

# Reduction/adsorption of Cr(VI) in aqueous solution using modified plum kernel shell with tartaric acid

## Abstract

This work investigates the adsorption of chromium ions, Cr(VI) on modified plum kernel shell with tartaric acid (MPKS). For adsorption studies, different parameters were optimized such as pH, MPKS dosage, and contact time through batch technique. Equilibrium models such as Langmuir, Freundlich and Dubinin–Radushkevich (D-R) were used to determine the isotherm parameters associated with the adsorption process. Maximum adsorption capacities of Cr(VI) were 181.8 mg/g.

**Keywords:** plum, shell, adsorption, isotherm

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**Abbreviations:** MPKS, modified plum kernel shell; PKS, plum kernel shell; HCl, hydrochloride; NaOH, sodium hydroxide

## Introduction

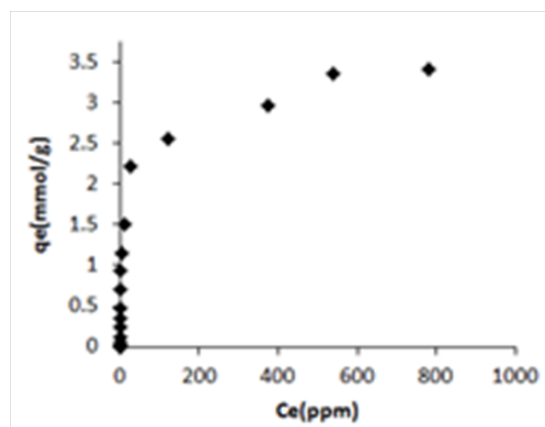
Water pollution is one of the most important issues to be guided in the context of emerging environmental problems. Water pollution is caused by toxic metals from industrial applications.<sup>1</sup> Toxic metals can seriously harm to human health, even at low concentrations in the water, resulting in serious health problems, even death. Chromium ions are the most hazardous toxic metals. Chromium has become a serious health concern due to its release into the environment.<sup>2</sup> The most common methods for removing heavy metal ions from water are: chemical precipitation, membrane filtration, ion exchange, reverse osmosis and adsorption.<sup>3-5</sup> Among all techniques, adsorption with MPKS is a green separation process. The application is easy; the purification is effective and cheap.

During selection of adsorbent; attention should be paid to features such as high adsorption capacity, low cost, high adsorption rate and reusability. Suitable adsorbent material for removing Cr(VI) due to their content is plum kernel shell (PKS) and it contains lignin and carbohydrate (cellulose and hemicelluloses). This adsorbent has cellulose and lignin which contain different polar functional groups, such as alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers which may be involved in the surface application. The modification of PKS by tartaric acid was subsequently investigated for the potential adsorbent for the removal of Cr(VI) from aqueous solutions. Effective parameters such as initial pH, initial metal concentration, contact time, and adsorbent dosage related to adsorption were investigated.

## Materials and methods

PKS was obtained from Konya-Turkey. It was cleaned, dried in sunlight ground to pass through a 125µm sieve. Then PKS was treated with 1.2M tartaric acid at 80°C for 8 h and labeled as MPKS. MPKS was then washed to neutral pH and dried at 50°C for 24h. All other chemicals were purchased from Merck Company. All chemicals used in the experiments were in analytic grade and ultrapure water was used to prepare required solutions. The pH of the solution was adjusted by mixing the appropriate amount of 0.1M (HCl/NaOH). A stock solution of Cr(VI) with a concentration of 1000ppm was prepared by dissolving K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in distilled water. The residual solution was investigated by a UV-vis Spectrophotometer (Schmadzu UV-1700)

(λ: 540nm) using a diphenylcarbazide reagent for determination of Cr(VI). For all parameters (pH, metal concentration, adsorbent dose and contact time), each experimental steps was replicated three times and average value was recorded.



**Figure 1** Equilibrium adsorption isotherm of Cr(VI) ions on MPKS.

## Results and discussion

The contact time for taking Cr(VI) ions with MPKS was ranged from 5 to 360minutes. The agitation time showed fast Cr(VI) adsorption during the first 5-30min of agitation period and then reached to the equilibrium at the end of 60 min of contact period. The initial rapid removal could be due to high initial Cr(VI) concentrations and free Cr(VI) binding sites at the functional groups of MPKS. All conditions for the Cr(VI) adsorption were kept constant and only MPKS dosage (1,2,4,6,8,10mg/L) was changed for a series of experiments. When the amount of MPKS increased (1g/L from 4g/L) the ability to capture Cr(VI) increased, but after increasing the amount of adsorbent, it was marginally reduced and the adsorption increased. With increase in the residence time, the adsorption was increased to a constant value. For this reason, the adsorbent dosage for Cr(VI) was taken as 4g/L in the experiments. The pH of the solution plays an important role in adsorption mechanism of Cr(VI) ions. The experiments were carried out at a pH range 1.5-6. The hydrolysis of solution, the pH of the solution, the redox reactions in the solution phase, the coordination groups on the surface of MPKS, and the ionic state can affect Cr(VI) removal. The adsorption capacity of MPKS is pH dependent and the maximum adsorption took place at pH 2.

**Table 1** Adsorption Isotherm Constants for Cr(VI)

Langmuir Isotherm				Freundlich Isotherm			D-R Isotherm			
$Q_m$	b	$R^2$	$R_L$	$K_f$	n	$R^2$	$X_m$	K	E	$R^2$
181.8	0.029	0.988	0.25	11.03	2.09	0.646	0.0099	0.0042	10.91	0.726

Adsorption studies of Cr(VI) at different concentrations in the range of 5-1500ppm (4g/L adsorbent) were shown by Freundlich, Langmuir, D-R Isotherm. Freundlich, Langmuir and D-R isotherms (Figure 1). Freundlich, Langmuir and D-R adsorption isotherms parameter were given in Table 1.  $K_f$  and  $n$  constant values were calculated to define the equilibrium fit Freundlich equation.  $n$  values were determined as 2.09. If this value is between 1 and 10, Freundlich isotherm can be selected for adsorption. From Dubinin-Radushkevich (D-R) isotherm,  $X_m$ ,  $K$  and  $E$  values were calculated. The adsorption energy ( $E_{ad}$ ) was calculated to be 10.91kJ/mol. The fitness of adsorption can be compared according to  $R_L$  value. If  $R_L$  is between 0 and 1, it specifies the relevance of Langmuir adsorption isotherm.<sup>6,7</sup>  $R_L$  values of Cr(VI) are 0.25. According to Langmuir isotherm, the maximum capacity ( $q_m$ ) is 181.8mg/g.

## Conclusion

The adsorption behavior of Cr(VI) was investigated in the batch experiments. Adsorption was found to depend on pH, adsorbent dose and contact time. The maximum adsorption for Cr(VI) was at pH 2.0. The MPKS attained equilibrium in 60min. Adsorption of Cr(VI) obeys Langmuir equation. Using the Langmuir model equation, the maximum capacities of MPKS for Cr(VI) was found to be 181.8mg/g. PKS can easily found in Turkey and it is expected that modified PKS will be economical to remove Cr(VI) from wastewater plants.

## Conflicts of interest

None.

## Acknowledgements

None.

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