Removal of Cr Ions from Aquatic Solutions Using Olive Leaves as Low-cost Bio-sorbent

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ABSTRACT: Contamination of water by chromium (Cr) creates serious pollution in terms of the environment and public health, since its different forms become released into air, water, soil and residential areas. In the present work, olive leaf powder (OLP) was evaluated as a novel low-cost sorbent due to its various functional groups such as amide, hydroxyl, carboxyl, and carbonyl which are responsible for the bio-removal of chromium ions from aqueous solutions. The chemical functional groups and microstructure of the OLP bio-sorbent were characterized by the Fourier Transform Infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) techniques. The bio-sorption conditions were optimized as pH 4, contact time 60 min, bio-sorbent dosage 40 g/L, temperature 40 °C. The bio-sorption isotherm was well fitted to the Langmuir model, and the predicted maximum bio-removal capacity of the OLP was estimated at 42.4 mg/g under the above-mentioned experimental conditions. The reuse performance of the bio-sorbent was determined after repeated sorption/desorption cycles. The thermodynamic examination showed that the chromium sorption by OLP was endothermic in thermal nature. The kinetic evaluations indicated that the bio-sorption process well followed with the pseudo-second-order model. The overall results demonstrated that the OLP can be thought as a potential bio-sorbent for cleaning of chromium-contaminated water and wastewater due to its advantageous properties such as low cost, availability, renewable nature, and remarkable bio-sorption capacity.

INTRODUCTION

Chromium is a known heavy metal and is present in water in two stable oxidation states as trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Cr(III) is an essential metal, but Cr(VI) is toxic and can cause different health effects. Chromium is used in various industrial processes such as for wood preservation, in tannery plants, for electroplating, leather industry, steel and alloys, dye manufacturing and mining.^{1,2} Extensive use of chromium, however, has led to pollution problems in water. Chromium concentration has been reported in the range of 0.5 and 270 mg/L in industrial wastewaters.³ According to the World

Health Organization (WHO), total chromium concentration must be lower than 0.05 mg/L in drinking water and 0.1 mg/L in surface waters.^{4,5} So, removal of chromium ions from water samples is very important for human, animal and environmental health.

Different chemical treatment methods such as chemical precipitation, solvent extraction, bioremediation, photocatalytic degradation, membrane process, electroplating and adsorption have been used for the removal of chromium and heavy metals from wastewater samples.^{6,7} Adsorption is an important method for the removal of heavy metals due to the efficient and low-cost adsorbents such as biomass, activated carbon, clay minerals,

nanoparticles, alginate, sand, chitosan, and polyaniline.^{8,9} The most important factor for the adsorption process is the selection of proper sorbents. The use of inexpensive, easy, high efficiency and environmentally friendly adsorbents is very important for the removal of heavy metals. Various adsorbents such as pomelo peel,¹⁰ rice husk,¹¹ corn cobs,¹² red algae,¹³ moss,¹⁴ modified laterite,¹⁵ polyacrylamides,¹⁶ nanoparticles,¹⁷ eggshells,¹⁸ diatomite,¹⁹ prawn shell activated carbon,²⁰ and algae biosorbents²¹ have been used for the removal of chromium ions from water samples. The biomass material has some advantages such as low cost, easy operation, disposal after regeneration and having some functional groups.²²⁻²⁷

The chemical structure of the OLP bio-sorbent includes the amide (-N-H), hydroxyl (-O-H), carbonyl (-C=O) groups and aromatic rings which play an important role in the sorption of metal ions. Therefore, in this work, the OLP was selected as a low cost and renewable bio-sorbent for bio-removal of chromium ions from aqueous solutions. The chemical functional groups and the morphological structure of the bio-sorbent were characterized by use of the Fourier Transform Infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) techniques. The adsorption isotherms were modeled using the Langmuir and Freundlich model equations. The thermal nature of chromium sorption onto the OLP bio-sorbent and adsorption mechanism was examined by thermodynamic and kinetic evaluations.

EXPERIMENTAL

Bio-sorbent preparation

The olive leaves were obtained from the Salihli district of Manisa city in Turkey. The leaves were crushed and sifted through 100 mesh. The olive leaf powdered (OLP) sample was washed several times with deionized water to remove some coloring agents, then dried at room temperature.

Reagents and instrumentation

All of the supplied chemical reagents were of analytical grade and used without further purification. The chemical structure of the OLP bio-sorbent was characterized by a Nicolet 6700 model FTIR spectrometer (Nicolet Instrument Corporation, USA). The dried samples were mixed using KBr powder and converted to a thin pellet prior to analysis. The microstructure of the OLP was investigated using a ZEISS model SEM instrument. The chromium concentration in the solution sample was determined by using a Varian SpectraAA 220FS model flame atomic absorption spectrometer (FAAS).

