Comparative study of adsorption properties of Turkish fly ashes
II. The case of chromium (VI) and cadmium (II)

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Abstract

The purpose of the study described in this paper was to compare the removal of Cr(VI) and Cd(II) from an aqueous solution using two different Turkish fly ashes; Afsin-Elbistan and Seyitomer as adsorbents. The influence of four parameters (contact time, solution pH, initial metal concentration in solution and ash quality) on the removal at $20 \pm 2\,^{\circ}$C was studied. Fly ashes were found to have a higher adsorption capacity for the adsorption of Cd(II) as compared to Cr(VI) and both Cr(VI) and Cd(II) required an equilibrium time of 2 h. The adsorption of Cr(VI) was higher at pH 4.0 for Afsin-Elbistan fly ash (25.46%) and pH 3.0 for Seyitomer fly ash (30.91%) while Cd(II) was adsorbed to a greater extent (98.43% for Afsin-Elbistan fly ash and 65.24% for Seyitomer fly ash) at pH 7.0. The adsorption of Cd(II) increased with an increase in the concentrations of these metals in solution while Cr(VI) adsorption decreased by both fly ashes. The lime (crystalline CaO) content in fly ash seemed to be a significant factor in influencing Cr(VI) and Cd(II) ions removal. The linear forms of the Langmuir and Freundlich equations were utilised for experiments with metal concentrations of $55 \pm 2\,$mg/l for Cr(VI) and $6 \pm 0.2\,$mg/l for Cd(II) as functions of solution pH (3.0–8.0). The adsorption of Cr(VI) on both fly ashes was not described by both the Langmuir and Freundlich isotherms while Cd(II) adsorption on both fly ashes satisfied only the Langmuir isotherm model. The adsorption capacities of both fly ashes were nearly three times less than that of activated carbon for the removal of Cr(VI) while Afsin-Elbistan fly ash with high-calcium content was as effective as activated carbon for the removal of Cd(II). Therefore, there are possibilities for use the adsorption of Cd(II) ions onto fly ash with high-calcium content in practical applications in Turkey.
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1. Introduction

Heavy metals discharged in wastewaters can be toxic to aquatic life and cause natural waters to be unsuitable as potable water sources. The ubiquitous nature of heavy metals, their toxicity even in trace quantities, their tendency for bioaccumulation in food chain and the stricter environmental regulations related to heavy metals discharges make it necessary to develop processes for the removal of heavy metals from wastewaters.

Chromium (Cr(VI)) and cadmium (Cd(II)) are two extremely toxic metals found in various industrial wastewaters, e.g. of electroplating, metal finishing, leather tanning, paint and paper manufacturing [1,2]. Various methods for the removal of metals from wastewaters include chemical precipitation, membrane filtration, ion exchange and adsorption, the latter process being a more useful method for metal removal than the other processes. Although, the adsorbents commonly recommended for removal of heavy metals are alumina, silica, iron oxide and activated carbon, they are expensive [3–5]. Therefore, some studies have been concerned with the development of new and especially cheap adsorbents for the removal of heavy metals from wastewaters. Among these studies, the use of fly ash, a coal combustion by-product, has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to the ash's content of alumina (Al_2O_3), silica (SiO_2), ferric oxide (Fe_2O_3) and calcium oxide (CaO). Fly ash is also an abundant waste material, i.e. Turkey utilities generate about 10 million tons of fly ash each year [6]. It is well documented that fly ash is capable of adsorbing Cr(VI) and Cd(II) ions from aqueous solutions [7–13]. However, most of these studies did not evaluate the ash quality for such removal.

The objective of this paper is to compare the different Turkish fly ashes (Afsin-Elbistan and Seyitomer) with respect to their ability to remove Cr(VI) and Cd(II) ions, from an aqueous solution and observe the effect of contact time, pH in solution and initial metal concentration in solution on these metal adsorptions by fly ash. Batch adsorption experiments were conducted to characterise and model the adsorption equilibrium. The removals obtained with fly ashes were also compared with results obtained with commercial activated carbon.

2. Materials and methods

2.1. Fly ash

Characterisation of the fly ashes is described in the first part of this investigation. The other characteristics of the fly ashes are also reported elsewhere [14].

2.2. Chemicals

The synthetic solution for the present study was prepared by dissolving 156 mg $K_2Cr_2O_7$ and 14 mg $3CdSO_4 \cdot 8H_2O$ in distilled water (1 l) to obtain 55 ± 2 mg/l Cr(VI) and 6 ± 0.2 mg/l Cd(II) concentrations. Solutions of 0.1 M HNO_3 and 0.1 M NaOH were used for pH adjustment. The electrolyte used to modify the ionic strength in the adsorption experiments

was 0.1N NaNO₃. All chemicals used were of analytical reagent grade and were obtained from Merck, Germany.

2.3. Adsorption experiments

The batch studies were conducted using a jar-test apparatus manufactured by Phipps and Bird Inc. The adsorption experiments of Cr(VI) and Cd(II) were conducted using the same procedures as the adsorption experiments of Ni(VI), Cu(II) and Zn(II) with respect to the effect of contact time, pH in solution, initial metal concentration in solution and fly ash origin. In these experiments, 500 ml of solution containing 55 ± 2 mg/l (or 1.0 ± 0.1 mg/l) of Cr(VI) and 6 ± 0.2 mg/l (or 0.2 ± 0.02 mg/l) of Cd(II) were poured into each jar of the jar-test apparatus and 10 g of fly ash added. The solution-fly ash mixtures were stirred at

Solution ($K_2Cr_2O_7$, $3CdSO_4 \cdot 8H_2O$)

0.1 N NaNO₃
0.1 M HNO₃ or NaOH   10 g Fly Ash or Activated Carbon

Mixing (at predetermined time)

Vacuum Filtration
(0.45 μm membrane filter)   Fly Ash + Metal-Laden

Filtrate   Deionized water
                                                    0.1 M HNO₃ or NaOH

