

ERKAN KALIPCI¹, OSMAN ONDER NAMAL¹

REMOVAL OF Cr(VI) USING A NOVEL ADSORBENT MODIFICATION. ULTRASONIC METHOD WITH APRICOT KERNEL SHELLS

Raw apricot kernel shells (AKS) and ultrasound-modified apricot kernel shells were used as adsorbents for the removal of Cr(VI) from aqueous solutions. For raw and modified AKS, the experimental data well fitted to the Langmuir isotherm and adsorption kinetics was suited to pseudo-second order kinetic model indicating chemisorption as the rate-limiting step. For raw and modified AKS, maximum adsorption capacities obtained from the Langmuir adsorption model were 6.5 mg/g and 9.9 mg/g, respectively. Maximum Cr(VI) adsorption was obtained at a pH 2 and optimum stirring speed was determined as 250 rpm. After ultrasound modification, an increase for Cr(VI) adsorption was observed. Raw AKS as low-cost natural biomaterial can be preferred for the removal of Cr(VI) when compared to other adsorbents. Ultrasonic modification can be used to improve the efficiency of Cr(VI) removal.

1. INTRODUCTION

Increase in metal usage together with industrial development reveals heavy metal pollution as an important environmental problem [1]. Especially wastewater including heavy metals in developing countries is directly or indirectly discharged to the environment with an increasing rate. Contrary to organic pollutants, heavy metals are non-biodegradable and have tendency to accumulate in living organisms, moreover, many heavy metal ions are known as toxic or cancerogenic. Nowadays, heavy metals are the primary pollutants of the environment and are one of the most important environmental problems [2].

Chromium contamination, one of the most frequent heavy metal pollutions, is caused by activities such as metal coating, metal cutting, leather tanning, dye and pigment production, mining and ore processing [3]. Chromium occurs in aqueous solutions

¹Department of Environmental Engineering, Nevsehir Hacı Bektas Veli University, 50300 Nevsehir, Turkey, corresponding author E. Kalipci, e-mail address: ekalipci@hotmail.com

in two oxidation states such as trivalent Cr(III) and hexavalent chromium Cr(VI) [4]. Due to their high solubility, Cr(VI) compounds are more toxic than Cr(III) ones [5]. When more than 0.1 mg/dm^3 of Cr(VI) is taken into the body via digestive system, it might cause health problems such as vomiting and cerebral bleeding [6]. Moreover, contact with chromium also leads to some health diseases such as skin irritation, lung carcinoma [7]. Thus, wastewater including chromium should be treated before discharge in order to prevent such negative effects.

According to literature data, adsorption method is preferred due to its low cost [8, 9]. Adsorption is one of the treatment methods used for the removal of heavy metals from aqueous solutions [1] with high removal efficiencies [2]. Activated carbon is one of the common adsorbents used for adsorption, however, it is relatively expensive. For the removal of heavy metal ions, searching alternative low-cost and easily available adsorbents has become a basic of a research study. In order to treat wastewater including heavy metals, agricultural wastes, various industrial products and wastes as well as natural compounds have been investigated as adsorbent materials. Apricot kernel shells (AKS) that are used within the scope of this study are also one of the low-cost agricultural wastes.

Various methods have been examined in order to activate the adsorbents. Some of them are acid activation, thermal activation and acoustic cavitation. Acoustic cavitation is based on application of ultrasonic radiation to the liquid medium. When ultrasound propagates in a liquid medium, cavitation bubbles are produced in the liquid due to the effect of high ultrasonic pressure. These bubbles get bigger until they reach unstable dimension and at the end they collapse very rapidly. During this collapse, extreme conditions occur (temperature of 5200 K and 50 MPa pressure) [10]. Since the diameters of bubbles produced at low ultrasonic frequencies about 20 kHz are relatively big, the intensity of hydromechanical shear force produced during cavitation collapse at low ultrasonic frequency is maximum. This mechanism of acoustic cavitation might be used for activation and increasing the capacities of adsorbents [11].

Within the scope of this study, raw AKS and those modified ultrasonically were used to examine the adsorption of Cr(VI) from aqueous solutions and check how such modification may improve adsorption properties of AKS.