Batch bio-sorption experiments

The bio-sorption experiments were carried out using the batch method. Each of the bio-sorbent samples (0.10 g) was added to 25 mg/L standard chromium solution (25 mL) into 100 mL beakers. The solutions were mixed using a temperature-controlled

magnetic stirrer at 400 rpm during a specified time. The pH of the solution was adjusted to different values by adding appropriate buffer solutions. The pH measurements were conducted by using a pH meter (Hanna HI83141 model). After appropriate contact time, the solution was filtered using a 0.45 µm filter paper (Millipore Corporation, USA). The chromium concentration in the filtered solution was determined using an AAS instrument in the acetylene-air flame at a wavelength of 357.9 nm. The bio-sorption experiments were repeated under various experimental conditions: initial metal concentration 10-500 mg/L, pH 2-9, contact time 10-60 min, bio-sorbent concentration 20-80 g/L and temperature 10-40°C. In order to obtain repeatable data, the concentration measurement was replicated three times. The average value was used in the calculation of the adsorption yield (%) which is formulated in Eq. (1):

$$\text{Adsorption yield (\%)} = \frac{(C_o - C_{exp})}{M} V \quad (\text{Eq. 1})$$

where C_o (mg/L) and C_{exp} (mg/L) are the initial chromium concentration in solution before and after the bio-sorption process, respectively. M (g) is the mass of the bio-sorbent and V (L) is the solution volume.

Reuse performance test

To determine the reuse performance, the developed OLP bio-sorbent was subjected to a sorption/desorption cycling process, repeated four times. Each cycle was carried out using ethanol solution (10 mL) as the desorbing solvent under the optimized batch conditions at pH 4, contact time 60 min, adsorbent dosage 40 g/L, and temperature 40 °C. The OLP was washed with distilled water after each cycle. The concentration of the chromium ions was determined by FAAS after each adsorption/desorption process.

RESULTS AND DISCUSSION

Characterization results

Fig. 1(a-c) and Fig. 1(d-f) show the SEM photographs of raw and chromium loaded-OLP bio-sorbent, respectively. As clearly seen, the surface of raw OLP includes the micro particles with shapes of fiber, star and needle-porous structures, while the surface morphologies of them were changed after chromium loading.

In the spectra of the unloaded bio-sorbent sample (Fig. 2a), the large absorption band at 3436 cm⁻¹ is associated with the stretching bands of the -OH and -NH₂ groups. The peaks at 2930 and 2852 cm⁻¹ are corresponding to -CH bending vibrations as the peaks at 1386 and 1456 cm⁻¹ are regarded with -C=C stretching vibrations and CH out-of-plane bending vibrations of aromatic rings. The strong peaks at 1732 and 1035 cm⁻¹ correspond to -C=O and -C-O stretching absorption bands of the acetate group of the bio-sorbent. After loading the chromium ions, the absorption bands regarding the -OH, -NH₂ -C=C and -C-O groups shifted to 1333,

Fig. 1 SEM photographs of (a-c) the surface of raw OLP bio-sorbent and (d-f) chromium loaded OLP bio-sorbent.

Fig. 2 (a) the FTIR spectra of raw OLP bio-sorbent and chromium-loaded bio-sorbent. (b) the change of bio-sorption efficiency with pH of solution (40 g/L dosage, 298K, 60 min contact time and 25 mg/L initial chromium concentration).

1447, 1368, and 1031 cm^{-1} , respectively. It means that these functional groups were involved in the chromium sorption of the OLP bio-sorbent.

pH effect on bio-removal yield

The pH value is one of the most vital parameters that impacts the surface charge intensity of the sorbent in metal ion included aqueous solutions. The chromium species in solution consist of H_2CrO_4 , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} and Cr^{3+} ions. Therefore, the bio-removal efficiency of total chromium is changed depending on the protonation degree of these species at different pH of the solution.¹⁴ At pH 2-3, the dominant species were the HCrO_4^- ions. At pH 4, the bio-sorption efficiency reached maximum, because of the coordination bonds between the chromium ions and the functional groups of the OLP. Over this pH value, the bio-sorption

efficiency was decreased due to the formation of hydroxylated chromium complexes. Fig. 2b shows the change in the bio-removal efficiency of the OLP bio-sorbent for the chromium ions under the optimized batch conditions: 40 g/L dosage, 298 K, 60 min contact time and 25 mg/L initial chromium concentration. As clearly seen from the curve, the best bio-sorption efficiency was achieved at pH 4. Nearly the same findings were reported for Cr(III) and Cr(VI) removal from aquatic medium using different sorbents.^{15,18,28,29}

