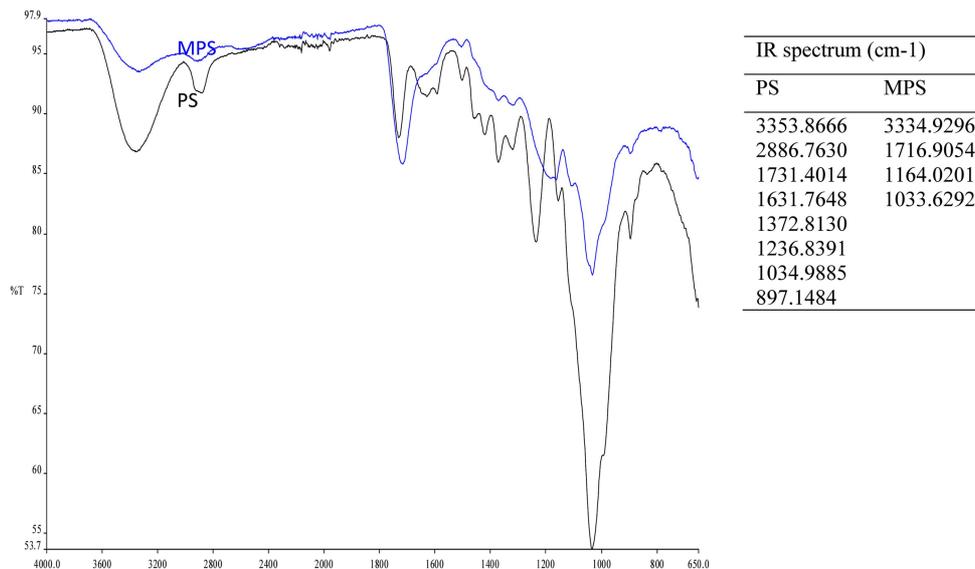


Fig. 1 IR Spectra of PS and MPS

Table 2 Elemental analysis of PS before and after modification

Weight percentage (%)	PS	MPS
C	42.5	44.3
H	5.2	6.0
O	52.3	49.7
C/O (Atomik)	0.8	0.9

the presence of unsaturated fatty acids, those are probably destroyed by modification since this peak is absent in modified sample; 1372 cm^{-1} CH_2 – deformation vibration and CH_3 symmetrical bending of aliphatic structures; 1236 cm^{-1} aliphatic CH_2 wagging vibration and C-O phenolic stretching vibration and OH deformation – this peak seems to be shifted to 1164 cm^{-1} and its intensity is reduced; 1034 cm^{-1} C-O stretching vibration and other bonds typical for cellulose, in modified sample is still a high content of this structures despite the modification; 897 cm^{-1} saturated aliphatic esters and symmetrical C-O stretching vibration, the content in MPS is reduced but still present. To sum it up, during modification, is the content of fatty acids is significantly reduced which can be seen by reduction of aliphatic carbon and COOH groups; further, reduction in number of OH groups can be attributed to the degradation of cellulose moieties.

2.4.2 Elemental analysis

Elemental analysis confirms that the higher C/H for PS implies higher content of aromatic carbon than in the MPS (Table 2). The C/O ratio suggests lower content of O per C in PS which suggests modification of polar groups in treated sample; potentially conversion of C-OH alcoholic to C=O aldehyde and ketonic to COOH groups occurred or modification lead to destruction of ester bonds followed by evaporation of alcohols.