2. MATERIALS AND METHODS

Raw AKS obtained from Malatya City of Turkey were washed with distilled water and then dried at $105 \text{ }^\circ\text{C}$ for 24 h. After that, they were ground and screened until the particle size was 1–2 mm. This screened material was again washed with distilled water and dried in an oven at $105 \text{ }^\circ\text{C}$ for 24 h. Some of this dried material was used directly for adsorption experiments. The rest of the material was modified using an ultrasound device. After addition of AKS to 100 cm^3 of distilled water, it was sonicated using a Bandelin UW 2200 device at a rate of 100% power (200 W) for 15 min. Then the

samples were filtered, washed with distilled water and then dried in an oven at 105 °C for 24 h. Both raw and modified AKS were kept in a desiccator to be used for adsorption experiments.

Batch experiments were carried out in 250 cm³ flasks with adsorbent doses: 1, 3, 5, 7, 9 g/dm³ using 100 cm³ of 25, 50 and 75 mg Cr⁶⁺/dm³ solutions. They were stirred in an agitated incubator (JSR, JSSI 100T) at 35 °C with 200, 250, 300 rpm stirring speeds for 0–140 min. pH of the solutions was adjusted with 0.1 mol/dm³ HCl or 0.1 mol/dm³ NaOH solutions. pH measurements were carried out with a multimeter instrument (Hach Lange, HQ40d multimeter). Cr⁶⁺ concentrations at equilibrium were measured spectrophotometrically (Hach Lange, DR 3900) in accordance with Standard Methods (3500-Cr B.). All samples were filtered using Sartorius, Germany filters having 0.45 µm pore diameter in order to prevent interferences. The removal efficiency was calculated as [26]:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where R is the removal percentage, C_0 and C_e (mg/dm³) are Cr(VI) initial and equilibrium concentrations, respectively. Adsorbed Cr(VI) amount at equilibrium, q_e (mg/g), was calculated by the following equation [27]:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where V (dm³) is the volume of the solution and W (g) is the amount of adsorbent.

3. RESULTS AND DISCUSSION

3.1. KINETIC INVESTIGATIONS

Kinetics is a significant explanatory stage for understanding the adsorption factors affecting the rate of adsorption process. In addition to pseudo-first and pseudo-second order models, the Elovich model, intraparticle diffusion model and exponential function models were also used for interpreting the adsorption kinetics [12].

Pseudo-first order kinetic model is expressed as follows [13]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

where k_1 (min⁻¹) is the adsorption rate constant for pseudo first order kinetics, q_e and q_t (mg/g) are adsorbed amounts per unit mass at equilibrium and at any time, respectively.

Pseudo-second order kinetic model is based on the assumption that the rate limiting step is chemisorption and is expressed by the following equation [14, 15]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 (g/(mg·min)) is the second order rate constant.

For porous adsorbents, diffusion of adsorbate molecules or ions in the pores comes into question. In such a situation, intraparticle diffusion model can be used to evaluate the effect of diffusion process and its kinetics equation is as follows [16]:

$$q_t = k_{\text{int}} t^{1/2} \quad (5)$$

where, k_{int} (mg/(g·min)) is the rate constant.

The Elovich model is based on the assumption of solid surfaces being heterogeneous in terms of energy and is expressed by the following equation [13]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta \ln t} \quad (6)$$

where, α (g/mg) and β (mg/(g·min)) expresses initial adsorption and desorption rate constants, respectively.

The film diffusion model is defined as [17]:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -K_4 t + A \quad (7)$$

where K_4 (1/min) and A are the diffusion constants.

