Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2012.3043

44 (2012) 180–189
June

Experimental study on the nickel (II) removal from aqueous solutions using silica fume with/without apocarbonic anhydrase

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Received 7 June 2011; Accepted 13 November 2011

ABSTRACT

The silica fume is a fine-grain, thin and very high surface area silica. Although the silica fume is a waste material of industrial applications, it has become the most valuable by-product among the pozzolanic materials due to its very active and high pozzolanic property. In this study, the potential use of silica fume in the remediation of polluted heavy metal water to remove nickel ions is presented. For studying metal adsorption, 1 g of silica fume has been taken as adsorbent and then it has been suspended in 50 ml of 3 mmol dm^{-3} $NiCl_2$, at pH between 3 and 9 and contacted batchwise in a thermostatic (t = 25°C ± 0.1°C) water-bath agitator for 1 h to enable equilibration of the sorbent and solution phases. The nickel concentrations in the samples taken from the silica fume treated aqueous solutions of polluted river water with/without apocarbonic anhydrase (apoCA) and $NiCl_2$ solution have been determined by spectrophotometric method using dithizone. The nickel concentration in the samples of silica fume treated leachates solutions decreased. It was determined that the adsorption of nickel ions increased with the addition of apoCA as compared with those of without apoCA. The experimental investigation results show that activated silica fume has a high level of adsorption capacity for nickel ion. Consequently, it is concluded that the silica fume can be successfully used for the removal of the nickel ions from the aqueous solutions with heavy metals.

Keywords: Waste water; Silica fume; Apocarbonic anhydrase; Aqueous solution; Nickel removal; Adsorption isotherms

1. Introduction

It is known that widespread contamination of aqueous environment by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain. Rapid industrialization has lead to an increased disposal of heavy metals into the environment. The presence of these heavy metals in the environment is of importance concern due to their toxicity and health effects on the human and living creatures [1–4]. Heavy metals and dyes are found in the wastewater streams of industrial processes, including textiles, paper, paint manufacture, leather tanning, battery manufacture, dyeing, and others. Their removal has attracted much practical and academic interest owing to increased concern with their environmental impact. The world industry comes across the ever-increasing need for decreasing of heavy metal ions contents in waters as well as industrial waste to the admissible level. For the past several years, high levels of heavy metals in drinking

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water and foods have been associated with several acute and chronic illnesses in humans throughout the world [4–8].

Nickel is one of toxic heavy metals which are common pollutants of the environment. It is an important metal in many industries such as electroplating, nickel-based alloys and nickel-cadmium battery manufacture. In the blood circulation, nickel is transported bound to albumin and then distributed to the kidney and further into other tissues [9]. It holds a special place among the heavy metals and its compounds are well-known carcinogens to humans. Several types of cellular damage have been identified that may contribute to their carcinogenic potentials, such as the induction of oxidative DNA damage and epigenetic alterations such as gene silencing by changes in DNA methylation patterns, as shown for particulate nickel compounds [10]. The higher concentration of nickel in ingested water may cause severe damage to stomach, intestine, lung, kidney, nervous system and constitute nausea, vomiting, diarrhea, pulmonary fibrosis, renal edema, skin dermatitis, allergic sensitization [11–16].

A survey of recent patents for water and wastewater treatments showed that significant amount of patents related to sorption technologies still include only carbon based materials [17–22] which are relatively expensive, act in a non-selective manner and exhibit unsatisfactory efficiency in the removal of inorganic contaminants. Although the adsorption technique is versatile and is easy to adopt in practical forms, the adsorbent materials are either costly or cannot be regenerated for large-scale applications. Hence research of the recent past mainly focused on utilizing low cost waste materials as alternatives to activated carbon for large scale waste water treatment [20–23]. For that reason, there is an increasing trend in searching for new heavy metal sorbents among commercially available materials such as by-products of various industries. Recent comparison of composite sorbents which are accessible, inexpensive and effective for treating a variety of contaminants have emphasized the outstanding metal removal capabilities of materials originating from agricultural and industrial by-products [15,24–32]. One of the most promising sorbent was found to be silica fume, a by-product of silicon material or silicon alloy metal factories. Although the silica fume is a waste material of industrial applications, it has become the most valuable by-product among the pozzolanic materials due to its very active and high pozzolanic property. Currently, it is widely used in concrete or mortar as an admixture [33]. The investigations show that silica fume can be successfully used in the geotechnical applications to improve the compacted clayey soils [34–37].