                                            Mixing (4 h)

                                    Vacuum Filtration
                                    (0.45 μm membrane filter)   Fly Ash Sludge

                                            Filtrate

Atomic Absorption Spectrophotometry (AAS)
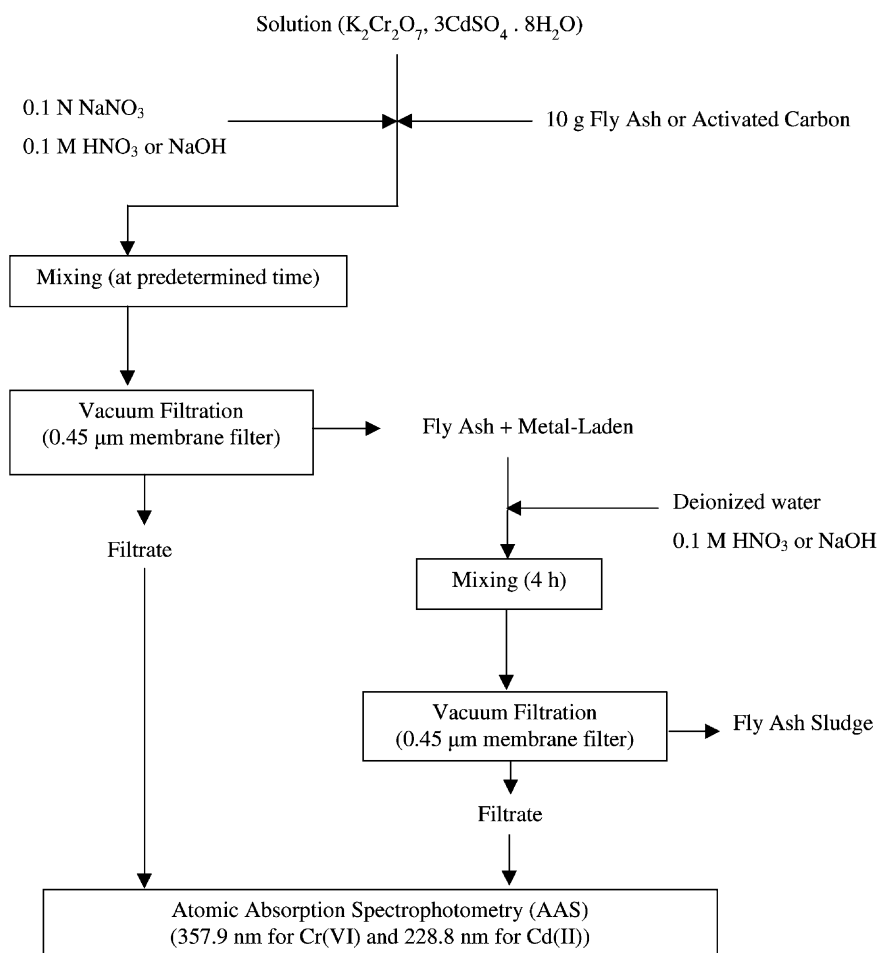(357.9 nm for Cr(VI) and 228.8 nm for Cd(II))

Fig. 1. Flowchart for experimental procedures followed.

100 rpm at varying time intervals (0.5, 1.0, 1.5, 2.0, 3.0, 4.0 h) in the pH range of 3.0–8.0 at $20 \pm 2\,^{\circ}$C. At the end of predetermined time intervals, the jars were withdrawn one by one from the jar-test apparatus, their contents filtered trough 0.45 µm membrane filter using a vacuum pump and the filtrate analysed for Cr(VI) and Cd(II) using a Perkin-Elmer model 3100 atomic absorption spectrophotometry at wavelengths of 357.9 nm for Cr(VI) and 228.8 nm for Cd(II). The experimental data obtained in the range of pH values (3.0–8.0) were also conducted in order to prepare adsorption isotherms. The same experiments were also conducted using activated carbon (untreated powder, 0.150–0.038 mm) derived from charcoal (Sigma, catalogue no. C 3345) to compare the adsorption effectiveness of carbon to fly ash.

Details of the experimental procedures are described in the first part of this investigation. A flowchart for the experimental procedures followed is also given in Fig. 1.

2.4. Statistical analysis

All batch kinetic studies were performed in duplicate and the average of the two residual Cr(VI) and Cd(II) concentrations in the filtrate presented. The criteria assigned for the relative error was 5%. When the relative error exceeded this criterion, the data were discarded and a third experiment conducted until the relative error fell within an acceptable range. The highest relative error for the data of both Cr(VI) and Cd(II) residues in the filtrate was <3% for all the experiments. All data in this study were analysed statistically using a Statcalc Statistical Package [15].