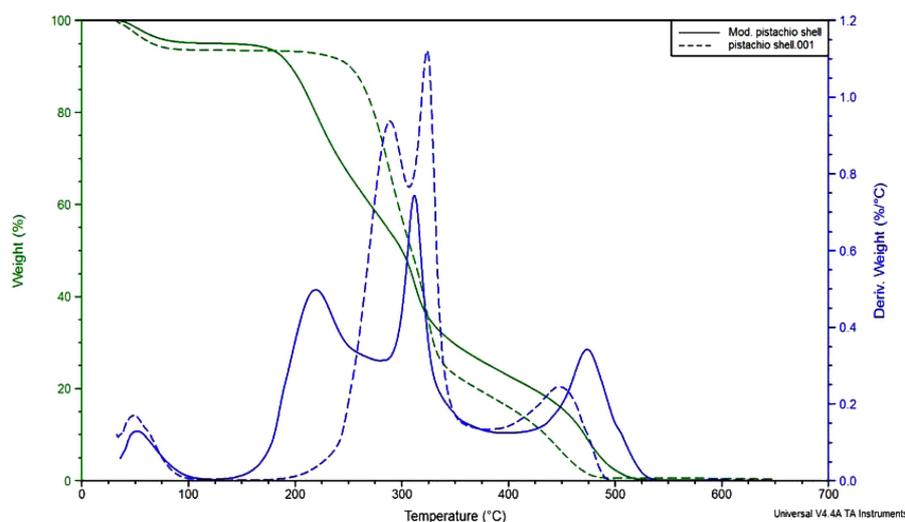


Fig. 2 TGA and DTG comparison of PS and MPS

2.4.3 TGA-DTG analysis

Fig. 2 shows the curve of TGA and DTG about PS and MPS. The records started around 30°C and immediately started the moisture evaporation followed by degradation. It can be seen that degradation of MPS started at lower temperatures in comparison with PS (175 vs. 241°C). Taking the results from elemental analysis into account, the C/O parameter decreased after modification which suggests formation of new functional groups containing oxygen generally, those are thermally unstable and incapable to resist the thermo-oxidative attack. In fact, it should be a possible reason of higher sorption capacity of this material. As it can be seen on the DTG curves, number of peaks is the same, but they occurred at different temperatures (Fig. 2). This can be partially caused by the difference in C/H. In fact, the modified sample has the lower C/H ratio and last peak (degradation of aromatics) was shifted to higher temperatures in comparison with MPS. Generally, it seems that the modification took part mainly on the surface, the “core” of the material seems to be unaltered. This is confirmed also by the mass loss at 600°C at which both materials are already decomposed.

2.4.4 SEM characterization

The SEM enables the direct observation of the surface microstructures of different adsorbents. SEM micrographs obtained before and after Cr(VI) adsorption onto PS (Figs. 3(a) and 3(b)) and MPS (Figs. 3(c) and 3(d)) are given. SEM characterization of the adsorbent has shown a clear difference in the native and Cr(VI) loaded adsorbents. It can be observed from (Figs. 3(b) and 3(d)) that the surface morphology of modified adsorbents is different of the studied original adsorbents. The citric acid treated adsorbent has porous structure with greater homogeneity, which can be

