Comparative study of adsorption properties of Turkish fly ashes
I. The case of nickel(II), copper(II) and zinc(II)

Belgin Bayat[*]

*Department of Environmental Engineering, Faculty of Engineering and Architecture,
Cukurova University, Balcali, Adana 01330, Turkey*

Abstract

The objective of this study was to compare two different Turkish fly ashes (Afsin-Elbistan and Seyitomer) for their ability to remove nickel [Ni(II)], copper [Cu(II)] and zinc [Zn(II)] from an aqueous solution. The effect of contact time, pH, initial metal concentration and fly ash origin on the adsorption process at $20 \pm 2\,^\circ\text{C}$ were studied. Batch kinetic studies showed that an equilibrium time of 2 h was required for the adsorption of Ni(II), Cu(II) and Zn(II) on both the fly ashes. The maximum metal removal was found to be dependent on solution pH (7.0–8.0 for Ni(II), 5.0–6.0 for Cu(II) and 6.0–7.0 for Zn(II)) for each type of fly ash. With an increase in the concentrations of these metals, the adsorption of Ni(II) and Zn(II) increased while the Cu(II) adsorption decreased on both the fly ashes. Adsorption densities for the metal ions were $Zn(II) > Cu(II) > Ni(II)$ for both the fly ashes. The effectiveness of fly ash as an adsorbent improved with increasing calcium (CaO) content. Adsorption data in the range of pH values (3.0–8.0) using Ni(II) and Cu(II) concentrations of 25 ± 2 mg/l and Zn(II) concentration of 30 ± 2 mg/l in solution were correlated using the linear forms of the Langmuir and Freundlich equations. The adsorption data were better fitted to the Langmuir isotherm since the correlation coefficients for the Langmuir isotherm were higher than that for the Freundlich isotherm. The fly ash with high calcium content (Afsin-Elbistan) was found to be a metal adsorbent as effective as activated carbon and, therefore, there are good prospects for the adsorptions of these metals on fly ash with high calcium content in practical applications in Turkey.
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Keywords: Adsorption; Nickel; Copper; Zinc; Fly ash; Langmuir's model; Freundlich's model

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[*] Tel.: +90-322-338-61-19; fax: +90-322-338-61-26.
E-mail address: obayat@cu.edu.tr (B. Bayat).

1. Introduction

The presence of heavy metals in the environment is a major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products. Thus, treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume followed by a secure disposal. The most commonly used techniques for removing metal ions from wastewaters include chemical precipitation, ion-exchange, reverse osmosis and solvent extraction. However, these techniques have certain disadvantages, such as high capital and operational costs or the treatment and disposal of the residual metal sludges.

In the last few years, adsorption has been shown to be an alternative method for removing trace metals from water and wastewater [1–4]. In spite of the usefulness of activated carbon as an effective adsorbent for heavy metals, the high cost of activated carbon has restricted its more widespread use.

Several studies reported that significant amounts of heavy metals were removed from solution by adsorption on fly ash, a waste product of thermal power units [5–12]. Gangoli et al. [5] examined the suitability of fly ash as an adsorbent for the removal of heavy metal ions from the aqueous solutions. They concluded that metal ions might adsorb on fly ash because of its high content of silica and alumina. Panday et al. [6] studied the removal of copper(II) by adsorption on fly ash and reported that fly ash exhibited Langmuir isotherm behaviour and had adsorption efficiencies of 70 wt.% for 2.0×10^{-4} M Cu(II) from aqueous solution at pH 6.5 and 30 °C. Viraraghavan and Dronamraju [8], investigated the removal of copper(II), nickel(II) and zinc(II) by fly ash at different contact times, pH, initial concentrations of the adsorbate and temperatures. Their results showed that the adsorption capacity of fly ash with respect to Cu(II), Ni(II) and Zn(II) increased with increase in the temperature. The optimum pH corresponding to the maximum adsorption was found to lie between 3.0 and 3.5 for the three metal ions. Two different fly ashes (Kardia and Megalopolis) were studied with respect to their ability to remove nickel(II) ions from aqueous solutions by Mavros et al. [9]. Their results showed that Kardia fly ash with a higher percentage of CaO compound (44%) exhibited much greater Ni(II) removal than Megalopolis fly ash with 22% of CaO. Ricou-Hoeffer et al. [12] also studied the removal of copper(II), zinc(II) and lead(II) by the adsorption on fly ash and fly ash/lime mixing and concluded that four parameters were dominant for adsorption: pH, sorbate/adsorbent mass ratio, fly ash/lime ratio and fly ash origin.

The purpose of this work is to compare two different Turkish fly ashes (Afsin-Elbistan and Seyitomer) with respect to their ability to remove Ni(II), Cu(II) and Zn(II) from an aqueous solution and to assess the influence of contact time, pH, initial metal concentration on metal adsorption by the fly ash. This work also involved isotherm studies conducted at several different pH in an attempt to understand the mechanisms of metal ion removal. In addition, the removals obtained with fly ashes were also compared with results obtained with commercial activated carbon.

2. Materials and methods

2.1. Fly ash

The lignite fly ashes used in the experiments were collected from the lignite-burning thermal power plants of Afsin-Elbistan (south-eastern Anatolia) and Seyitomer (north-western Anatolia). The pH values of the fly ash samples were determined by mixing 2 g of fly ash with 100 ml of deionized water and recording pH at 1 h intervals for a period of 24 h. The results showed that the pH of the solutions was almost constant at approximately 12.5 for Afsin-Elbistan fly ash and 10.5 for Seyitomer fly ash.

Dry mechanical sieving and laser beam techniques (Malvern Series 2600) were used to determine the particle size of materials coarser and finer than 0.075 mm, respectively. It was found that Afsin-Elbistan fly ash has a very small particle size with greater than about 50 wt.% passing a number 200 sieve (0.075 mm) while only 15 wt.% of Seyitomer fly ash particles is less than 0.075 mm. The specific surface area of the particles of Afsin-Elbistan and Seyitomer fly ashes was determined by the laser beam method (Malvern Series 2600). They were 0.342 and 0.115 m^2/g, respectively.

The surface charge was determined by electrophoretic measurements using a zeta-meter (ZM-77 manufactured by Zeta-Meter, USA), and the zero point charge (ZPC) found to be at over pH 7.0 for Afsin-Elbistan fly ash and pH 3.5 for Seyitomer fly ash.

The loss on ignition (LOI) was determined by heating a pre-weighed dry sample (left at 105 °C in an oven and then cooled in desiccators) to 600 °C over a period of 2 h (Table 1). Elemental analysis was determined by a wet chemical method involving hydrofluoric acid digestion and measurement of elemental concentration using an atomic absorption spectrophotometry (AAS) (Perkin-Elmer, model 3100). Results indicated that Seyitomer fly ash is a Class F fly ash grouping of ASTM designation C 618 with alumina (Al_2O_3) and silica (SiO_2) components as major constituents ($\geq$70 wt.%), whereas Afsin-Elbistan fly ash is a Class C fly ash with 23.66% lime (CaO) as a major constituent (Table 2) [13–15].

In order to provide a better understanding of the environmental impacts of fly ash disposal or utilization, the solubility characteristics of various chemical species associated with fly ash were examined. One gram samples of ash were equilibrated in 200 ml distilled water for 2 h. After filtration, the major chemical constituents in the filtrate were measured by AAS (Table 3). Other characteristics of the fly ashes are reported elsewhere [16].

Table 1
Major physical properties of Afsin-Elbistan and Seyitomer fly ashes [16]

Property	Afsin-Elbistan	Seyitomer
pH	12.5	10.5
Particle size	65%; $\leq$75 μm	15%; $\leq$75 μm
Specific surface area (m^2/g)	0.342	0.115
Bulk density (g/cm^3)	1.05	0.88
Specific gravity (g/cm^3)	2.70	1.58
pH_{ZPC}	7.0	3.5
LOI	2.31	3.78

Table 2
Chemical composition of Afsin-Elbistan and Seyitomer fly ashes [16]

Element oxide	Afsin-Elbistan (wt.%)	Seyitomer (wt.%)
SiO_2	15.14	53.50
Al_2O_3	7.54	15.71
Fe_2O_3	3.30	8.81
CaO	23.66	0.29
MgO	4.50	2.94
K_2O	0.28	1.19
Na_2O	0.57	0.77
TiO_2	1.03	0.12
SO_3	13.22	1.11
Cd[a]	8.00	–
Pb[a]	80.00	79
Zn[a]	80.00	112.6
Cu[a]	40.00	98.8
Cr[a]	298.00	454.5
Ni[a]	119.00	1975.9
Mn[a]	219.00	790.4

[a] Measured in mg/l.