3. Results and discussion

3.1. Contact time

The kinetics of Cr(VI) and Cd(II) adsorption by two different types of Turkish fly ashes was studied by mixing for a predetermined time interval 10 g of fly ash in 500 ml of solution containing 55 ± 2 mg/l Cr(VI) and 6 ± 0.2 mg/l Cd(II) at pH 4.0 for Afsin-Elbistan fly ash and pH 3.0 for Seyitomer fly ash in the case of Cr(VI) and pH 7.0 for both fly ashes in the case of Cd(II). The plots for Cr(VI) concentration versus time (Fig. 2) and Cd(II) concentration versus time (Fig. 3) showed that equilibrium was attained in 2 h for the adsorption of both Cr(VI) and Cd(II) by two of the fly ashes. In general, the percentage of metal removal increased rapidly up to approximately 30 min and thereafter, rose slowly before attaining a saturation value. It can be inferred from Figs. 2 and 3 that metal removals in the first 30 min were approximately 20 and 25.46% for Cr(VI) and 85.08 and 40.16% for Cd(II) by Afsin-Elbistan and Seyitomer fly ashes, respectively. Approximately 93.5% removal for Afsin-Elbistan fly ash and 65% removal for Seyitomer fly ash was observed in the case of Cd(II), while it was only about 25.5 and 32% removal in the case of Cr(VI) for Afsin-Elbistan and Seyitomer fly ashes, respectively, in the initial 2 h and the adsorption of Cr(VI) and Cd(II) did not increase with time after the initial 2 h for both fly ashes. In all subsequent experiments, the equilibrium time was maintained at 2 h, which was considered as sufficient for the removals of both Cr(VI) and Cd(II) ions by each type of fly ashes.
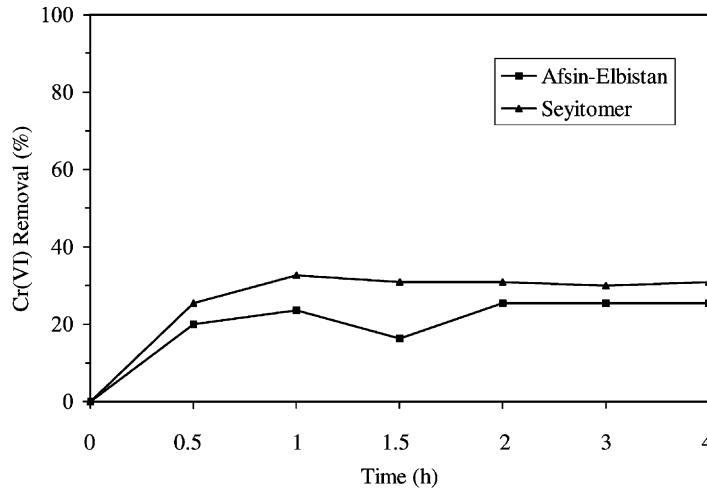
Fig. 2. Equilibrium time for the adsorption of Cr(VI) on Afsin-Elbistan and Seyitomer fly ashes.

The same equilibrium time (2 h) observed for Cr(VI) and Cd(II) adsorption on two different type of fly ash is interesting since Afsin-Elbistan fly ash has a larger specific surface area ($0.342 \, m^2/g$) compared to $0.115 \, m^2/g$ for Seyitomer fly ash. This result showed that the 15.14% silica (SiO_2), 7.54% alumina (Al_2O_3), 3.30% iron oxide (Fe_2O_3) and 23.66% lime (CaO) in Afsin-Elbistan fly ash as compared to the 53.50% silica (SiO_2), 15.71% alumina (Al_2O_3), 8.81% iron oxide (Fe_2O_3) and 0.29% lime (CaO) in Seyitomer fly ash could also contribute to the contact time for the adsorption of these two metals onto fly ash. This consideration is in good agreement with similar findings in the literature. The 3 h
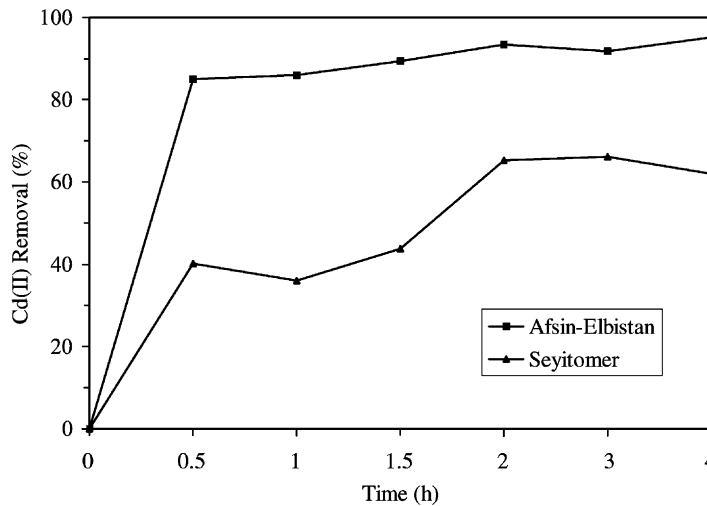

Fig. 3. Equilibrium time for the adsorption of Cd(II) on Afsin-Elbistan and Seyitomer fly ashes.
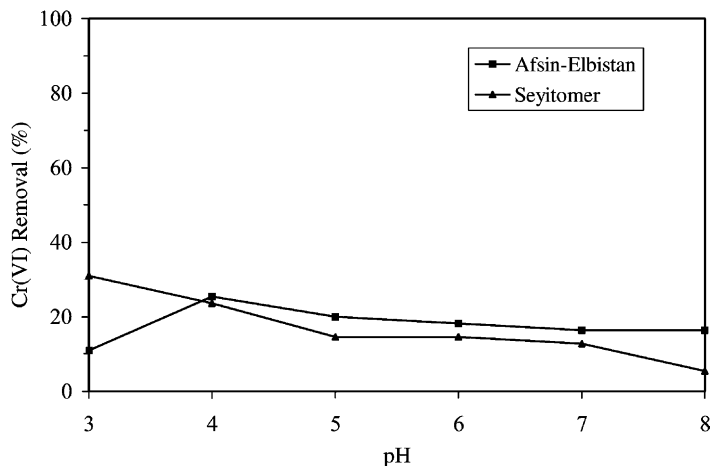
Fig. 4. Effect of pH on the adsorption of Cr(VI) by Afsin-Elbistan and Seyitomer fly ashes.

equilibrium time obtained by Viraraghaven and Rao [4] for Cr(VI) and Cd(II) adsorption on Saskatchewan fly ash consist of 50.70% SiO_2, 21.80% Al_2O_3, 4.50% Fe_2O_3 and 11.50% CaO, with high specific surface area ($1.7\,m^2/g$) suggests that the adsorption of Cr(VI) and Cd(II) on fly ash is very much dependent on the soluble lime (CaO) content of fly ash studied.

3.2. Adsorption at various pH levels

The effect of pH on the degree of metal removal for Cr(VI) and Cd (II) ions was investigated; the results are presented in Figs. 4 and 5. In these experiments, the fly ash loading was 10 g in 500 ml of solution containing 55 ± 2 mg/l Cr(VI) and 6 ± 0.2 mg/l Cd(II) at $20\pm2\,°C$ in all cases. The equilibrium time was 2 h, as discussed earlier. To avoid precipitation of the metal ions, all the experiments were conducted at a maximum pH of 8.0.