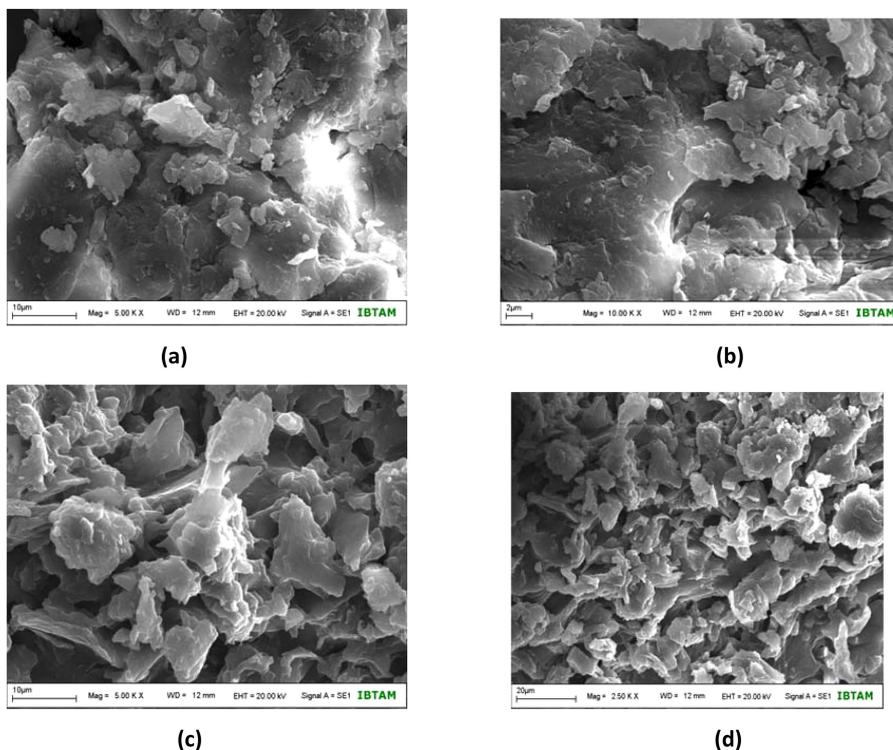


Fig. 3 (a) SEM of PS, (b) SEM of Cr(VI)-loaded PS, (c) SEM of MPS, (d) SEM of Cr(VI)-loaded MPS

clearly seen in the magnified view of the SEM (Figs. 3(a) and 3(c)).

3. Results and discussion

3.1 Effect of solution initial pH on the Cr(VI) adsorption

The chemical composition of PS determined by Yeganeh *et al.* (2006) and the chemical composition of them may differ depending on the geographical site and the season of cultivation. Experiments which were performed according to TSE (Turkish Standards Institute) and ASTM methods showed that pistachio shells contain 60.62% cellulose and 12.80% acid-insoluble lignin (Apaydin-Varol *et al.* 2007, Yeganeh *et al.* 2006, Özsin 2011).

It is well known that the dominant form of Cr(VI) at pH 2 is HCrO_4^- . Increasing the pH will shift the concentration of HCrO_4^- to other forms, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. The effect of pH on adsorption of Cr(VI) was studied at room temperature by varying the pH of Cr(VI) solution in MPS suspension from 1.5 to 7.0. Maximum adsorption at pH 1.8 indicates that it is the HCrO_4^- form of Cr(VI) which is the predominant species between pH 1 and 2. Similar results were displayed by several other researchers working Cr(VI) adsorption (Kobya 2004, Jain *et al.* 2010).

The interactions of Cr(VI) ions with MPS surface molecules are complex, dominated by adsorption, complexation and chelation. The variation in equilibrium pH for MPS is shown in Fig. 4. The equilibrium pH decreases non-linearly in the pH range of 1.5–4.0. The percent adsorption decreased in the pH range of 2.0–5.0 and remains stable until pH 7.0. 77% of the Cr(VI) adsorbed onto MPS from the solution when the optimum pH was around 1.8.

Different studies have shown that the solution pH seems to be the most important parameter in the adsorptive process of natural adsorbents (Dönmez and Aksu 2002, Gupta *et al.* 2001, Altun and Pehlivan 2012, Pehlivan *et al.* 2012, Karthikeyan *et al.* 2005). Different types of pH dependent equilibrium between adsorbent and adsorbate can exist in the batch reactor. As the pH is shifted, the

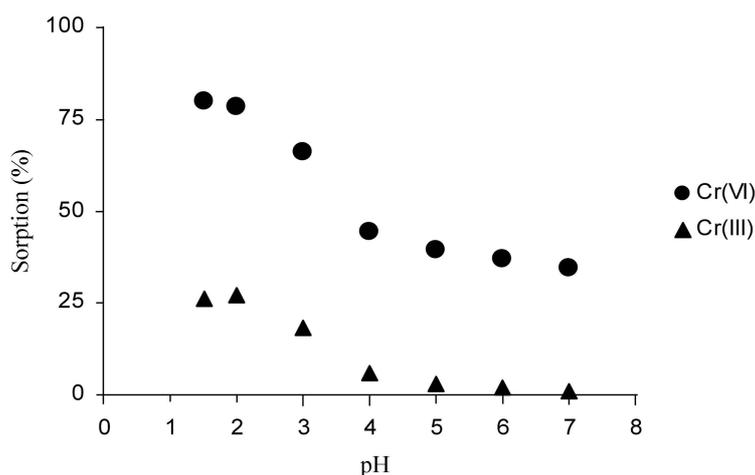


Fig. 4 Effect of pH on the biosorption of Cr(VI) using MPS. Biosorption conditions; initial concentration of Cr(VI): 2×10^{-3} mol/L, 0.1 g adsorbent, 40 mL of biosorption medium, temperature: $25 \pm 1^\circ\text{C}$, contact time: 120 min