Table 3
Soluble concentrations of some elements in water from Afsin-Elbistan and Seyitomer fly ashes [16]

Fly ash	Total concentration in solution (mg/l)														
	Si	Al	Fe	Ca	Mg	K	Na	Ti	Cd	Pb	Zn	Cu	Co	Ni	Mn
Afsin-Elbistan	3.1	0.2	–	280	3.6	1.0	4.0	–	–	–	–	–	–	–	–
Seyitomer	5.0	0.5	–	30	0.9	3.0	6.0	–	–	0.2	0.2	–	–	–	–

2.2. Chemicals

The synthetic solution for this study was prepared by dissolving 124 mg $Ni(NO_3)_2 \cdot 6H_2O$, 95 mg $Cu(NO_3)_2 \cdot 3H_2O$ and 63 mg $ZnCl_2$ in 1 l of distilled water to obtain 25 ± 2 mg/l of both Ni(II) and Cu(II) and 30 ± 2 mg/l Zn(II), the typical concentrations found in the wastewaters of metal plating industries [17]. 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 0.1 N $NaNO_3$. 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. To determine the contact time necessary for adsorption, 500 ml of solution containing 25 ± 2 mg/l of Ni(II) and Cu(II) and 30 ± 2 mg/l of Zn(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 100 rpm, and at the end of predetermined time intervals (0.5, 1.0, 1.5, 2.0,

3.0, 4.0 h), the jars were withdrawn one by one from the jar-test apparatus, their content was filtered, and the filtrate analyzed for Ni(II), Cu(II) and Zn(II). The effect of pH on the adsorption of Ni(II), Cu(II) and Zn(II) on fly ash was studied by the addition of 10 g of fly ash to each of the six jars containing 500 ml of solution with 25 ± 2 mg/l of Ni(II) and Cu(II) and 30 ± 2 mg/l of Zn(II). The pH of the solution was adjusted to be in the range 3.0–8.0 by the addition of either 0.1 M HNO_3 or 0.1 M NaOH. After mixing at 100 rpm for the equilibrium time, the solutions were filtered and the concentrations of Ni(II), Cu(II) and Zn(II) determined. The experimental data obtained in the range of pH values (3.0–8.0) were also conducted in order to prepare the adsorption isotherms. To determine the performance of fly ash as an adsorbent in wastewater with low initial metal concentrations (0.1–0.3 mg/l of Ni(II), up to 0.8 mg/l of Cu(II) and 0.7–1.6 mg/l of Zn(II), the typical concentrations found in municipal effluents [18]), batch tests were conducted for the equilibrium time mixing at a constant speed of 100 rpm after adjusting the pH to the optimum value for maximum adsorption. A constant 10 g fly ash in 500 ml of solution was used.

After the adsorption experiments conducted by mixing 10 g of fly ash with 500 ml of solution containing 25 ± 2 mg/l of Ni(II) and Cu(II), and 30 ± 2 mg/l of Zn(II) at optimum pH for maximum adsorption for the equilibrium time, the metal-laden fly ash was separated from the solution by filtration and mixed with a 500 ml deionized water. Mixing was carried out for the equilibrium time, which was the same time as the adsorption equilibrium time. Conditions were 100 rpm at $20 \pm 2\,^{\circ}C$. After mixing, the deionized water was filtered and analyzed for the concentrations of Ni(II), Cu(II) and Zn(II). The desorption experiments were performed at pH values varying from 3.0 to 8.0.

The adsorption of Ni(II), Cu(II) and Zn(II) from aqueous solutions by activated carbon (untreated powder, 0.150–0.038 mm) derived from charcoal (Sigma, catalog no. C 3345) was studied to compare to the adsorption effectiveness of fly ash. The adsorption experiments with activated carbon were conducted using the same procedures as used in the adsorption experiments with the fly ash to determine the equilibrium time and the optimum pH for maximum adsorption.

To correct for any adsorption of Ni(II), Cu(II) and Zn(II) on glass beakers, control experiments were conducted without adsorbent as before; there was negligible adsorption by the glass beaker walls.

Ten grams of fly ash were also added to 500 ml of deionized water to assess the leaching of Ni(II), Cu(II) and Zn(II) during the adsorption equilibrium time period. The concentrations of Ni(II), Cu(II) and Zn(II) in the supernatant were measured using a Perkin-Elmer model 3100 AAS at wavelengths of 232 nm for Ni(II), 324.8 nm for Cu(II) and 213.9 nm for Zn(II). If necessary, samples were diluted with distilled water. All the samples were filtered through a 0.45 μm membrane filter (Whatman) using a vacuum pump, and acidified with concentrated HNO_3 prior to Ni(II), Cu(II) and Zn(II) measurement. A flowchart for the experimental procedures followed is given in Fig. 1.

2.4. Statistical analysis

All the batch kinetic studies were performed in duplicate and the average of the two residual Ni(II), Cu(II) and Zn(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
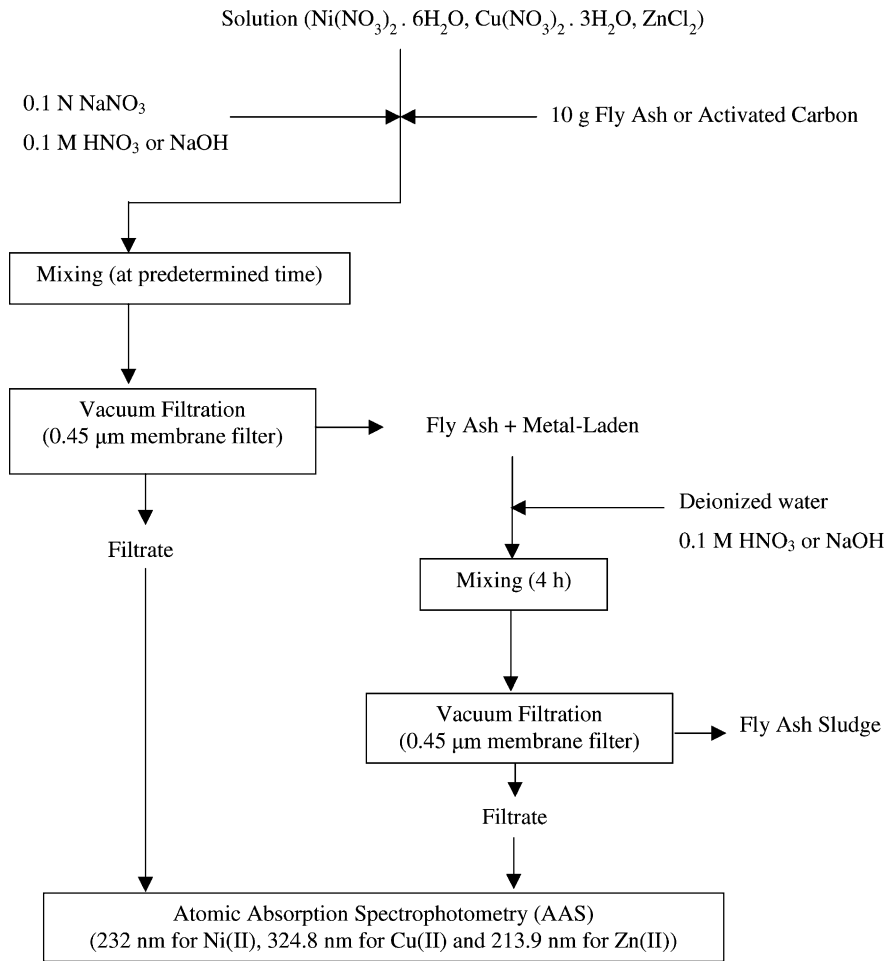
Solution ($Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $ZnCl_2$)

0.1 N $NaNO_3$

0.1 M HNO_3 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 HNO_3 or NaOH

Mixing (4 h)

Vacuum Filtration
(0.45 μm membrane filter)   → Fly Ash Sludge

Filtrate

Atomic Absorption Spectrophotometry (AAS)
(232 nm for Ni(II), 324.8 nm for Cu(II) and 213.9 nm for Zn(II))

Fig. 1. Flowchart for experimental procedures followed.

discarded and a third experiment conducted until the relative error fell within an acceptable range. The highest relative error for the data of Ni(II), Cu(II) and Zn(II) residues in the filtrate was less than 3% for all the experiments. All the data in this study were analyzed statistically using a Statcalc statistical package [19].