Hamadi et al. [18] performed experiments of Cr(VI) adsorption from aqueous solution with natural adsorbents. It was observed that adsorption reached an equilibrium in 120 min, similarly as in the present paper. Adsorption capacities of raw AKS at 25, 50 and 75 mg Cr⁶⁺/dm³ initial concentrations were determined as 3.8, 5.4 and 6.5 mg/g; whereas for the modified AKS, they were higher: 5.2, 7.8 and 9.6 mg/g. Contrary to increasing initial concentrations for modified and raw AKS, the time for the system to reach equilibrium increased, however, removal efficiency decreased. The removal efficiencies obtained for 25, 50 and 75 mg Cr⁶⁺/dm³ initial concentrations for raw material were 45.6%, 32.4% and 25.8% while for modified material – 62.4%, 47.2% and 38.4%. At high concentrations, the amount of heavy metal ions is higher than available adsorption sites. For this reason, removal of heavy metals decreases with the increase in initial metal concentration [19]. In the kinetic studies carried out with modified AKS, removal

Table 1

Results of kinetic studies carried out with raw AKS

Coefficient	Value		
Initial concentration, mg Cr ⁶⁺ /dm ³	25	50	75
Pseudo-first order kinetic model			
q_e , exp, mg/g	3.8	5.4	6.5
q_e , calc, mg/g	2.2	5.7	7.9
k_1 , 1/min	276.4×10^{-4}	428.4×10^{-4}	474.4×10^{-4}
R^2	0.925	0.961	0.899
Pseudo-second order kinetic model			
q_e , calc, mg/g	3.9	5.7	6.8
k_2 , g/(mg·min)	788.9×10^{-4}	482.6×10^{-4}	315.4×10^{-4}
R^2	0.996	0.987	0.984
Intraparticle diffusion model			
k_{int} , mg/(g·min ^{0.5})	0.3	0.5	0.6
R^2	0.823	0.908	0.922
Elovich model			
α , g/mg	3.7	8.1	10.7
β , mg/(g·min)	0.133	0.069	0.054
R^2	0.996	0.969	0.954
Film diffusion model			
K_4 , min ⁻¹	0.027	0.047	0.052
A	-0.583	-0.17	-0.27
R^2	0.925	0.937	0.899

Table 2

Results of kinetic studies carried out with modified AKS

Coefficient	Value		
Initial concentration, mg Cr ⁶⁺ /dm ³	25	50	75
Pseudo-first order kinetic model			
q_e , exp, mg/g	5.2	7.9	9.6
q_e , calc, mg/g	3.5	5.4	10.3
k_1 , 1/min	518.2×10^{-4}	386.9×10^{-4}	531.9×10^{-4}
R^2	0.792	0.936	0.938
Pseudo-second order kinetic model			
q_e , calc, mg/g	5.4	8.4	10.4
k_2 , g/(mg·min)	0.039	0.015	0.009
R^2	0.994	0.998	0.999
Intraparticle diffusion model			
k_{int} , mg/(g·min ^{0.5})	0.4	0.7	0.8
R^2	0.775	0.828	0.851

Table 2

Results of kinetic studies carried out with modified AKS

Elovich model			
α , g/mg	5.8	6.5	11.3
β , mg/(g·min)	0.088	0.056	0.046
R^2	0.812	0.943	0.994
Film diffusion model			
K_4 , l/min	0.052	0.039	0.012
A	-0.40	-0.37	-0.53
R^2	0.792	0.936	0.714