equilibrium will also shift. Depending on the solution pH values, Cr(VI) species may exist as dichromate ($\text{Cr}_2\text{O}_7^{2-}$), hydrochromate (HCrO_4^-), or chromate (CrO_4^{2-}). In the pH range of 1.0–6.0, chromium species co-exist in different forms, such as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ of which HCrO_4^- predominates. As the pH of the solution increases, predominant species of chromium become CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. At lower pH ranges, due to the high electrostatic force of attraction, the percentage of Cr(VI) removal from solution phase is high and the surface of adsorbent would be surrounded in a restrictive manner by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the adsorbents by greater attractive forces (Karthikeyan *et al.* 2005, Verma *et al.* 2006, Demirbas *et al.* 2008, Jain *et al.* 2010).

It has been proved that, when Cr(VI) comes in contact with soluble reducing certain substances, usually in an acidic solution, it is readily reduced to the Cr(III), because Cr(VI) has high redox potential value (Park *et al.* 2005a, Park *et al.* 2005b). Cr(VI) can be removed from the aqueous phase by biomass through two mechanisms: (A) and (B). In mechanism (A) (direct reduction), Cr(VI) is directly reduced to Cr(III) in the aqueous phase by contact with the electron-donor groups of the adsorbent, i.e., groups having lower reduction potential values than that of Cr(VI). Mechanism (B) (indirect reduction); however, consists of three steps; (1) the binding of anionic Cr(VI) ion species to the positively-charged groups present on the adsorbent surface; (2) the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups; and (3) the release of the Cr(III) ions into the aqueous phase due to electronic repulsion between the positively-charged groups and the Cr(III) ions, or the complexation of the Cr(III) with adjacent groups capable of Cr-binding (Park *et al.* 2005a). As seen in the Fig. 4, some of Cr(VI) were reduced to Cr(III) and the reduction rate of Cr(VI) increased with decreasing solution pH as the protons were consumed during the reduction period. Cr(III) ions passed to the solution phase were measured and recorded in Fig. 4.

3.2 Effect of contact time

The effect of time on the adsorption of Cr(VI) ions by the MPS was studied by taking 0.1 g

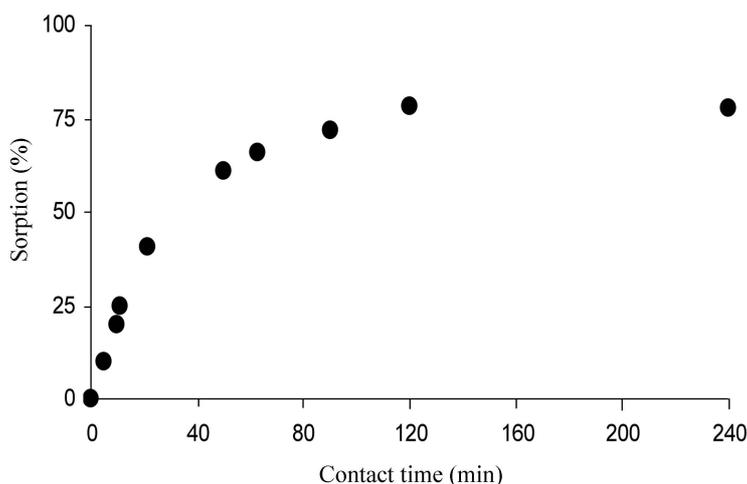


Fig. 5 Effect of contact time on the sorption of Cr(VI) by MPS. Biosorption conditions; initial concentration of Cr(VI): 2×10^{-3} mol/L, 0.1 g adsorbent, 40 mL of biosorption medium, temperature: $25 \pm 1^\circ\text{C}$, pH 2.0