It is readily apparent from Fig. 4 that the maximum adsorption of Cr(VI) occurred at pH 4.0 for Afsin-Elbistan fly ash and pH 3.0 for Seyitomer fly ash. As it also seen in Fig. 4, the removal efficiency of Cr(VI) decreased from 32 to 5.5% with the rise of pH from 3.0 to 8.0 by Seyitomer fly ash while it increased from 11 to 25.5% with an increase in pH of solution from 3.0 to 4.0 and thereafter decreased appreciably (16%) in the pH range investigated (4.0–8.0) by Afsin-Elbistan fly ash. The higher adsorption of Cr(VI) on fly ash at low pH may be due to the neutralisation of negative surface charge by an excess of hydrogen ions, thereby facilitating the diffusion of dichromate ions and their adsorption on the prepared adsorbent. A significant reduction in the adsorption of Cr(VI) at higher pH is possibly due to the abundance of OH^- ions resulting in an increased hindrance to the diffusion species [16]. The results obtained at pH 3.0 and 4.0 using Afsin-Elbistan fly ash with a high-lime content may be explained by the sulphate ion (SO_4^{2-}) concentrations in solution as this ionic species is considered to be a more significant factor than OH^- and NO^{3-} ions according to the pC–pH diagrams given by Snoeyink and Jenkins [17]. Since,
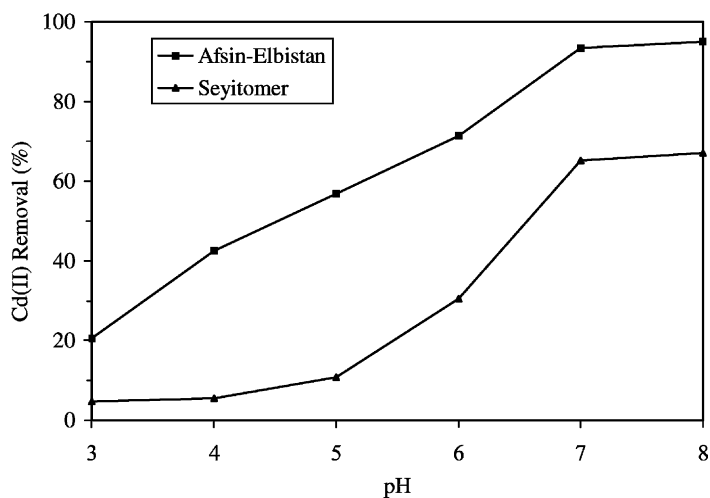
Fig. 5. Effect of pH on the adsorption of Cd(II) by Afsin-Elbistan and Seyitomer fly ashes.

at pH 3.0, $SO_4{}^{2-}$ ions react with H^+ ions to form bisulphate ions ($HSO_4{}^{2-}$), H^+ ions in solution decrease for the neutralisation of negative surface charge, the removal of Cr(VI) decreases. Nevertheless, at pH 4.0 the reaction rate of $SO_4{}^{2-}$ ions with H^+ ions to form $HSO_4{}^{2-}$ ions decreases because of the high-soluble lime content of Afsin-Elbistan fly ash. As a result, H^+ ions in solution increase for the neutralisation of negative surface charge, hence, the removal of Cr(VI) increases [16,17].

Alternatively, the phenomena of chromium adsorption at different pH may be explained with an equation given below:

$$2H^+ + 2HCrO_4{}^- \Leftrightarrow 2H_2CrO_4 \Leftrightarrow 2H_2O + Cr_2O_7{}^{2-} \overset{2H^+}{\Leftrightarrow} 2CrO_3 + H_2O \qquad (1)$$
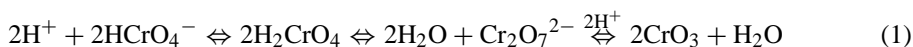
The H_2CrO_4 and CrO_3 probably exist as polynuclear species, along with their anhydrous forms, at high chromium concentration and at low pH. Thus, a high degree of adsorption Cr(VI) is due to the ability of Cr(VI) to stabilise itself, by forming undissociate polynuclear species as well as CrO_3 crystals. The formation of undissociated H_2CrO_4 followed by CrO_3 crystallisation is a proton consuming process and requires constant sources of protons. Hence, maximum adsorption was taken place at low pH values [18]. The results of the removal of Cr(VI) obtained at various pH values may also be attributed to the surface charge development of the fly ash and the degree of ionisation and speciation of Cr(VI) ions, since they are pH-dependent [19,20]. As shown in Table 1 in Part I of this study, Afsin-Elbistan and Seyitomer fly ashes exhibit a pH_{ZPC} of 7.0 and 3.5, respectively. This indicates that at pH lower than 7.0 and 3.5, the surface of Afsin-Elbistan and Seyitomer fly ashes is positively charged, respectively and Cr(VI) is present mainly as $Cr_2O_7{}^{2-}$ in the range of pH 3.0–4.0 at which maximum removal was observed under equilibrium conditions for both fly ashes. In this case, the adsorption of Cr(VI) onto the fly ashes occurred by electrostatic attraction [21]. In addition, the functional oxidised groups (SiO_2, Al_2O_3 and Fe_2O_3) present on the