3. Results and discussion

3.1. Contact time

Initial batch studies conducted to assess the time taken for the equilibrium to be attained were performed for two different types of Turkish fly ashes (Afsin-Elbistan and Seyitomer).
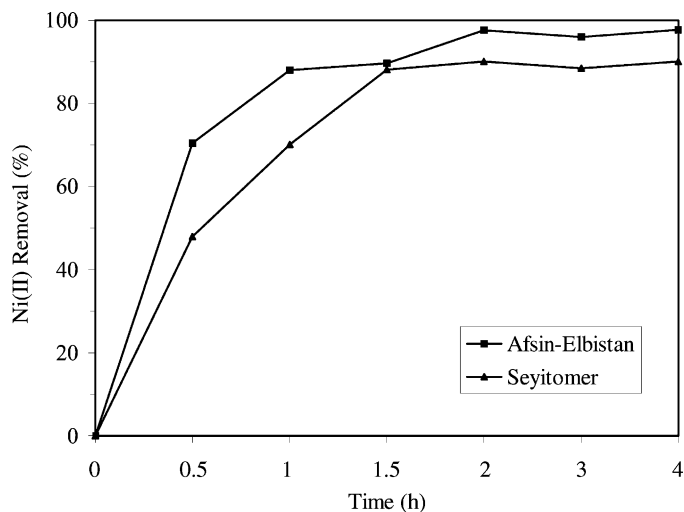
Fig. 2. Equilibrium time for the adsorption of Ni(II) on Afsin-Elbistan and Seyitomer fly ashes.

In these tests, 10 g of fly ash in 500 ml of aqueous solution containing 25 ± 2 mg/l of Ni(II) and Cu(II), and 30 ± 2 mg/l of Zn(II) were used. The pH was 8.0 for Ni(II), 6.0 for Cu(II) and 7.0 for Zn(II), corresponding to the pH values at which the maximum removal was observed for both the fly ashes. The metal concentrations were determined at varying time intervals. The results are shown for Ni(II), Cu(II) and Zn(II) in Figs. 2–4, respectively. As shown, the removal of Ni(II), Cu(II) and Zn(II) by Turkish fly ashes increased with increasing time up to120 min, and thereafter the removal was not significant, indicating that
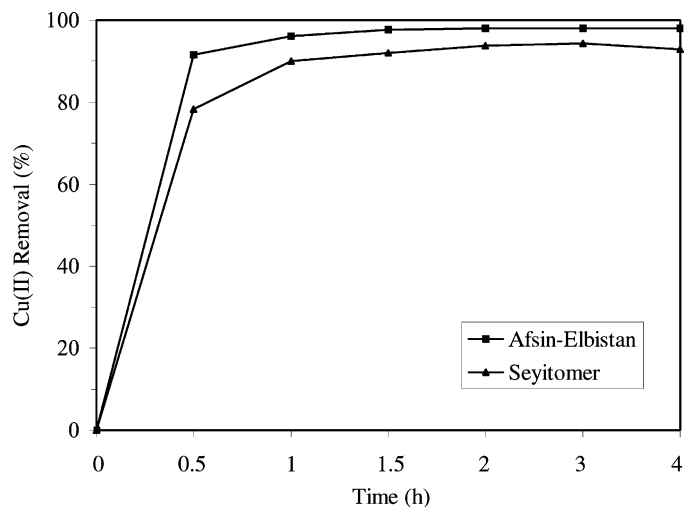
Fig. 3. Equilibrium time for the adsorption of Cu(II) on Afsin-Elbistan and Seyitomer fly ashes.
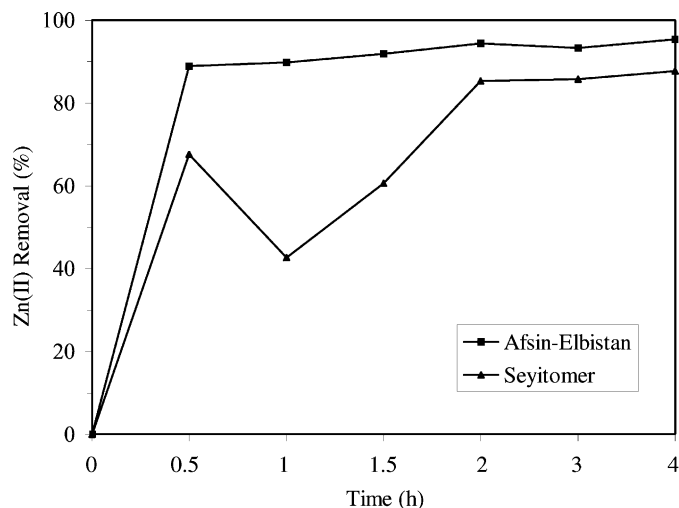
Fig. 4. Equilibrium time for the adsorption of Zn(II) on Afsin-Elbistan and Seyitomer fly ashes.

the minimum contact time necessary for a good heavy metal removal was 120 min. It can be seen in Figs. 2–4 that the metal removal in the first 30 min was 92 and 89% of the maximum removal in the case of Cu(II) and Zn(II), respectively, while it was 70% of the maximum for Ni(II) by the Afsin-Elbistan fly ash. Nevertheless, metal removal by the Seyitomer fly ash, was slower in the initial stages and was 78, 68 and 48% of the maximum Cu(II), Zn(II) and Ni(II) removal, respectively, during first 30 min. The maximum removal efficiencies of 98 and 94% Cu(II), 98 and 90% Ni(II), and 94 and 85% Zn(II) were also attained with the Afsin-Elbistan and Seyitomer fly ashes, respectively, in the initial 120 min. Therefore, the equilibrium time was fixed at 120 min in the case of Ni(II), Cu(II) and Zn(II) in all the further tests.

   Although the Afsin-Elbistan fly ash with high calcium oxide (CaO) content (Table 2) is a more effective adsorbent than the Seyitomer fly ash at equilibrium conditions for the three metals tested, the contact time is the same for both fly ashes for each metal (Figs. 2–4). 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 contribute to the contact time for the adsorption of these three metals on the fly ash. Viraraghavan and Dronamraju [8], conducted their study at 21 °C using Ni(II), Cu(II) and Zn(II) concentrations of 1.15, 1.232 and 1.05 mg/l, respectively, while this study was conducted at 20 ± 2 °C with Ni(II) and Cu(II) concentrations of 25 ± 2 mg/l and Zn(II) concentration of 30 ± 2 mg/l. Viraraghavan and Dronamraju [8], also determined the appropriate contact time was 120 min for the adsorption of Ni(II), Cu(II) and Zn(II) on Saskatchewan fly ash which consists of 50.70% SiO_2, 21.80% Al_2O_3, 4.50% Fe_2O_3 and 11.50% CaO. In addition, the larger specific surface area (1.7 m^2/g) of the fly ash used by Viraraghavan and Dronamraju [8] as compared with the specific surface areas of 0.342 and 0.115 m^2/g for Afsin-Elbistan and Seyitomer fly ashes, respectively, used in this study suggests that the
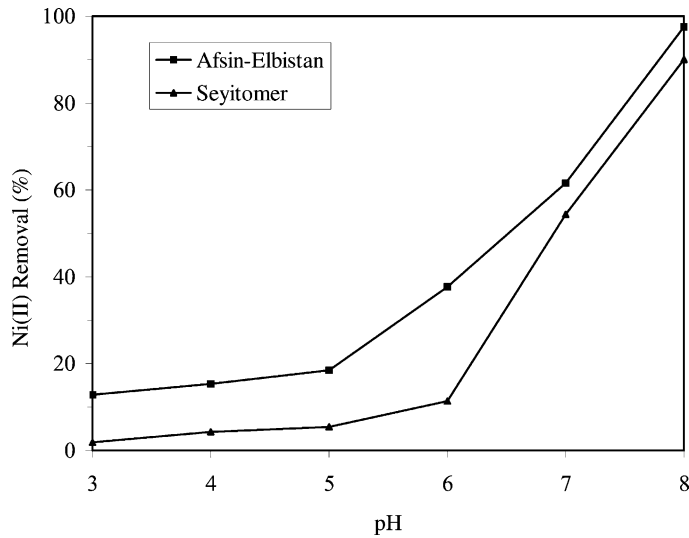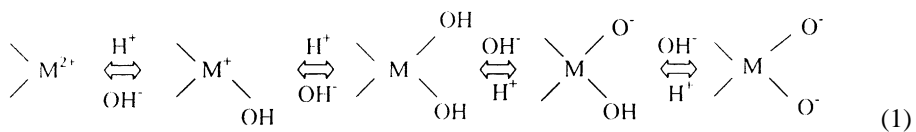
Fig. 5. Effect of pH on the adsorption of Ni(II) by Afsin-Elbistan and Seyitomer fly ashes.