A number of methods are available for the removal of metal ions from aqueous solutions. These are ion exchange, solvent extraction, reverse osmosis, electrodialysis, precipitation, flocculation and membrane separation processes [15,38–41]. However, these techniques have certain disadvantages, such as high capital and operational costs or the treatment and disposal of the residual metal sludge. Adsorption compared with other methods appears to be an attractive process due to its efficiency and the ease with which it can be applied in the treatment of heavy metal containing wastewater. In recent years, a number of adsorptive materials were used in heavy metal removal from wastewaters [1,2,15,23–31,42–44].

The carbonic anhydrase (CA), which catalyses the reversible hydration of carbon dioxide (CO_2), was one of the first proteins for which a crystal structure was obtained [45–47]. CA is categorized into three main classes: α, β and γ, which share no significant similarity in primary sequence or overall structure [48], but which all, rely on Zn for activity. Whereas α- and γ-CA use three histidine residues to coordinate the Zn atom, β-CA uses two cysteine residue and one histidine residue [49–51].

When the zinc covalently bound to active site is removed, the apocarbonic anhydrase (apoCA) obtained, resulting in the deactivated enzyme [52]. The apoCA can connect metal ions to its structure in the media. It is thought that apoCA both can connect Ni^{2+} to its active center and facilitate connection of Ni^{2+} to the silica fume surface [53].

In the current research, we studied the adsorption capacities of the silica fume waste material for the removal of nickel ions from wastewater with apoCA and without apoCA. We wanted to determine whether this material might be cost-effective and be an alternative adsorbent that could replace the expensive resins now used for wastewater treatment. The nickel ions were absorbed by silica fume from polluted river water and $NiCl_2$ solution and the results were shown on the adsorption behavior of nickel heavy metal in silica fume with apoCA and without apoCA.

2. Materials and methods

2.1. Silica fume

Silica fume, also known as micro silica, is a byproduct of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. It is also collected as a by-product in the production of other silicon alloys such as ferrochromium, ferromanganese, ferromagnesium and calcium silicon. Silica fume has been obtained from Ferro-Chromate Factory in Antalya [31].

The silica fume was thoroughly washed with distilled water until it became neutral. The suspension was wet sieved through a 200 mesh screen. A little amount of the suspension remained on the sieve and was discarded. The solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last suspension was filtered, and the residual solid was then dried at 105°C, ground in a mortar, and sieved through a 200 mesh sieve. The product was used in the study. Its chemical and index properties are summarized in Tables 1 and 2, respectively.

2.2. Preparation of apoCA from human erythrocytes

The apoCA was purified by a Sepharose-4B-L tyrosine sulphailamide affinitiy chromatography from human erythrocytes [54]. For obtaining apo enzymes, CA was dialyzed against 0.075 M dipicolinic acid. By using this method almost 100% pure apoenzyme was obtained. 5 ml of the apoenzyme reagent can be prepared by using 100 mg of apoCA [52]. ApoCA was concentrated by using membrane filter and this concentrated enzyme was used at dose of 5 mg apoCA g^{-1} silica ume.