Isotherm modeling results

The Langmuir and Freundlich isotherm models are used to estimate the sorption capacity of the adsorbent and explain the adsorption mechanism. The Langmuir model presumes that the monolayer sorption process occurred on the homogenous surface

Fig. 3 (a) Langmuir isotherm plot obtained for the bio-removal of chromium using OLP (40 g/L dosage, 298K, pH 4, 60 min contact time and 10-500 mg/L initial chromium concentration). (b) Freundlich isotherm plot obtained for the bio-removal of chromium using OLP (40 g/L dosage, 298K, pH 4, 60 min contact time and 10-500 mg/L initial chromium concentration).

Fig. 4 (a) PFO model results obtained for bio-sorption of chromium ions onto OLP bio-sorbent, (b) PSO model results obtained for bio-sorption of chromium ions onto OLP bio-sorbent, and (c) the change of KD parameter with temperature.

of the adsorbent, while the Freundlich model assumes multilayer sorption taking place onto a heterogeneous surface of the adsorbent. These models can be described in linear form in Eqs. (2) and (3), respectively:^{30,31}

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \quad (\text{Eq. 2})$$

$$\ln q_e = \ln K_f + \frac{1}{n} C_e \quad (\text{Eq. 3})$$

where C_e (mg/L) and q_m (mg/g) are the concentration of the non-adsorbed species and maximum adsorption quantity, respectively, as K_L (L/mg), K_f (mg/g) and n constants are model constants. The model plots are demonstrated in Fig. 3a and Fig. 3b, respectively.

As clearly seen from the data tabulated on Fig. 4 and 5, the R^2 value was estimated as 0.9523 and 0.8320 for the Langmuir and Freundlich models, respectively. These values evidently showed that the relationship of q_e with C_e corresponds to a relatively higher correlation for the Langmuir model compared to the values obtained from the Freundlich model. It also means that no sorption process was carried out after monolayer covering of the sorbent surface by chromium ions. Additionally, according to the Langmuir model, the q_m value was determined as 42.4 mg/g. Moreover, the K_L , K_f and n constants were computed to be 40.5, 1.82 and 1.73, respectively.

Kinetic results

Kinetic evaluation of the adsorption data is needed to archive time

efficiency of the adsorption process in large-scale practices. With this regard, to examine the adsorption mechanism of chromium ions onto the OLP bio-sorbent and decide the rate limiting step throughout the adsorption process, the pseudo-first-order (PFO) and pseudo-second-order (PSO) models were handled. The PFO model is generally effective in the initial phase of the sorption process and assumes the presence of faint interface between the surface of the sorbent and the sorbed species. The PSO model is another approach to characterize the sorption mechanism. The PFO and PSO models are described by the respective equations:^{32,33}

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{Eq. 4})$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{Eq. 5})$$

where q_e and q_t are the quantity (mg) of the adsorbed species at equilibrium time and any t time, respectively, as k_1 (min⁻¹) and k_2 (g/mg.min) are the kinetic rate constants. The suitability of these models is generally checked by comparing the experimental data ($q_{e,\text{exp}}$) with the theoretical values ($q_{e,\text{cal}}$), in addition to considering the correlation coefficient, R^2 values. The kinetic results obtained from the PFO and PSO models are shown in Fig. 4a and Fig. 4b, respectively. The model parameters obtained by inspecting these plots were also presented in Table 1. As can be seen from these findings, the $q_{e,\text{exp}}$ values at the studied temperatures do not agree with $q_{e,\text{cal}}$; and the R^2 values are relatively lower (0.914 - 0.948).

Table 1. PFO and PSO Kinetic Model Parameters Obtained for Bio-sorption of Chromium Ions onto OLP Bio-sorbent

Temperature (K)	$q_{e,exp}$ (mg/g)	PFO model			PSO model		
		k_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg.min)	$q_{e2,cal}$ (mg/g)	R^2
303	15.9×10^{-2}	2.1×10^{-2}	7.4×10^{-2}	0.948	6.6×10^{-2}	15.6×10^{-2}	0.990
313	18.2×10^{-2}	3.0×10^{-2}	8.6×10^{-2}	0.914	8.7×10^{-2}	18.4×10^{-2}	0.992
323	18.4×10^{-2}	4.6×10^{-2}	9.6×10^{-2}	0.919	15.1×10^{-2}	18.6×10^{-2}	0.994

Table 2. Comparison of OLP with the Bio-sorption Capacity of Different Kinds of Sorbents in Literatures