surface area of fly ash is a less effective parameter than the chemical content of fly ash to establish the contact time for the adsorption of these three metals on fly ash.

3.2. Adsorption at various pH levels

The removal of pollutants from wastewaters by adsorption is highly dependent on the pH of the solution, which affects the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate [6,7,20]. It is readily apparent from Figs. 5–7 that the amount of metal removal by adsorption increased with an increase of pH level up to about pH 8.0 for Ni(II), pH 7.0 for Zn(II) and pH 6.0 for Cu(II). These results correspond to the pH values at which the maximum removal was observed under equilibrium conditions. Thereafter, the removal was more or less constant in the pH range investigated for both the fly ashes (Afsin-Elbistan and Seyitomer). To avoid precipitation of the metal ions, all the experiments were conducted at pH values less than 8.0. The maximum degree of metal removal was in the ranges of 98.0–98.39 and 93.77–93.89% at pH 6.0–7.0 in the case of Cu(II), 94.39–96.01 and 85.29–85.89% at pH 7–7.5 in the case of Zn(II) and 97.69 and 90.04% at pH 8.0 in the case of Ni(II) for Afsin-Elbistan and Seyitomer fly ashes, respectively.

The basis of aqua-complex formation and its subsequent acid–base dissociation at the solid–solution interface seems to be responsible for the following results obtained at various pH values:

$$
\begin{array}{c}
\diagdown \\
\diagup
\end{array}
M^{2+}
\underset{OH^-}{\overset{H^+}{\rightleftharpoons}}
\begin{array}{c}
\diagdown \\
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\end{array}
M^+
\underset{OH^-}{\overset{H^+}{\rightleftharpoons}}
\begin{array}{c}
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M
\underset{H^+}{\overset{OH^-}{\rightleftharpoons}}
M
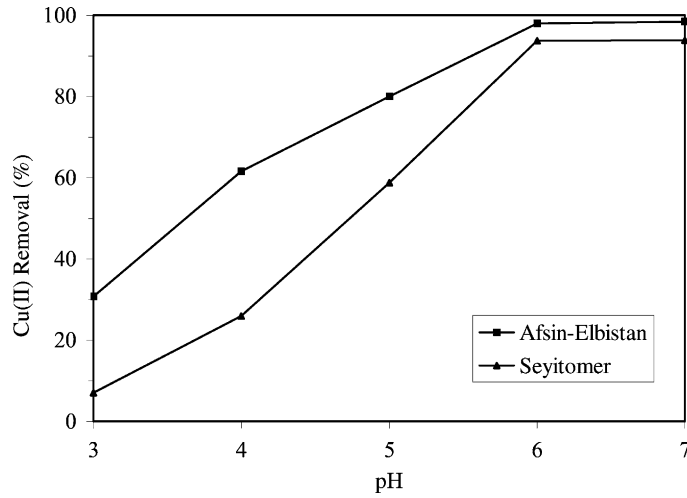\underset{H^+}{\overset{OH^-}{\rightleftharpoons}}
M \tag{1}
$$

Fig. 6. Effect of pH on the adsorption of Cu(II) by Afsin-Elbistan and Seyitomer fly ashes.

where, M represents Si, Al, Fe or Ca [8]. In addition, the functional oxidized group (SiO_2, Al_2O_3 and Fe_2O_3) present on the surface of the fly ash and pH of the system largely affect the adsorption of the various ionic species of Ni(II), Cu(II) and Zn(II) present in wastewater. Gangoli et al. [5], reported that the surface of silica (SiO_2) might exhibit considerable affinity towards metal ions. The central ion of silicates (Si^{4+}) has a very strong affinity for electrons; therefore, the oxygen atoms that are bound to the silicon ions have a low basicity, making the silica surface act as a weak acid. The oxygen atoms on the silica surface are free
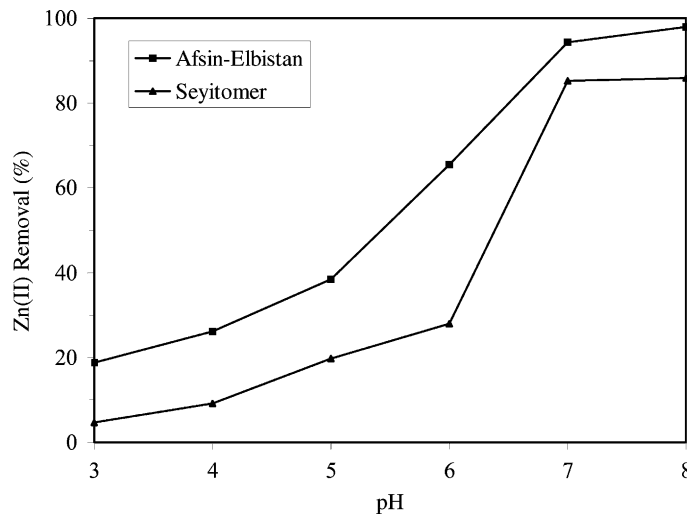

Fig. 7. Effect of pH on the adsorption of Zn(II) by Afsin-Elbistan and Seyitomer fly ashes.
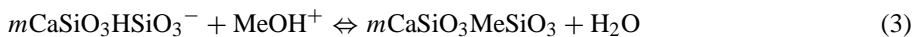
to react with water, forming surface silanol (SiOH) groups. The acidity of the silanol (SiOH) groups determines the dependence of the charge of the silica surface on pH. At low pH, a positively charged silica surface results, and at high pH values negatively charged surface prevails. The pH_{ZPC} of pure silica is generally close to 2.0 [6]. 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 ZPC at pH 6.7, while that of alumina (Al_2O_3) is at pH 8.5 [21]. Taking into account the dominating metal species, which are Ni^{2+}, $NiOH^+$, Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2$, Zn^{2+} and $ZnOH^+$ according to the simple species diagrams constructed by Mavros et al. [9], Panday et al. [6] and Huang and Rhodas [22] for Ni(II), Cu(II) and Zn(II), respectively, at the pH values where the maximum adsorption of the metal took place, the maximum Ni(II) and Zn(II) adsorption capacity of the fly ashes can be attributed to the electrostatic interaction of the adsorbate with surface silica and iron sites. In the case of Cu(II), adsorption is supposed to be occur by the electrostatic interaction with only surface silica sites. These metals are perhaps adsorbed on the alumina surface in the fly ashes by a strong tendency towards chemical bonding between the metal groups and the alumina. Ricou-Heffer et al. [23] have reported that alumino silicate compounds in the fly ashes may also be involved in the adsorption phenomena through a SiO bond with metallic ions.

According to the experimental results, Afsin-Elbistan fly ash with high soluble calcium oxide (CaO) content (Tables 2 and 3) is 5–10% more effective than Seyitomer fly ash at equilibrium conditions for the removal of three metals due to the formation of Ca and Si complexes such as calcium silicates $(2CaO·SiO_2)$. 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 idealized 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 represents the bivalent metal ions. $Me(OH)_2$ can not be deposited on the solid phase because as a result of reactions (3) and (4) it turns into less soluble $MeSiO_3$ [24].