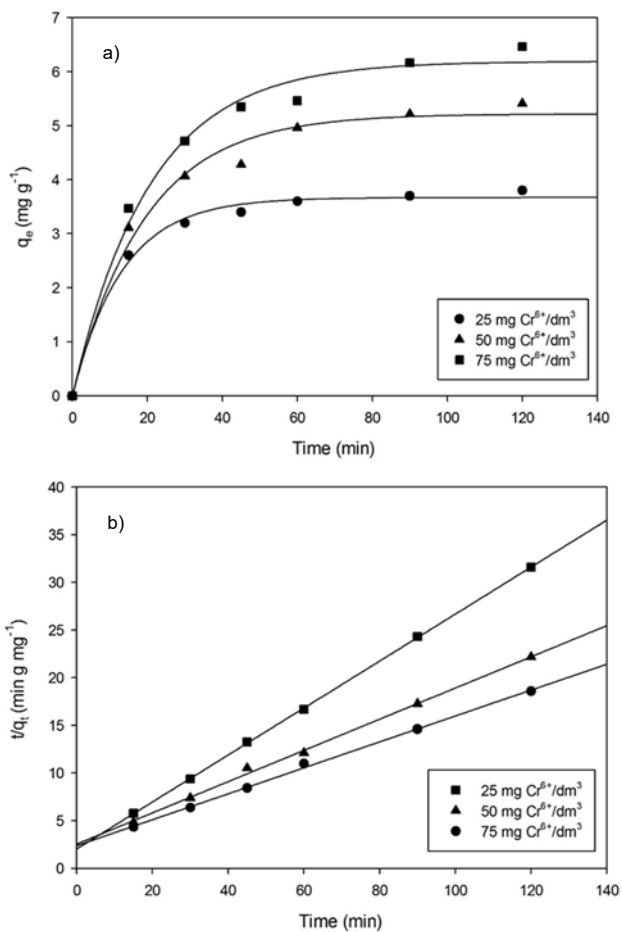


Fig. 1. Pseudo-second order kinetic model obtained for raw AKS at various initial metal concentrations (temperature 35 °C, AKS dose 3 g/dm³, stirring speed 250 rpm, and pH 3)

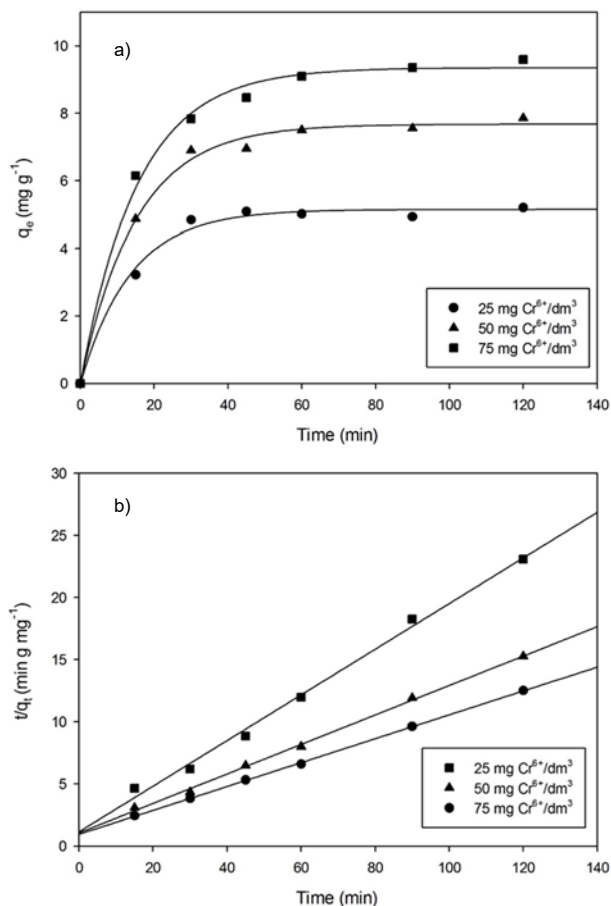


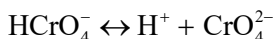
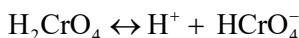
Fig. 2. Pseudo-second order kinetic model obtained for modified AKS with different initial metal concentrations (temperature 35 °C, AKS dose 3 g/dm³, stirring speed 250 rpm and pH 3)

efficiencies were found higher when compared to raw AKS. This situation is related with the changes in the structure of the material after ultrasound modification and with the increase in accessible sites. The results obtained from kinetic studies were assessed in terms of various kinetic models. The coefficients of these models are given in Tables 1 and 2. When the regression coefficients calculated for modified and raw AKS were taken into consideration, the adsorption process can be best defined with pseudo-second order kinetic model (Figs. 1, 2). The R^2 values obtained at 25, 50 and 75 mg Cr⁶⁺/dm³ initial concentrations for raw material were as 0.996, 0.987 and 0.984, respectively, while those for modified material – 0.994, 0.998 and 0.999, respectively. The difference between empirical equilibrium concentrations and equilibrium concentrations calculated according to second order kinetic model was low. Therefore, it can be stated that the rate limiting stage of the adsorption process might be chemisorption. Since surface of

the adsorbent is constituted of various acidic functional groups, physicochemical interactions took part in removal of Cr(VI) [6].