Table 1
Langmuir constants at different pH for Cd(II)

pH	Afsin-Elbistan fly ash			Seyitomer fly ash		
	Langmuir constants		Equilibrium parameter, R_L	Langmuir constants		Equilibrium parameter, R_L
	b (l/mg)	Q^0 (mg/g)		b (l/mg)	Q^0 (mg/g)	
3.0	6.1818	0.0809	0.0250	6.2219	0.0077	0.0249
4.0	4.2025	0.1489	0.0364	3.7556	0.0162	0.0406
5.0	11.2583	0.1794	0.0139	3.7978	0.0345	0.0404
6.0	27.4481	0.2306	0.0058	2.2753	0.0925	0.0652
7.0	179.4000	0.2949	0.0009	11.0836	0.2160	0.0141

surface of fly ash play a major role with the change in pH of the system in removing Cr(VI) ions from solutions. SiO_2 in fly ash could adsorb either positive or negative contaminants depending on the pH of the solution [22]. The central ion of silicates has an electron affinity, giving the oxygen atoms bound to it low basicity. This condition allows the silica surface to act as a weak acid, which can react with water, forming surface silanol (SiOH) groups. As a result, at low pH the silica surface is positively charged and at high pH values it is negatively charged. The pH_{ZPC} of silica is generally in the neighbourhood of 2.0 [23]. Other solid materials such as alumina and iron also show this same phenomenon of developing positive or negative charges depending on pH. Iron as Fe_2O_3 has a zero point of charge (ZPC) at pH 6.7 while that of alumina (Al_2O_3) is at pH 8.5 [24]. This condition indicates that the maximum Cr(VI) adsorption capacity of the fly ashes can be attributed to the electrostatic interaction of the adsorbate with surface iron and alumina sites. This consideration also explains why Seyitomer fly ash with high Al_2O_3 and Fe_2O_3 content is a more effective adsorbent than the other (Afsin-Elbistan) at equilibrium conditions for Cr(VI) ions (Table 2 in Part I and Fig. 4).

The removal of Cd(II) by adsorption on both fly ashes was found to increase with an increase in pH of the solution from 3.0 to 8.0 at $20 \pm 2\,^\circ$C and the maximum adsorption of Cd(II) was found to occur at pH 7.0 for both fly ashes (Fig. 5). This finding may be attributed to the surface charge development of the fly ash and the concentration distribution of metal ions since both of them are pH dependent [19,20]. Regarding the pH_{ZPC} of the fly ashes (Table 1 in Part I), the adsorption of Cd(II) ions, which is present mainly as Cd^{2+} at pH 7.0 where maximum removal was observed under equilibrium conditions for both

Table 2
Langmuir equations for the adsorption of Cd(II)

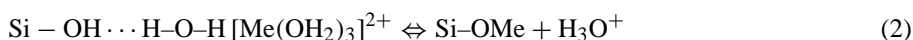| pH	Afsin-Elbistan fly ash		Seyitomer fly ash	
	Langmuir equation	Correlation coefficient	Langmuir equation	Correlation coefficient
3.0	$C/q_e = 1.9996 + 12.3609C$	0.9935	$C/q_e = 20.8731 + 129.8701C$	0.8570
4.0	$C/q_e = 1.5895 + 6.6800C$	0.9930	$C/q_e = 16.4364 + 61.7284C$	0.8930
5.0	$C/q_e = 0.4951 + 5.5741C$	0.9984	$C/q_e = 7.6930 + 28.9855C$	0.9567
6.0	$C/q_e = 1.1580 + 4.3365C$	0.9978	$C/q_e = 4.7514 + 10.8108C$	0.9653
7.0	$C/q_e = 0.0189 + 3.3907C$	0.9996	$C/q_e = 0.4177 + 4.6296C$	0.9935

Table 3
The *t*-test values for the adsorption of Cd(II) on Afsin-Elbistan and Seyitomer fly ashes

pH	Afsin-Elbistan fly ash calculated value	Seyitomer fly ash calculated value	Table value[a]
3.0	17.503	3.327	2.776
4.0	16.750	3.968	2.776
5.0	34.923	6.577	2.776
6.0	29.903	7.390	2.776
7.0	66.435	17.444	2.776

[a] Table values of *t* are at 5% level of significance.

fly ashes, occurred by electrostatic attraction [25]. Also, taking into account the pH_{ZPC} of SiO_2, Fe_2O_3 and Al_2O_3, which is 2.0, 6.7 and 8.5 [23,24], respectively, at pH where the maximum adsorption of the Cd(II) occurred, the maximum Cd(II) adsorption capacity of both fly ashes can be attributed to the electrostatic interaction of the adsorbate with surface silica and iron sites. The Cd(II) ions are perhaps adsorbed on the alumina surface in the fly ashes by a strong tendency towards chemical bonding between the Cd(II) ions and the alumina. Ricou-Hoeffer et al. have [12] reported that alumina silicate compounds in the fly ashes may also be involved in the adsorption phenomena through a SiO bond with metallic ions. Afsin-Elbistan fly ash with low SiO_2, Al_2O_3 and Fe_2O_3 and high-soluble lime (crystalline CaO) content (Tables 2 and 3 in Part I) is about 30% more effective than the other (Seyitomer) at equilibrium conditions for the removal of Cd(II) ions due to the formation of Ca and Si complexes such as calcium silicates ($2CaO·SiO_2$; Fig. 5). If it is assumed that adsorption takes place mainly on the surface of $2CaO·SiO_2$, it can be presented the interaction of the hydrolysis metal forms with the surface in an idealised manner as follows:

In acid solutions

$$Si - OH \cdots H–O–H \, [Me(OH_2)_3]^{2+} \Leftrightarrow Si–OMe + H_3O^+ \tag{2}$$

In neutral solutions

$$mCaSiO_3HSiO_3^- + MeOH^+ \Leftrightarrow mCaSiO_3MeSiO_3 + H_2O \tag{3}$$

In alkaline solutions

$$mCaSiO_3HSiO_3^- + Me(OH)_2 \Leftrightarrow mCaSiO_3MeSiO_3 + H_2O + OH^- \tag{4}$$
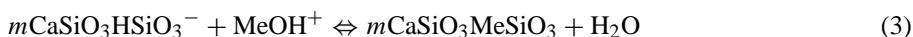
where Me is bivalent metal ions. $Me(OH)_2$ cannot be deposited on the solid phase because as a result of reactions (3) and (4) it turns into less soluble $MeSiO_3$ [26].