adsorbent with 40.0 ml of 0.002 M Cr(VI) solution in different plastic beakers. The beakers were shaken for different time intervals in a temperature-controlled shaker. Fig. 5 illustrates the effect of the adsorption time on the adsorption efficiency. The removal rate of Cr(VI) ions increases with the increase of the adsorption time. However, it remains constant after an equilibrium time of 120 min, which indicates that the adsorption tends toward saturation at 120 min. Therefore, the adsorption time was set to 120 min in each experiment.

3.3 Effect of amount on adsorption

The effect of the MPS amount on the removal of metal ions is shown in Fig. 6. Adsorption increased from 56.0 to 79.0% MPS with increase in adsorbent dose from 0.025 to 0.2 g in the case of chromium ion and then became almost constant.

3.4 Effect of initial Cr(VI) concentration

The effect of Cr(VI) concentration on the sorption by the MPS was investigated by varying the Cr(VI) concentration (0.2-2.0 mmol/L) at a pH of 2.0 for 120 min equilibrium time. Percentages of removal by MPS were 75.0% for Cr(VI) ion. The percent Cr(VI) ions removal efficiency of MPS increased with increasing Cr(VI) concentration. The Langmuir isotherm is conclusive for the dynamic equilibrium adsorption processes on completely homogenous surfaces with negligible interaction between adsorbed molecules. The Langmuir and Freundlich isotherm models were used for modeling of the adsorption equilibrium data between Cr(VI) ion and PS in the solution phase (Eqs. (2) and (3)). The Langmuir type adsorption isotherm was found to be the best one that represents the equilibrium data related to the adsorption phenomena of Cr(VI) ion on PS.

Langmuir equation

$$\frac{C_e}{q_e} = \frac{C_e}{A_s} + \frac{1}{A_s K_b} \quad (2)$$

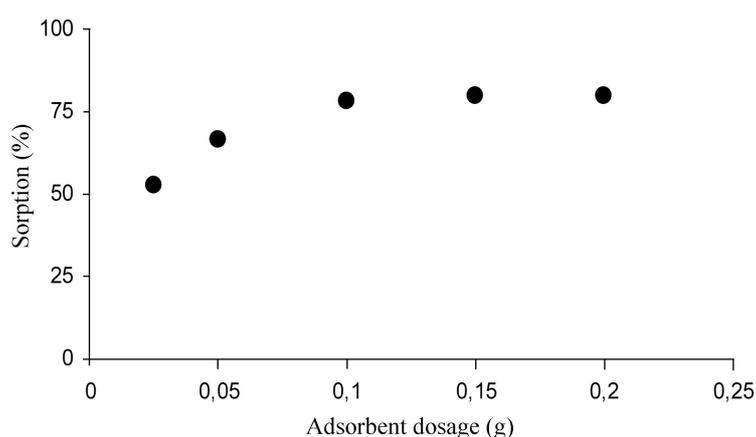


Fig. 6 Effect of adsorbent dosage on the sorption of Cr(VI) on MPS. Biosorption conditions; initial concentration of Cr(VI): 2×10^{-3} mol/L, volume 40 mL of biosorption medium, temperature: $25 \pm 1^\circ\text{C}$, pH 2.0, contact time: 120 min

where A_s (mol g^{-1}) and K_b (L mol^{-1}) are the coefficients, q_e is the weight adsorbed per unit weight of adsorbent and C_e is the Cr(VI) concentration in bulk solution at equilibrium.

Freundlich equation

$$\left(\frac{x}{m}\right) = kC_e^{1/n} \quad (3)$$

where n is the Freundlich constant and k is the adsorption coefficient, x/m is the weight adsorbed per unit weight of adsorbent and C_e is the equilibrium metal concentration in fluid. Taking logs and rearranging the Eqs. (3) and (4) was obtained. The adsorption data in the linear forms gave satisfactory correlation coefficients for a part of the covered concentration range.