3.2. THE EFFECT OF pH ON ADSORPTION EFFICIENCY

Since pH of the adsorption system affected surface properties of activated carbon and different ionic forms of chromium solutions, it determines the adsorption capacity. Within the pH range of 1–5, while different chromium ions such as Cr_2O_7^- , HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ were dominant, chromium was present in the form of H_2CrO_4 at pH = 1. Chromium forms present in different oxidation stages and their stability depend on the pH of the system. Equilibrium between different chromium species is as follows [20]:



pH affected Cr(VI) adsorption significantly (Fig. 3). Maximum Cr(VI) adsorption was achieved at pH 2 for both modified and raw AKS. At pH 2, Cr(VI) ions were present as hydrogen chromate (HCrO_4^- , 90%), dichromate (Cr_2O_7^- , 5%) and chromic acid (H_2CrO_4 , 5%). At pH higher than 2, CrO_4^{2-} is known as the dominant Cr(VI) species [21].

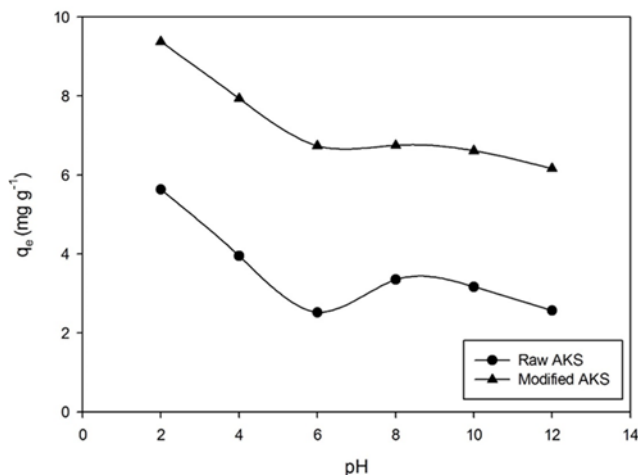


Fig. 3. Effect of pH on the adsorption process carried out with raw and modified AKS (stirring period 120 min, initial concentration $50 \text{ mg Cr}^{6+}/\text{dm}^3$, temperature $35 \text{ }^\circ\text{C}$, stirring speed 250 rpm and AKS dosage $3 \text{ g}/\text{dm}^3$)

At low pH, the number of H^+ ions on the surface of AKS increased. Moreover, after ultrasound modification, the functional groups on the surface of AKS enhanced Cr(VI) adsorption due to electrostatic attraction between surfaces of positively charged AKS and Cr(VI) ions. For this reason, adsorption capacity at pH 2 was high (for raw AKS, $R = 33.8\%$, $q_e = 5.6$ mg/g, for modified AKS, $R = 56.2\%$, $q_e = 9.4$ mg/g). At increased pH values, negative charges on the surface of the adsorbent are dominant and thus, adsorption of Cr(VI) on the surface decreased. For this reason, the value of pH 2 was determined as the most appropriate value for maximum Cr(VI) adsorption. Hence, in the study of Kalipci et al. [10], while the highest efficiency was obtained at pH 2, adsorption efficiency decreased as the value of pH was increased.

3.3. ADSORPTION ISOTHERMS

In order to evaluate experimental equilibrium data, various isotherm models have been suggested [12]. The Langmuir adsorption isotherm is expressed as follows [22]:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

where q_e is the amount of material adsorbed at equilibrium (mg/g), Q_m is the maximum adsorption capacity (mg/g), K_L is the model constant related with adsorption energy (dm^3/mg) and C_e is the adsorbate concentration in liquid phase at equilibrium (mg/dm^3). In the Langmuir model, R_L equilibrium parameter, known as the separation factor, was suggested by Hall et al. [23] in order to interpret the K_L Langmuir constant. R_L values might provide necessary information about adsorption process. The relation between R_L and K_L is given as follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

where C_0 is the initial concentration of adsorbate in the solution (mg/dm^3).

Classification of R_L values and their interpretation are given in Table 3.