3.3. Adsorption isotherm

The experimental equilibrium data for the adsorption of Ni(II), Cu(II) and Zn(II) by both fly ashes at $20 \pm 2\,°C$ using Ni(II) and Cu(II) concentrations of $25 \pm 2\,mg/l$ and Zn(II) concentration of $30 \pm 2\,mg/l$ in the pH range of 3.0–8.0 were correlated using the linear forms of the Langmuir and Freundlich equations [25–27]:

Langmuir equation:

$$\frac{C}{q_e} = \frac{1}{Q^0 b} + \frac{C}{Q^0} \tag{5}$$

Table 4
Langmuir equations for the adsorption of Ni(II), Cu(II) and Zn(II)

Metal	pH	Afsin-Elbistan fly ash		Seyitomer fly ash	
		Langmuir equation	Correlation coefficient	Langmuir equation	Correlation coefficient
Nickel	5.0	–	–	$C/q_e = 5.2367 + 16.1290C$	0.9260
	6.0	$C/q_e = 2.8895 + 2.0833C$	0.9580	$C/q_e = 2.5815 + 8.0645C$	0.9790
	7.0	$C/q_e = 0.5751 + 1.1099C$	0.9930	$C/q_e = 2.0145 + 2.8902C$	0.9730
	8.0	$C/q_e = 0.4842 + 1.0130C$	0.9960	$C/q_e = 0.4688 + 0.8619C$	0.9890
Copper	3.0	$C/q_e = 5.6670 + 2.9412C$	0.9890	$C/q_e = 25.6608 + 11.1111C$	0.9400
	4.0	$C/q_e = 0.3983 + 1.1611C$	0.9930	$C/q_e = 5.8849 + 2.6247C$	0.9970
	5.0	$C/q_e = 0.1117 + 0.9276C$	0.9986	$C/q_e = 1.9802 + 1.2970C$	0.9966
	6.0	$C/q_e = 0.0293 + 0.7401C$	0.9995	$C/q_e = 0.0646 + 0.07972C$	0.9993
Zinc	3.0	$C/q_e = 8.2146 + 3.9841C$	0.9820	$C/q_e = 40.1268 + 14.0845C$	0.9730
	4.0	$C/q_e = 3.2762 + 1.7953C$	0.9830	$C/q_e = 20.8747 + 6.9930C$	0.9750
	5.0	$C/q_e = 2.4286 + 1.2531C$	0.9870	$C/q_e = 18.6644 + 3.3223C$	0.9740
	6.0	$C/q_e = 0.5999 + 0.8375C$	0.9890	$C/q_e = 2.0718 + 2.8011C$	0.9730
	7.0	$C/q_e = 0.0720 + 0.6173C$	0.9980	$C/q_e = 0.1757 + 0.7687C$	0.9780

where C (mg/l) is the equilibrium concentration, q_e (mg/g) the amount adsorbed at equilibrium, and b (l/mg) the "affinity" parameter or the Langmuir constant, and Q^0 (mg/g) the "capacity" parameter. When C/q_e is plotted versus C, the slope is equal to $1/Q^0$ and the intercept is equal to $1/Q^0b$.

Freundlich equation:

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C) \tag{6}$$

where, C and q_e have the same definitions presented for the Langmuir isotherm. K_F and n are the constants that can be related to the adsorption capacity and the adsorption intensity, respectively. Values of K_F and n may be calculated by plotting $\log(q_e)$ versus $\log(C)$. The slope is equal to $1/n$ and the intercept is equal to $\log(K_F)$.

The adsorption data of Ni(II), Cu(II) and Zn(II) were found to fit well with the Langmuir equation (Table 4), while the Freundlich equation did not fit the adsorption data well. The latter fit had lower correlation coefficients with points showing scatter for both fly ashes. Detailed analysis of the variance also showed that the Langmuir model described the adsorption data better. The "t" test (for equations with relatively higher correlation) showed that the coefficient of X was significant for the 95% confidence level and hence X and Y were related (Table 5). The values of F in the analysis of variance (ANOVA) (for equations with the best correlation) were also significant at the 95% confidence level. The F values are very large especially at pH 8.0 for Ni(II), pH 6.0 for Cu(II) and pH 7.0 for Zn(II) 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 (modeling data). Hence, the linear model is well correlated. If F is approximately equal to 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 the dependent and independent variables.

Table 5
The *t*-test values for the adsorption of Ni(II), Cu(II) and Zn(II) on Afsin-Elbistan and Seyitomer fly ashes

Fly ash	pH	Calculated value			Table value[a]
		Ni(II)	Cu(II)	Zn(II)	
Afsin-Elbistan	3.0	–	13.368	16.135	2.776
	4.0	–	17.239	17.926	2.776
	5.0	–	37.475	12.340	2.776
	6.0	6.834	145.097	74.309	2.776
	7.0	17.022	–	109.455	2.776
	8.0	22.751	–	–	2.776
Seyitomer	3.0	–	5.529	10.797	2.776
	4.0	–	26.754	8.748	2.776
	5.0	4.893	24.254	9.401	2.776
	6.0	9.693	54.225	10.720	2.776
	7.0	8.466	–	11.046	2.776
	8.0	13.633	–	–	2.776

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

The smaller the *P* value, the greater the probability that there is an association. The values of the *P* in the analysis of variance were found to be smaller than 0.05 at all pH values for each metal for both the fly ashes. Traditionally, the independent variable can be used to predict the dependent variable when $P < 0.05$ [28].

The linear plots of C/q_e versus C at varying pH values suggest the applicability of the Langmuir isotherm for Ni(II), Cu(II) and Zn(II) adsorption by both the fly ashes, showing the formation of monolayer coverage of the adsorbate at the outer surface of adsorbent [29]. Figs. 8–13 present the typical plots of the Langmuir isotherm for Ni(II), Cu(II) and Zn(II)) adsorption by Afsin-Elbistan and Seyitomer fly ashes at the pH values for which the maximum adsorption was observed.