3.3. Adsorption isotherm

The linear forms of the Langmuir and Freundlich equations, described in the first part of this investigation, were conducted at the metal concentrations of 55 ± 2 mg/l for Cr(VI) and 6 ± 0.2 mg/l for Cd(II) as functions of solution pH under equilibrium conditions for both fly ashes. In the case of the adsorption of Cr(VI) on both fly ashes, the resulting adsorption data were found not to fit either the Langmuir isotherm or the Freundlich isotherm because
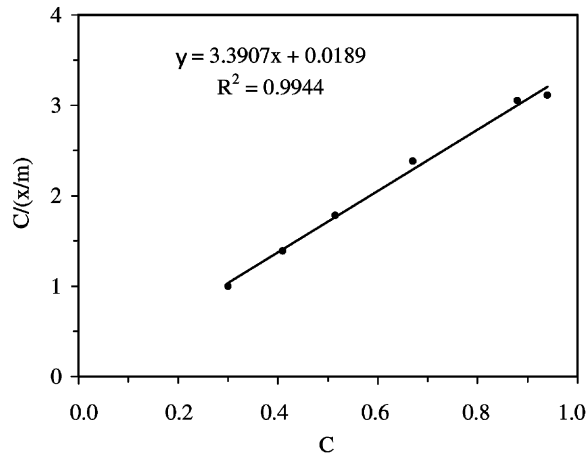
$$y = 3.3907x + 0.0189$$
$$R^2 = 0.9944$$

Fig. 6. Langmuir isotherm for Cd(II) adsorption on Afsin-Elbistan fly ash at pH 7.0 and $20 \pm 2\,°C$.

of the negative values for both isotherm constants. Because the Langmuir constants, Q^0 and b, are indicative of the adsorption capacity and the surface binding energy, respectively and the Freundlich constants, K_F and n, are also related to the adsorption capacity and the adsorption intensity, respectively, as given in the first part of this investigation. Therefore, these models inadequate to explain the adsorption process of Cr(VI) on both fly ashes. The adsorption data of Cd(II) on both fly ashes were found to fit well with the Langmuir equation (Eq. (5) in the Part I), however, the Freundlich equation (Eq. (6) in Part I), did not fit the adsorption data well in comparison, since it had lower correlations coefficients with points showing scatter.

The linear plots of C/q_e versus C at varying pH values suggest the applicability of the Langmuir isotherm for the present systems, showing the formation of monolayer coverage of the adsorbate at the outer surface of adsorbent [27]. The typical plots of the Langmuir isotherm for Cd(II) adsorption by Afsin-Elbistan and Seyitomer fly ashes at pH 7.0 are shown in Figs. 6 and 7, respectively. The values of Q^0 and b at varying pH values were determined from the slopes and intercepts of the respective plots and presented in Table 1 with equilibrium parameter (R_L). It is evident from this table that the adsorption capacity (Q^0) of Afsin-Elbistan and Seyitomer fly ashes for the removal of Cd(II) increased from 0.0809 to 0.2949 and 0.0077 to 0.2160 mg/g, respectively, with the rise of the pH of the solution from 3.0 to 7.0 at $20 \pm 2\,°C$. Furthermore, for all pH values, Q^0 for Afsin-Elbistan is greater than that of Seyitomer, indicating Afsin-Elbistan has a larger capacity for Cd(II) adsorption than Seyitomer. In addition to this result, the Langmuir model was found to be more applicable for the Afsin-Elbistan fly ash than for the Seyitomer fly ash, since the correlation coefficients for the former were higher (Table 2). The validity of the Langmuir model was further confirmed by the analysis of variance (ANOVA). The values of t (for equations with relatively higher correlation; Table 3) were significant at a 95% confidence level, indicating the linear nature of the model for both fly ashes. The values of F in the ANOVA (for equations with the best correlation) were also significant at 95% confidence
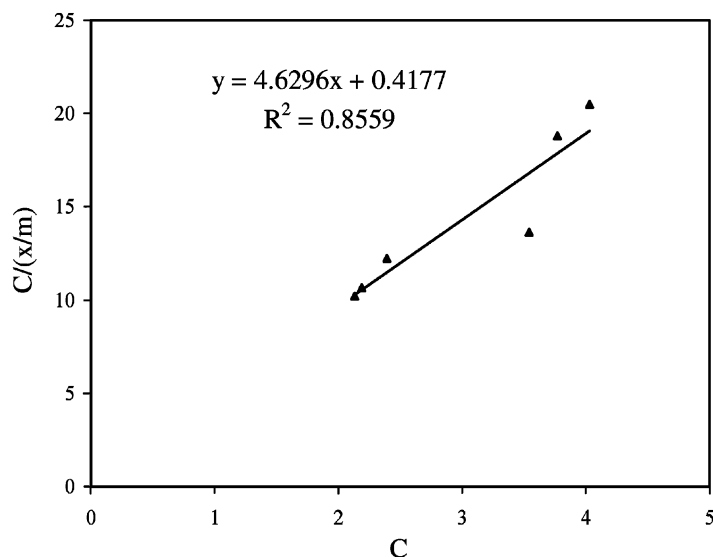
Fig. 7. Langmuir isotherm for Cd(II) adsorption on Seyitomer fly ash at pH 7.0 and $20 \pm 2\,^{\circ}$C.

level and have very large numbers ($F > 1$) especially at pH 7.0 for both fly ashes. If F is a large number, one can conclude that the independent variables (experimental data) contribute to the prediction of the dependent variables (modelling data), hence the linear model is well correlated. If F is approximately 1, one can conclude that there is no association between the variables. The P value is the probability of being wrong in concluding that there is an association between dependent and independent variables. The smaller the P value, the greater the probability that there is an association. The values of the P in the ANOVA were found to be smaller than 0.05 at all pH values for both fly ashes. Traditionally, it is concluded that the independent variable can be used to predict the dependent variable when $P < 0.05$ [28].