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C_e \quad (4)$$

The effect of adsorbate concentration is shown in Fig. 7. In the case of low Cr(VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is larger and subsequently the fractional adsorption becomes independent of initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration. The amount of Cr(VI) ions adsorbed per unit mass of the PS and MPS increased with the initial Cr(VI) concentration as expected. The sorption capacities were 21.142 and 64.356 mg of Cr(VI) per g of PS and MPS, respectively. The Langmuir equation was more applicable than the Freundlich although both described the sorption data adequately. We found the Langmuir isotherms, to have the highest correlation coefficients 0.99

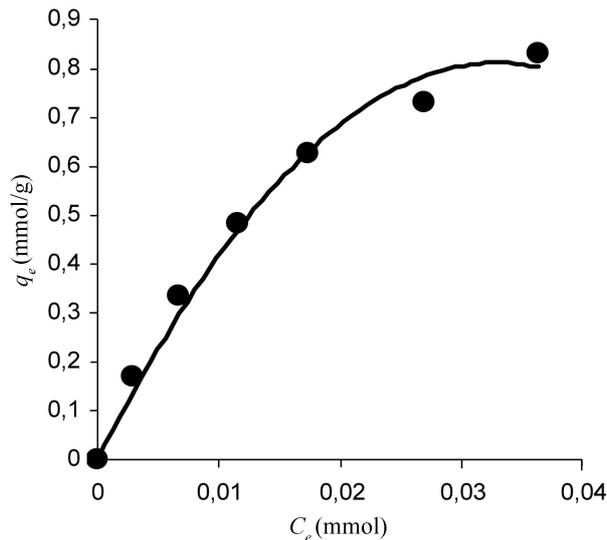


Fig. 7 Sorption isotherms of Cr(VI) ion on MPS as a function of initial Cr(VI) concentration at pH 2.0; 0.1 g adsorbent, temperature: $25 \pm 2^\circ\text{C}$, contact time: 120 min

Table 3 Freundlich and Langmuir isotherm parameters of MPS

Freundlich isotherm			Langmuir isotherm		
k^a	n	R^2	K_b	A_s^a	R^2
0.745	1.590	0.979	55.2	1.240	0.997

^ammol/g dry adsorbent

Table 4 Cr(VI) metal ion adsorption capacities of some adsorbents reported in literature

Adsorbent	Adsorption capacity (mmol/g)	Reference
Almond shell	0.0654	Pehlivan and Altun (2008)
Olive stones	0.1731	Fiol <i>et al.</i> (2003)
Sawdust	0.3042	Dakiky <i>et al.</i> (2002)
Citric acid modified Pistachio shell	1.2375	This study
<i>p-tert</i> -butylcalix[8]areneoctamide	7.8621	Qureshi <i>et al.</i> (2009)

for MPS (Table 3). Some of adsorbents used for Cr(VI) removal studied by several investigators were given in Table 4.

4. Conclusions

The removal of Cr(VI) from aqueous solution using MPS has been investigated in batch mode with various operating parameters such as initial pH, agitation time, initial chromium concentration and adsorbent dosage. It is apparent that the equilibrium concentration in solution phase decreases with increasing adsorbent amount for a given initial Cr(VI) ion concentration. FTIR analysis suggests the importance of functional groups such as amino, hydroxyl and carboxyl during Cr(VI) removal. Two possible mechanisms for reduction of Cr(VI) to Cr(III) can be suggested in Cr(VI) removal. The sorption capacities of adsorbents were calculated as 21.142 and 64.356 mg of Cr(VI) per g of PS and MPS respectively. The Langmuir type adsorption isotherms was preferred for the adsorption equilibrium of Cr(VI) ion on MPS. This study has demonstrated that using MPS as adsorbent for the removal of Cr(VI) from aqueous solution phase was efficient.

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