The values of Q^0 and b at varying pH values were determined from the slopes and intercepts of the respective plots. The data are found in Table 6. The Q^0 and b generally increased with solution pH, reflecting the increased ease of removal. Increasing values of the Langmuir constant, Q^0, with increasing solution pH also indicate that the adsorption capacity of the fly ashes increased with the increase in the solution pH for each metal (Ni(II), Cu(II) and Zn(II)). In addition to this result, the adsorption capacity of both fly ashes increased in the order Ni(II) < Cu(II) < Zn(II) according to the Q^0 values at the pH where the maximum removal was observed (pH 8.0 for Ni(II), pH 6.0 for Cu(II) and pH 7.0 for Zn(II)). On the other hand, this ranking, comparing the Q^0 values at a constant pH value, changed in the order Ni(II) < Zn(II) < Cu(II) for both the fly ashes. This classification could be explained with the first hydrolysis product of the metallic ions as well as the absolute hardness [24,30–32]. Furthermore, for all but pH 8.0 for Ni(II), Q^0 for Afsin-Elbistan fly ash is greater than that of Seyitomer fly ash, indicating the Afsin-Elbistan fly ash has a larger capacity for each metal adsorption than the Seyitomer fly ash.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which describes the
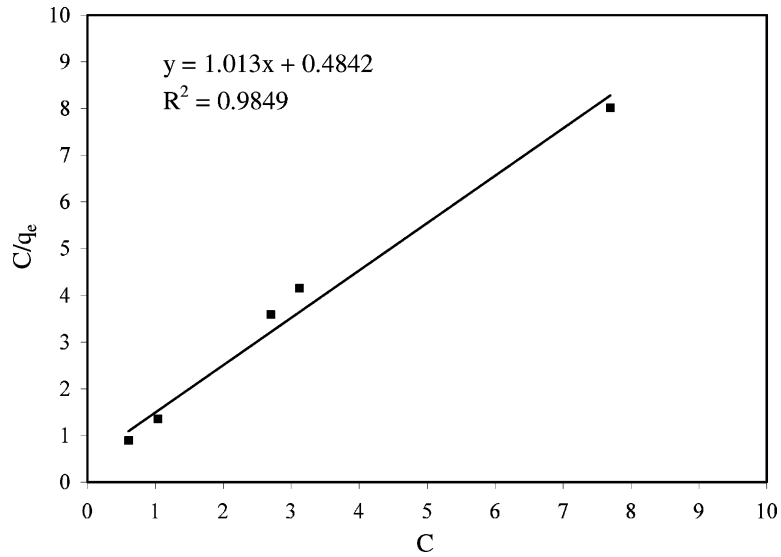
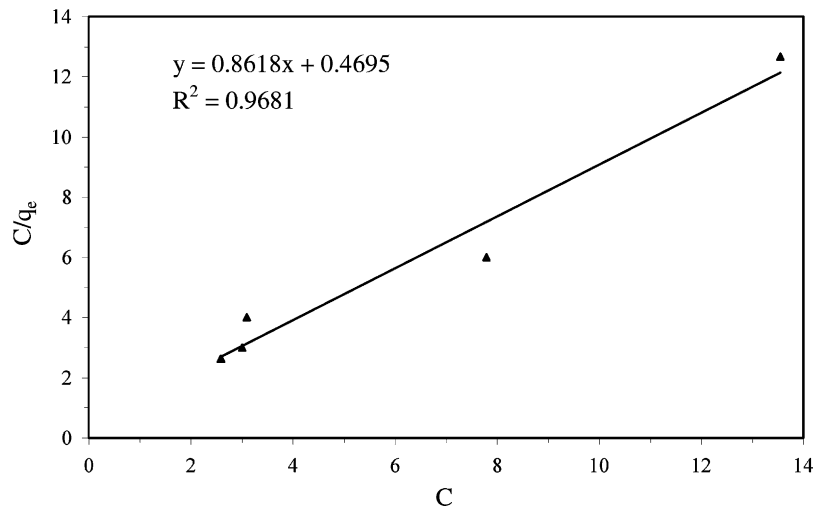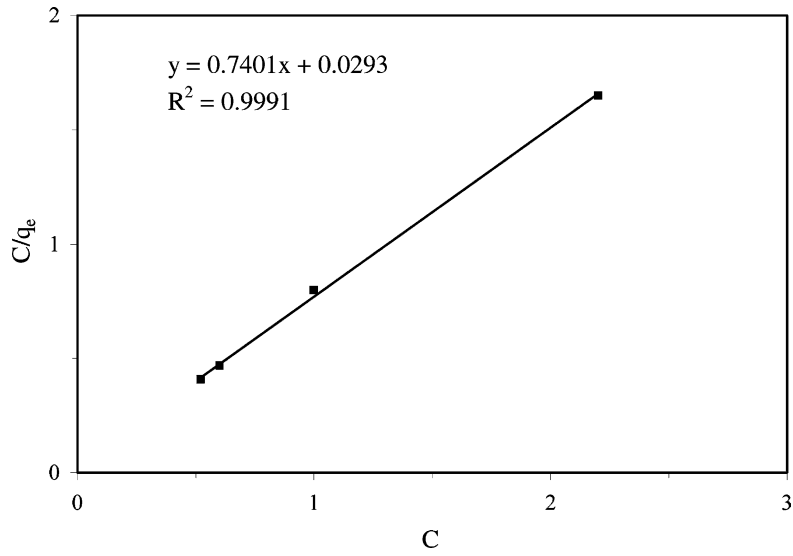Fig. 8. Langmuir isotherm for Ni(II) adsorption on Afsin-Elbistan fly ash at pH 8.0 and 20 ± 2 °C.

Fig. 9. Langmuir isotherm for Ni(II) adsorption on Seyitomer fly ash at pH 8.0 and 20 ± 2 °C.

type of isotherm [33] and is defined by,

$$R_{\mathrm{L}} = \frac{1}{1 + bC_0} \tag{7}$$

where, b (l/mg) is the Langmuir constant and C_0 (mg/l) the initial concentration of Ni(II), Cu(II) and Zn(II). R_{L} indicates the type of isotherm as follows:

Value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

$$y = 0.7401x + 0.0293$$
$$R^2 = 0.9991$$

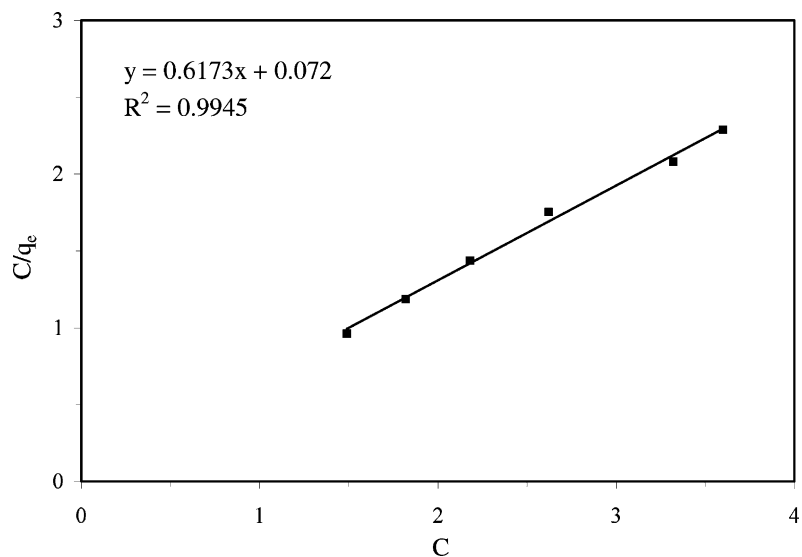Fig. 10. Langmuir isotherm for Cu(II) adsorption on Afsin-Elbistan fly ash at pH 6.0 and $20 \pm 2\,^\circ$C.

$$y = 0.7972x + 0.0646$$
$$R^2 = 0.9987$$
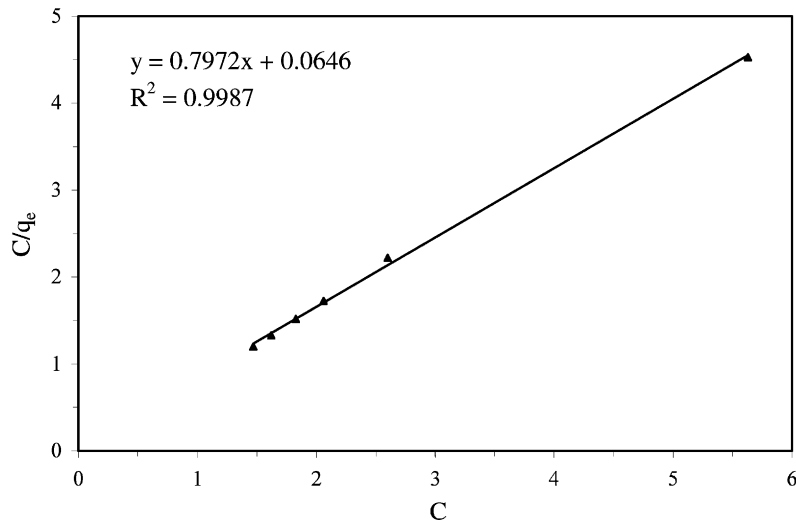
Fig. 11. Langmuir isotherm for Cu(II) adsorption on Seyitomer fly ash at pH 6.0 and $20 \pm 2\,^\circ$C.

Fig. 12. Langmuir isotherm for Zn(II) adsorption on Afsin-Elbistan fly ash at pH 7.0 and $20 \pm 2\,^{\circ}\text{C}$.
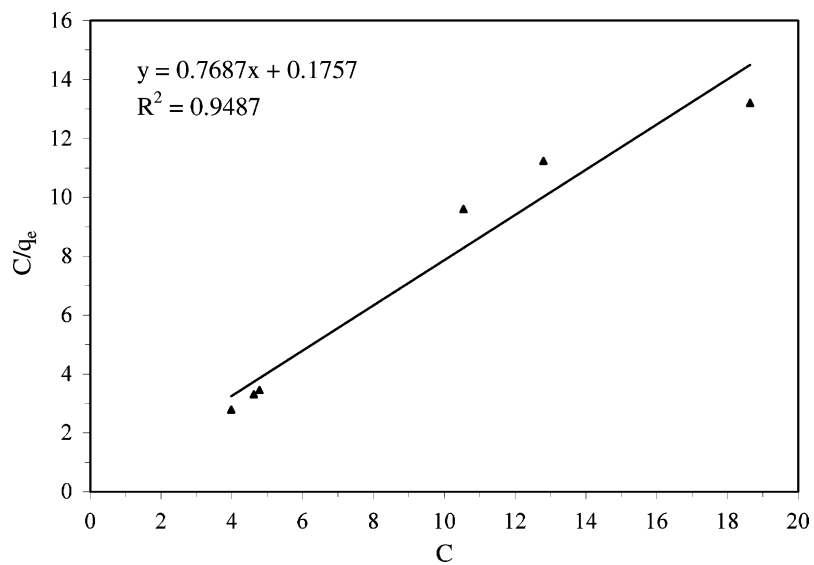

Fig. 13. Langmuir isotherm for Zn(II) adsorption on Seyitomer fly ash at pH 7.0 and $20 \pm 2\,^{\circ}\text{C}$.