The essential characteristic of the Langmuir isotherm expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_{L}, was determined according to the Eq. (7) given in the Part I of this investigation. The value of R_{L}, whether the process in unfavourable ($R_{L} > 1$) or favourable ($R_{L} < 1$) [29]. Table 1 shows the R_{L} values for the adsorption isotherms of Cd(II) adsorption on both fly ashes. The R_{L} values were found to be <1 and >0 indicating favourable adsorption of Cd(II) on both fly ashes in the pH range 3.0 to 7.0.

3.4. Initial metal concentration

The removal of Cr(VI) by Afsin-Elbistan and Seyitomer fly ashes decreased from 50 to 25.46 and 56.45 to 30.91%, respectively, by increasing the Cr(VI) concentration from 1 ± 0.1 to 55 ± 2 mg/l at $20 \pm 2\,^{\circ}$C and pH 4.0 for Afsin-Elbistan and pH 3.0 for Seyitomer fly ashes. However, the removal of Cd(II) increased from 44.4 to 93.48% for Afsin-Elbistan fly ash

and from 39.33 to 65.24% for Seyitomer fly ash with the increase of solution concentration from 0.2 ± 0.02 to 6 ± 0.2 mg/l at 20 ± 2 °C and pH 7.0. These results show that the removal of Cr(VI) and Cd(II) is highly concentration dependent.

According to the above observations, Seyitomer fly ash with high SiO_2, Al_2O_3 and Fe_2O_3 contents is the better adsorbent at larger soluble Cr(VI) concentrations due to the electrostatic interaction of the adsorbate with surface iron and alumina sites (Table 2 in Part I), whereas, at larger soluble Cd(II) concentrations, Afsin-Elbistan fly ash is the better adsorbent, because of its higher soluble lime (CaO) content (Tables 2 and 3 in Part I) and larger specific surface area (Table 1 in Part I). The removal efficiencies of both fly ashes in the solutions of lower initial Cr(VI) (1 ± 0.1 mg/l) and Cd(II) (0.2 ± 0.02 mg/l) ions concentrations are also sufficient for permissible levels in mixed industrial effluent discharge for Cr(VI) (0.5 mg/l) and Cd(II) (0.1 mg/l) in Turkey [30], showing the removal of trace quantities of pollutants from the solution is not expected to pose any special problem in the system under investigation.

3.5. Desorption studies

Desorption studies were conducted by mixing approximately 10 g of fly ash with metal-laden filtrated from the solution which was obtained at the end of the adsorption experiments conducted at the constant concentrations of Cr(VI) and Cd(II) (55 ± 2 and 6.0 ± 0.2 mg/l, respectively). The pH values for these experiments corresponded to the maximum removal that was observed with 500 ml of deionised water for 4 h at 100 rpm and 20 ± 2 °C in the range of pH values (3.0.0–8.0) (Fig. 1). These studies showed that Cr(VI) was desorbed from both the fly ashes at basic pH values (Fig. 8) while the desorption of Cd(II) ions from both fly ashes was observed only in acidic pH values (Fig. 9) during the 4 h study period and was generally rather low (<0.5 mg/l for Cr(VI) and 0.1 mg/l for Cd(II)) for both fly ashes.
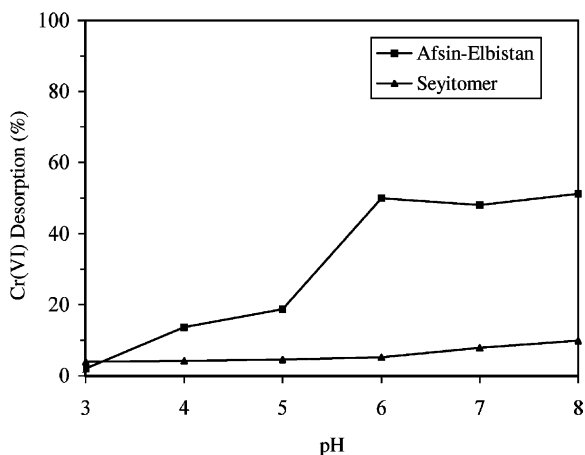

Fig. 8. Removal of Cr(VI) from fly ashes; influence of pH; Cr(VI) initially deposited on Afsin-Elbistan and Seyitomer fly ashes 0.22 and 1.63 mg/g, respectively.
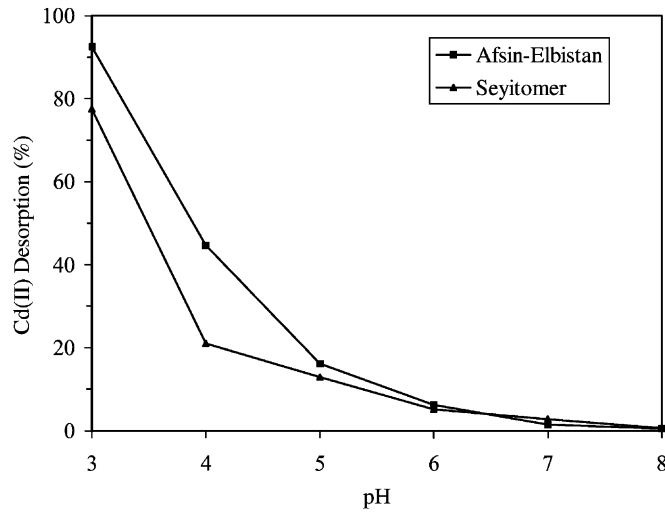
Fig. 9. Removal of Cd(II) from fly ashes; influence of pH; Cd(II) initially deposited on Afsin-Elbistan and Seyitomer fly ashes 0.60 and 0.434 mg/g, respectively.