Adsorbents	Maximum sorption capacity (mg/g)	References
Chemically modified nanoparticles	27.8–66.2	(8)
Pomelo peel (PP)	0.60	(10)
FeCl ₃ -modified pomelo peel (FPP)	21.6	(10)
<i>Rhizoclonium heiroglyphicum</i>	11.81	(21)
<i>Spirogyra condensata</i>	14.8	(21)
Eucalyptus bark biochar	21.3	(22)
Eucalyptus bark	45.0	(25)
Biocomposite	32.5–43.7	(35)
Magnetic biochar	19.0	(36)
Chitosan@ hydrotalcite composite	15.4	(37)
Wheat straw biochar	28.1	(38)
Olive leaf powder (OLP)	42.4	In this work

These results show that the PFO model does not properly elucidate the bio-sorption mechanism of chromium ions onto OLP bio-sorbent. On the other hand, the closeness of $q_{e,exp}$ values to $q_{e,cal}$ data and relatively higher R^2 values indicated that the PSO model is more appropriate to illuminate the bio-sorption process, which is carried out mainly via chemisorption.

Thermodynamic evaluation results

To describe the thermal nature of the bio-sorption process of chromium ions onto the OLP bio-sorbent, the main thermodynamic parameters, free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) change were calculated for four different temperatures using the following equations:

$$\Delta G = -RT \ln K_d \quad K_d = \frac{q_e}{C_e} \quad (\text{Eq. 6})$$

$$\ln K_d = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{RT} \right) \quad (\text{Eq. 7})$$

The ΔG° function was calculated to be -5.76, -6.72, -7.73 and -8.54 kJ/mol for 283, 293, 30 and 313 K, respectively. These data mean that the spontaneity of bio-sorption of chromium ions onto the OLP bio-sorbent was increased with increasing temperature. Moreover, by handling the slope of the plot shown in Fig. 4c, the ΔH° and ΔS° functions were calculated as 20.73 kJ.mol⁻¹ and 93.62 J.mol⁻¹, respectively. The positive ΔH° signified that the endothermic nature of the bio-sorption of chromium ions onto the OLP bio-sorbent as the positive ΔS° means that the arbitrariness between the surface of the adsorbent and the metal-included solution was boosted during the bio-sorption process. The endothermic character was found for the bio-sorption of Cr(VI) from aqueous solution of *Cupressus lusitanica* bark.³⁴

Comparison of bio-sorption capacity of the OLP with literature

To evaluate the OLP in terms of chromium removal potential from aqueous solution, its bio-sorption capacity was compared with those of various sorbents in Table 2.^{8,10,21,22,25,35-38} As can be seen from the tabulated data, the OLP has a comparably high chromium removal capacity and thus, it can be evaluated as a hopeful bio-sorbent for elimination of chromium ions from wastewaters.

Reuse performance of OLP bio-sorbent

The reuse performance of a sorbent used for the removal of heavy metal ions from aqueous solution is the preferred criterion which affects its cost-effectiveness in large-scale pollution control systems. With this in mind, the reuse yield of the OLP bio-sorbent was investigated by conducting four cycled-sorption/desorption processes. The results revealed that the recovery performance of the OLP bio-sorbent decreased to 15 % recovery at the 4th cycle.

CONCLUSIONS

Olive leaf powder (OLP) was evaluated as a low-cost and renewable bio-sorbent for removal of total chromium ions from aquatic media. The morphology and chemical functional groups of the bio-sorbent were characterized by using FTIR and SEM analysis techniques. From the Langmuir isotherm model, the sorption capacity of the OLP bio-sorbent was estimated as 42.4 mg/g under the optimized bath conditions. The bio-sorption mechanism compared well with the PSO kinetic model. The ΔH° and ΔG° parameters confirmed that the bio-sorption process was

endothermic and spontaneous with increasing temperatures from 10 to 40 °C. Consequently, the OLP can be evaluated as a potential bio-sorbent for cleaning of chromium-contaminated wastewaters due to its advantageous properties such as low cost, availability, renewable nature, and remarkable bio-sorption capacity. However, to be able to propose the OLP bio-sorbent for real high scale chromium removal applications, its performance should be investigated in case of availability of other co-existing ions such as Cd, Cu, Pb and Zn, etc., in wastewaters or drinking waters. The regeneration performance of the OLP bio-sorbent has to be determined by using different types of desorbing solutions. Moreover, its removal efficiency must be estimated by conducting a breakthrough test in a real-size column system based on some key factors such as flow rate, sampling volume and chromium concentration.

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Notes

The authors declare no competing financial interest.

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