Table 6
Langmuir constants (b and Q^0) at different pH for Ni(II), Cu(II) and Zn(II)

Fly ash	pH	Ni(II)		Cu(II)		Zn(II)	
		b (l/mg)	Q^0 (mg/g)	b (l/mg)	Q^0 (mg/g)	b (l/mg)	Q^0 (mg/g)
Afsin-Elbistan	3.0	–	–	0.519	0.344	0.485	0.251
	4.0	–	–	2.913	0.862	0.548	0.557
	5.0	–	–	8.305	1.078	0.516	0.798
	6.0	0.721	0.480	25.260	1.351	1.396	1.194
	7.0	1.930	0.901	–	–	8.574	1.162
	8.0	2.092	0.987	–	–	–	–
Seyitomer	3.0	–	–	0.433	0.090	0.351	0.071
	4.0	–	–	0.446	0.381	0.335	0.143
	5.0	3.080	0.062	0.655	0.771	0.178	0.301
	6.0	3.124	0.124	12.340	1.254	1.352	0.357
	7.0	1.435	0.346	–	–	4.375	1.301
	8.0	1.839	1.160	–	–	–	–

The values of R_L obtained in this study were found to lie between 0 and 1, indicating favorable adsorption (Table 7).

3.4. Initial metal concentration

The removal of Ni(II) and Zn(II) increased with an increase of the metal ion concentration in the solution while the removal of Cu(II) decreased slightly for each fly ash. With the increase of the initial concentration of Ni(II), Cu(II) and Zn(II) from 0.45 ± 0.03 to 25 ± 2, 0.35 ± 0.03 to 25 ± 2 and 0.50 ± 0.05 to 30 ± 2 mg/l, respectively, the percentage removal increased from 14.29 to 97.65 for Ni(II) and 55.56 to 94.39 for Zn(II), while it decreased from 100.00 to 98.00 for Cu(II) when Afsin-Elbistan fly ash was used under equilibrium conditions. In the case of Seyitomer fly ash, the removal of Ni(II) and Zn(II) increased from

Table 7
Equilibrium parameter, R_L

Fly ash	pH	Ni(II)	Cu(II)	Zn(II)
Afsin-Elbistan	3.0	–	0.0690	0.0597
	4.0	–	0.0130	0.0532
	5.0	–	0.0046	0.0560
	6.0	0.051	0.0015	0.0220
	7.0	0.020	–	0.0036
	8.0	0.018	–	–
Seyitomer	3.0	–	0.0816	0.0810
	4.0	–	0.0794	0.0840
	5.0	0.0123	0.0555	0.1480
	6.0	0.0122	0.0031	0.0220
	7.0	0.0261	–	0.0070
	8.0	0.0205	–	–

78.57 to 90.04 and 80.00 to 85.29%, respectively, by increasing the initial concentration
from 0.45 ± 0.03 to 25 ± 2 mg/l for Ni(II) and from 0.50 ± 0.05 to 30 ± 2 mg/l for
Zn(II), whereas, the removal of Cu(II) decreased from 100.00 to 93.77% when the ini-
tial concentration of Cu(II) increased from 0.35 ± 0.03 to 25 ± 2 mg/l under equili-
brium conditions. These results are similar to the results obtained by Panday et al. [6]
and Viraraghavan and Dronamraju [8].

Although the two fly ashes behave similarly for the changing metal concentrations,
Afsin-Elbistan fly ash is the better adsorbent at higher soluble Ni(II), Cu(II) and Zn(II)
concentrations as a result of its higher soluble lime content (Tables 2 and 3) and larger spe-
cific surface area (Table 1). It is also known from the experimental data that in the solutions
of higher initial Ni(II), Cu(II) and Zn(II) ions concentrations the removal efficiencies of
both fly ashes are sufficient for permissible levels in mixed industrial effluent discharge for
Ni(II) and Cu(II) (3 mg/l), and for Zn(II) (5 mg/l) in Turkey [34].

3.5. Desorption studies

Desorption studies were conducted by mixing approximately 10 g of fly ash with metal-
laden filtrate from the solution which was obtained at the end of the adsorption experiments
conducted at the constant concentrations of Ni(II) (25 ± 2 mg/l), Cu(II) (25 ± 2 mg/l) and
Zn(II) (30 ± 2 mg/l) at pH values corresponding to the maximum removal deionized water
(500 ml) for 4 h at 100 rpm and $20 \pm 2\,^{\circ}$C in the range of pH values 3.0.0–8.0 (Fig. 1). The
dissolution of Ni(II), Cu(II) and Zn(II) which were previously deposited on fly ash, back
into the deionized water was observed only in acidic pH values during the 4 h study period
and was generally rather low (<3 mg/l for Ni(II) and Zn(II) and 2 mg/l for Cu(II)) for both
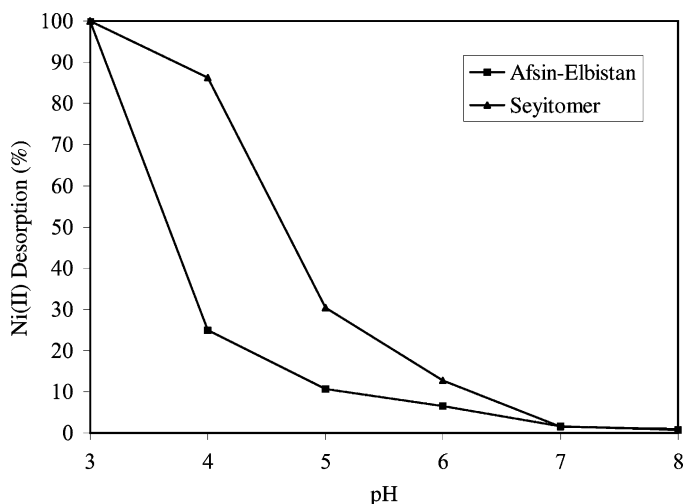the fly ashes (Figs. 14–16).

Fig. 14. Removal of Ni(II) from fly ashes; influence of pH; Ni(II) initially deposited on Afsin-Elbistan and
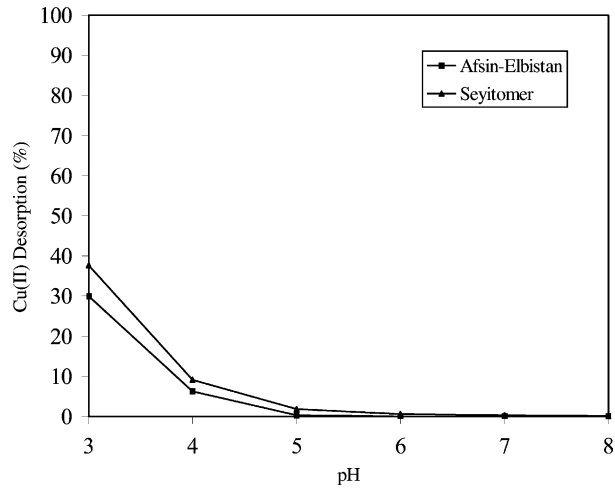Seyitomer fly ashes 2.15 and 2.51 mg/g, respectively.
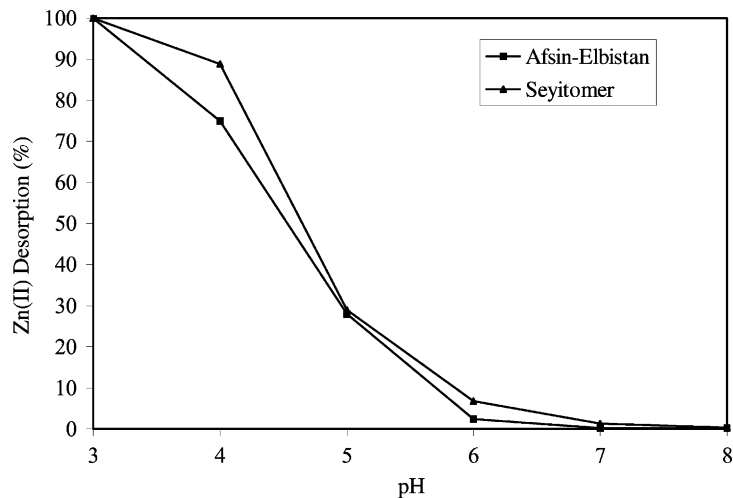
Fig. 15. Removal of Cu(II) from fly ashes; influence of pH; Cu(II) initially deposited on Afsin-Elbistan and Seyitomer fly ashes 2.17 and 2.75 mg/g, respectively.