Table 3

Adsorption properties according to R_L value

R_L	$R_L > 1$	$R_L = 1$	$0 < R_L < 1$	$R_L = 0$
Adsorption	unfavorable	linear	favorable	irreversible

Freundlich isotherm defines adsorption as a reversible process, not limited to one layer. One of the most important disadvantages of the Freundlich equation is that maximum adsorption cannot be predicted [24]. This model, which is more suitable for heterogeneous systems, is given as follows [12].

$$q_e = K_F C_e^{1/n} \quad (10)$$

where q_e is the amount of adsorbate adsorbed by the solid phase at equilibrium (mg/g), C_e is the adsorbate concentration in liquid phase at equilibrium (mg/dm³), K_F is a constant (mg/g)(mg/dm³)^{-1/n}, $1/n$ is a heterogeneity constant. A high K_F value indicates good adsorption capacity. $n > 1$ means that adsorption of adsorbate on the adsorbent is favorable and adsorption intensity is higher for higher n values [15].

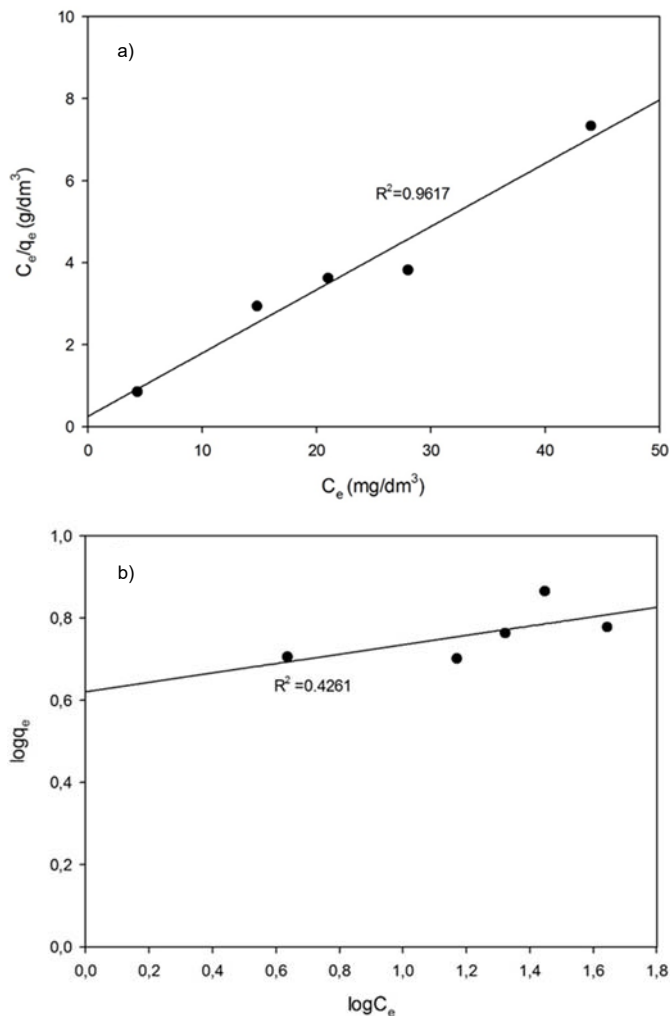


Fig. 4. Plots of the Langmuir (a) and Freundlich (b) adsorption models for raw AKS (stirring period 120 min, initial metal concentration 50 mg Cr⁶⁺/dm³, temperature 35 °C, stirring speed 250 rpm, AKS dose 3 g/dm³, and pH 3)