3.6. Comparative studies

The removal capacity of two different type of fly ash (Afsin-Elbistan, C class fly ash and Seyitomer, *F* class fly ash) [31–33] for Cr(VI) and Cd(II) ions was compared with that of charcoal activated carbon (Figs. 10 and 11). These results showed that the removal Cr(VI)
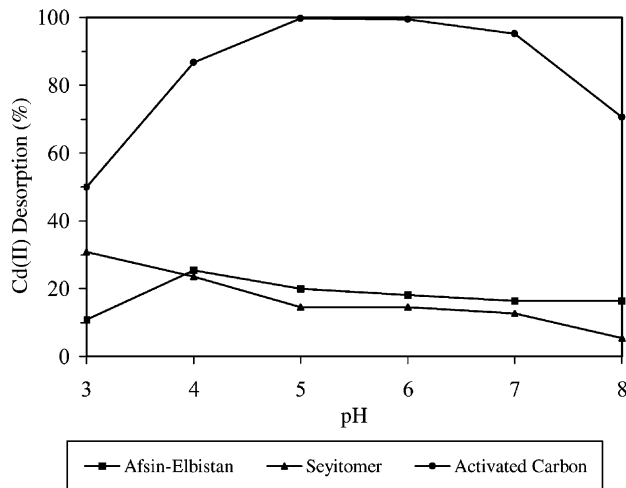

Fig. 10. Effectiveness of an activated carbon-compared to Afsin-Elbistan and Seyitomer fly ashes on the removal of Cr(VI).
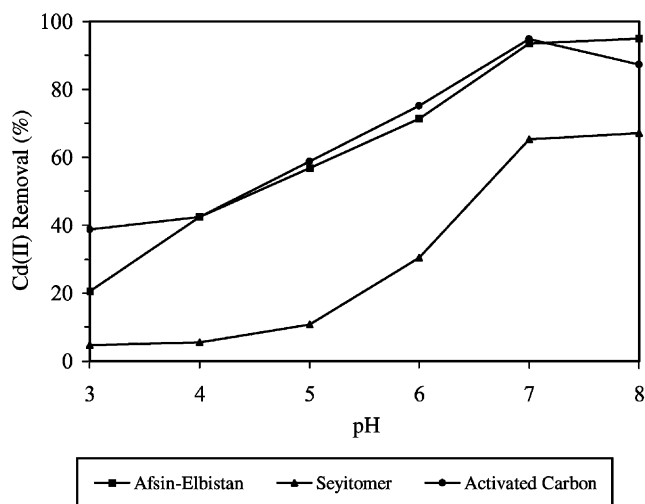
Fig. 11. Effectiveness of an activated carbon-compared to Afsin-Elbistan and Seyitomer fly ashes on the removal of Cd(II).

was in the order: activated carbon > Seyitomer fly ash > Afsin–Elbistan fly ash and the equilibrium period was 1.5 h for activated carbon and Seyitomer fly ash at pH values at which maximum removal was observed, namely, pH 5.0 for activated carbon, pH 4.0 for Afsin-Elbistan fly ash and pH 3.0 for Seyitomer fly ash. However, this ranking changed in the order activated carbon > Afsin–Elbistan fly ash > Seyitomer fly ash for the removal of Cd(II) at pH 7.0 at which maximum removal was observed. These results also indicated that the adsorption capacities of both fly ashes are nearly three times less than that of activated carbon for the removal of Cr(VI) while Afsin-Elbistan fly ash with high-lime content is as effective as activated carbon for the removal of Cd(II) (Table 4).

Table 4

Comparative study of the adsorptive properties of activated carbon, Afsin-Elbistan and Seyitomer fly ashes for Cr(VI) and Cd(II)

Adsorbent	Equilibrium period (h)	Percentage removal	
		Cr(VI)	Cd(II)
Activated carbon	1.5	99.92	94.58
	2.0	99.71	94.85
	3.0	84.38	58.57
Afsin-Elbistan fly ash	1.5	16.36	89.37
	2.0	25.46	93.48
	3.0	25.46	91.83
Seyitomer fly ash	1.5	30.91	43.81
	2.0	30.91	65.24

While the removals of Cr(VI) and Cd(II) ions by fly ash were much less than those by activated carbon, fly ash can be obtained cheaply in large quantities and used as a neutralising agent in the treatment process due to the high-lime content. Fly ash after use as an adsorbent can be employed as a filling material in pavement linings, in soil stabilisation, in cement and concrete industries, or can be disposed off in a landfill [5].

4. Conclusion

The results presented in this study clearly reveal the adsorption capacity of Turkish fly ash with high-lime content (Afsin-Elbistan) which is available in abundance, for the removal of Cd(II) from aqueous solutions. From the results obtained in this study, the following conclusions are deduced:

1. The kinetics studies indicated that equilibrium in the adsorption of Cr(VI) and Cd(II) on the fly ashes was reached in 2 h of contact time between the fly ash and the solution.
2. The optimum pH corresponding to the maximum adsorption was found to be at pH 4.0 for Afsin-Elbistan fly ash and pH 3.0 for Seyitomer fly ash in the case of Cr(VI) while Cd(II) was adsorbed to a greater extent at pH 7.0 for both fly ashes.
3. Cr(VI) adsorption on both fly ashes was not described by both the Langmuir and Freundlich isotherms, while Cd(II) adsorption on both fly ashes satisfied only the Langmuir isotherm model.
4. The adsorption of Cd(II) increased with an increase in the concentrations of these metals in solution while Cr(VI) adsorption decreased by both fly ashes.
5. The quality of fly ash seemed to be a significant factor in influencing Cr(VI) and Cd(II) ions removal. Afsin-Elbistan fly ash with high-lime content was the most efficient for the removal of Cd(II), while Cr(VI) ions were adsorbed by Seyitomer fly ash with high silica and alumina content much more than Afsin-Elbistan fly ash.
6. Activated carbon was found to have a much higher adsorption capacity for Cr(VI) and Cd(II); however, fly ash which is easily available at a fraction of the cost of activated carbon, may be suitable for small-scale wastewater treatment plants in Turkey.
7. The results obtained with the fly ashes may be testified using metal plating industry wastewaters containing these metals since fly ash is definitely inexpensive compared to activated carbon.

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