3.6. Comparative studies

The type of fly ash investigated was also compared with adsorption on charcoal activated carbon according to responses to Ni(II), Cu(II) and Zn(II) percentage removal values obtained in the pH range of 3.0–8.0 (Figs. 17–19). These results showed that the removals of Cu(II) and Zn(II) are in the order: activated carbon > Afsin-Elbistan fly ash > Seyitomer

Fig. 16. Removal of Zn(II) from fly ashes; influence of pH; Zn(II) initially deposited on Afsin-Elbistan and Seyitomer fly ashes 0.90 and 3.13 mg/g, respectively.
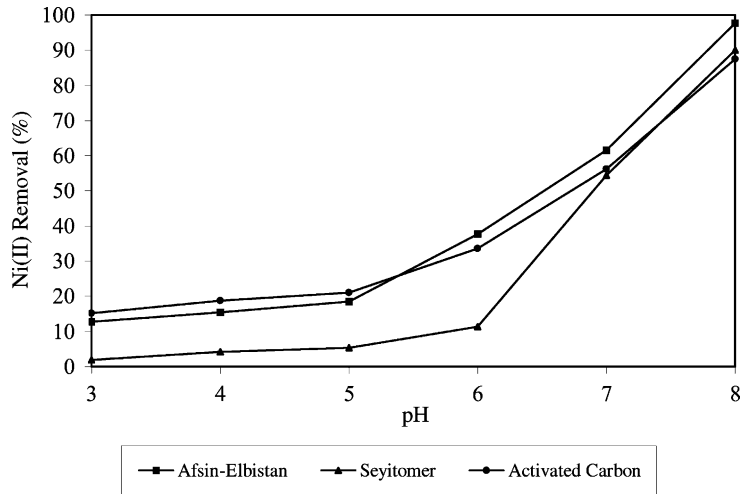
Fig. 17. Effectiveness of an activated carbon compared to Afsin-Elbistan and Seyitomer fly ashes on the removal of Ni(II).

fly ash (Figs. 18 and 19) and the equilibrium period is minimum (1.5 h) for activated carbon at higher pH (pH 6.0 for Cu(II) and pH 7.0 for Zn(II)) (Table 8). However, Afsin-Elbistan fly ash (high lime content) is the most efficient for the removal of Ni(II) at pH 8.0 at which maximum removal was observed and also Seyitomer fly ash is slightly more efficient than activated carbon (Fig. 17).
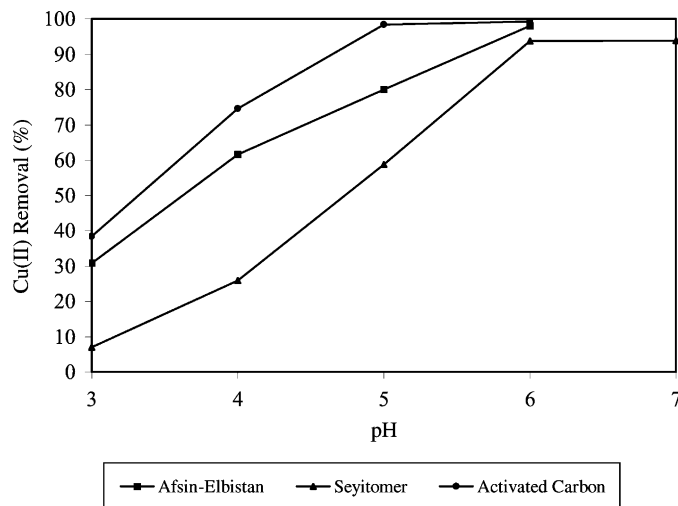

Fig. 18. Effectiveness of an activated carbon compared to Afsin-Elbistan and Seyitomer fly ashes on the removal of Cu(II).
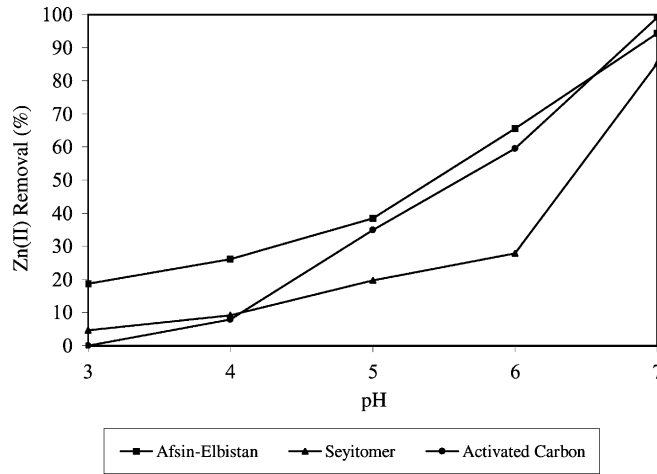
Fig. 19. Effectiveness of an activated carbon-compared to Afsin-Elbistan and Seyitomer fly ashes on the removal of Zn(II).

According to previous work [35], the adsorption capacities of the fly ashes are less than that of activated carbon. However, fly ash is definitely less expensive than activated carbon. Fly ash can be obtained cheaply in large quantities in Turkey. Fly ash can also be utilized as a fill material in roads and construction sites, in cement and concrete industries [10], in soil stabilizations. Most of the Turkish soils are calcareous and alkaline except for Black Sea coast [16]. Thus, any use or disposal of the "spent" fly ash for a soil stabilization process may not add metals to the soil. It can be disposed off in a landfill especially in old mining sites.

Table 8
Comparative study of the adsorptive properties of activated carbon, Afsin-Elbistan and Seyitomer fly ashes for Ni(II), Cu(II) and Zn(II)

Adsorbent	Equilibrium period (h)	Percentage removal		
		Ni(II)	Cu(II)	Zn(II)
Activated carbon	1.5	79.89	98.46	97.14
	2.0	87.50	99.23	99.09
	3.0	85.58	99.23	98.92
Afsin-Elbistan fly ash	1.5	89.62	97.69	91.94
	2.0	97.65	98.00	94.39
	3.0	96.00	98.00	93.29
Seyitomer fly ash	1.5	88.08	92.08	60.62
	2.0	90.04	93.77	85.29
	3.0	88.46	94.35	85.79

4. Conclusion

Afsin-Elbistan fly ash with a high CaO content was shown to be effective for Ni(II), Cu(II) and Zn(II) removal from aqueous solutions. The adsorption in these systems is highly dependent on pH, initial metal concentration and fly ash origin. The effects observed were: increase in metal removal with increasing solution pH (up to pH 6.0 for Cu(II), pH 7 for Zn(II) and pH 8.0 for Ni(II)), initial metal concentration (except for Cu(II)) and the CaO content of fly ash. The Langmuir isotherm successfully represented the adsorption phenomenon at a specific pH value. Hence, the Langmuir equation can be used to determine the amount of fly ash required for the removal of Ni(II), Cu(II) and Zn(II) from the wastewater. The results obtained may be useful for metal plating industry wastewaters containing these metals since fly ash is definitely inexpensive compared to activated carbon. No regeneration of the adsorbent such as fly ash is economically advantageous. Fly ash after use as an adsorbent can be employed as a filling material in roads and construction sites, in cement and concrete industries, in soil stabilization without any subsequent danger of aquifer contamination, or can be disposed off in a landfill.

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