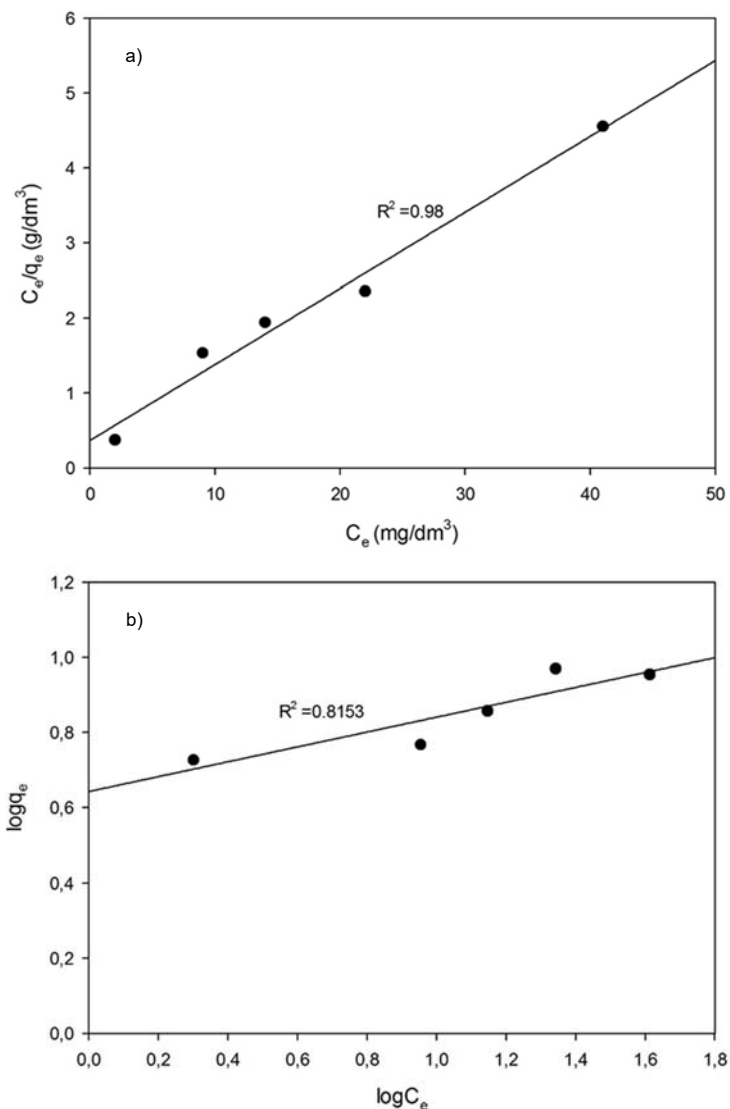


Fig. 5. Plots of the Langmuir (a) and Freundlich (b) adsorption models for modified AKS (stirring period 120 min, initial metal concentration $50 \text{ mg Cr}^{6+}/\text{dm}^3$, temperature $35 \text{ }^\circ\text{C}$, stirring speed 250 rpm , AKS dose 3 g/dm^3 and pH 3)

In this study, adsorption of Cr(VI) ions was investigated in terms of the ability to describe it by means of the Langmuir and Freundlich adsorption isotherms. Results obtained for modified and raw AKS are given in Figs. 4 and 5. The coefficients of the models are listed in Table 4. As can be seen, adsorption process fitted well to Langmuir isotherm model (R^2 values for raw and modified AKS were found as 0.96 and 0.98,

respectively). This result confirmed that adsorption was a single layer process for both raw and modified AKS. R_L values for Langmuir adsorption isotherm were between 0 and 1. Q_m values for Langmuir adsorption isotherm were calculated as 6.5 mg/g for raw AKS, and 9.9 mg/g for modified AKS. This result is an indication of improved adsorption capacity after ultrasound modification.

Table 4

Isotherm coefficients for raw and modified AKS

Model	Raw AKS	Modified AKS
Langmuir isotherm		
Q_m , mg/g	6.5	9.9
K_L , dm ³ /mg	0.039	0.037
R_L	0.339	0.351
R^2	0.962	0.980
Freundlich isotherm		
n	8.8	5.1
K_F , (mg/g)(mg/dm ³) ^{-1/n}	4.2	4.4
R^2	0.426	0.815

3.4. THE EFFECT OF STIRRING SPEED ON ADSORPTION EFFICIENCY

Depending on the stirring rate of the liquid-particle system, adsorption system is controlled by either film diffusion or particle diffusion.

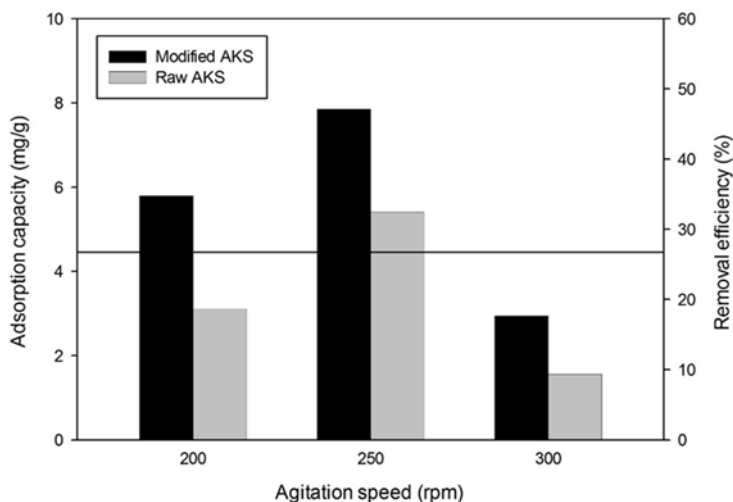


Fig. 6. Effect of stirring speed on adsorption capacity and Cr(VI) removal by raw and modified AKS (stirring period 120 min, initial metal concentration 50 mg Cr⁶⁺/dm³, temperature 35 °C, AKS dose 3 g/dm³ and pH 3)

At low stirring speeds, liquid film surrounding the particles is thinner and film diffusion is the rate limiting step. At high stirring speeds, film diffusion reaches its maximum value and pore diffusion becomes the rate limiting step. While the transport rate of dissolved material to sub-surface layer at high stirring speeds reaches its maximum, the volume of sub-surface reaches a constant minimum value [16]. In Figure 6, the effect of stirring speed on the removal efficiency and adsorption capacity of raw and modified AKS is shown. The optimum stirring speed under experimental conditions was determined as 250 rpm. In other words, diffusion of pollutant molecules on the surface of adsorbent material reached a maximum level. It was observed that the boundary layer resistance at the stirring speeds of 200 and 300 rpm was higher and mobility of the system was lower than that at the speed of 250 rpm. As a result, a longer time is required to reach equilibrium at lower stirring speeds.

3.5. ADSORPTION PROCESS OPTIMIZATION

The time needed to reach equilibrium was approximately 120 min. Optimum adsorption was observed at pH 2 for both raw and modified AKS. Maximum adsorption capacity at pH 2 was 5.63 mg/g and 9.37 mg/g for raw and modified AKS, respectively. The adsorption reached optimum value at the stirring speed of 250 rpm (5.41 and 7.86 mg/g for raw and modified AKS, respectively).

Every year, a large amount of apricot kernel shells emerges as an agricultural waste after harvest and it is used to provide energy in furnaces on large scale. Their adsorption ability has been known for a long time. It is quite cheap when compared to other low cost adsorbents. Moreover, apricot kernel shells are a renewable resource. Conventional modification procedures including the furnaces is more costly according to ultrasound modification. Energy consumption of furnaces is very high and modification can take a long time [28].

4. CONCLUSIONS

In the study, adsorption kinetics, effect of pH on adsorption, adsorption isotherms and effect of stirring speed were investigated. After ultrasound modification, a remarkable increase was determined in the adsorption capacity of the material. From this point of view, ultrasound modification is a suitable modification method for the removal of Cr(VI). Despite of the increase in initial concentration, a decrease in removal efficiency was observed depending on limiting of the system by adsorption sites. Adsorption system has been described by a pseudo-second order kinetic model and accordingly, it can be stated that chemisorption is the rate limiting step for this adsorption process. In other words, physicochemical interactions took place during Cr(VI) removal. Depending on the electrostatic interactions between adsorbent surfaces and Cr(VI) ions, the maximum

adsorption was determined at pH 2 for both raw and modified apricot kernel shells. The stirring rate played an active role throughout the adsorption process and optimum stirring speed was determined as 250 rpm. The adsorption system well fitted to the Langmuir isotherm which was an indication of single layer adsorption process. Low-cost AKS can be preferably used for Cr(VI) removal and ultrasound modification is an alternative method which improves and increases the removal of Cr(VI).

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