Table 1
Chemical compositions of silica fume used in the study

Property	Silica fume
Compound	
SiO_2, %	85–95
Al_2O_3, %	1–3
Fe_2O_3	0.5–1.0
CaO, %	0.8–1.2
MgO, %	1–2
TiO_2, %	–
Heat loss, %	0.5–1

Table 2
Engineering properties of silica fume used in the study

Property	Silica fume
Density	
Density, (mg m^{-3})	2–2.5
Grain size	
Gravel (>2000 μm), %	–
Sand (2000–75 μm), %	–
Silt, (2–75 μm), %	20
Clay (<2 μm), %	80
Specific surface area	
Specific surface area, m^2 g^{-1}	20.12

2.3. Analysis methods

2.3.1. Preparation o calibration curve

For single Ni determination, 1 ml of sample solution containing preferably 8.0×10^{-5}–8.0×10^{-4} mmol (4.7–47 μg) Ni was taken; 1 ml of 1.6×10^{-2} M Dz (20-fold of maximum amount of Ni) followed by 1 ml of distilled water and 1 ml of concentrated NH_3 solution were added to yield a final volume of 4 ml.

2.3.2. Adsorption of nickel ion on silica fume

For studying metal adsorption, 1 g of silica fume as adsorbent was taken and it was then suspended in 50 ml of 3 mM $NiCl_2$, at pH between 2 and 9 and contacted batchwise in a thermostatic (t = 30°C ± 0.1°C) water-bath agitator for 1 h to enable equilibration of the sorbent and solution phases with/without apoCA. At each pH, it was waited on for a term of 1 h. The suspension was centrifuged at 3000 rpm for 10 min, and the supernatant was filtered through a 0.45 μm pore, cellulosic membrane filter to make possible the measurement of the heavy metal concentration in the filtrate. After centrifuging, the amount of decreasing nickel at the top level of liquid solution was measured. The nickel ion concentration was determined by spectrophotometric method using dithizone [32,55]. The amount of nickel ions adsorbed was calculated as:

$$q_e = \frac{(C_0 + C_e)V}{m} \qquad (1)$$

where q_e (mg g^{-1}) is the amount of adsorbed nickel ions, C_0 (mg l^{-1}) is the initial concentration of nickel, C_e (mg l^{-1}) is the concentrations of nickel at equilibrium, V (l) is the volume of solution, and m (g) is the weight of silica fume adsorbent.

2.4. Equilibrium studies

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of an adsorption system. In an adsorption isotherm study, several equilibrium models have been developed to describe adsorption isotherm relationships. The Langmuir and Freundlich equations are the world-widely used models because of their simplicity [4]. Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of an adsorbent and it is given as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

where q_e (mg g^{-1}) is the adsorption amount of adsorbent at equilibrium, q_m (mg g^{-1}) is the maximum adsorption amount of metal ions, C_e (mg l^{-1}) is the equilibrium concentration of adsorbate in solution and K_L (l mg^{-1}) is the equilibrium adsorption constant which is related to the affinity of the binding sites. The Langmuir constants K_L and q_m are calculated with the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

where C_e (mg l^{-1}) is the equilibrium concentration of adsorbate in solution, q_e (mg g^{-1}) is the adsorption amount of adsorbent at equilibrium, q_m (mg g^{-1}) is the maximum adsorption amount of metal ions and K_L (l mg^{-1}) is the equilibrium adsorption constant which is related to the affinity of the binding sites. The Freundlich isotherm is based on the assumption that adsorption is on a heterogeneous surface and exponential distribution of sites and their energies [4], which can be expressed by the following equation:

$$q_m = K_F C_e{}^{1/n} \tag{4}$$

where q_m (mg g^{-1}) is the maximum adsorption amount of metal ions, C_e (mg l^{-1}) is the equilibrium concentration of adsorbate in solution. K_F (mg g^{-1}) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption, respectively. They can be calculated in the following linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where q_e (mg g^{-1}) is the adsorption amount of adsorbent at equilibrium, C_e (mg l^{-1}) is the equilibrium concentration of adsorbate in solution, K_F (mg g^{-1}) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption. The Langmuir and Freundlich isotherms were obtained from the experiments.

3. Results and discussion

3.1. Image analysis

The scanning electron microscope (SEM) was used to examine the surface of the adsorbent. Images of native adsorbent and metal loaded adsorbent were magnified 5000 times by SEM. The SEM photographs show progressive changes in the surface of the particles. Fig. 1(a) illustrates the SEM of native adsorbent that is considered helpful for the accessibility of nickel to the adsorbent surface. The SEM of exhausted adsorbent clearly indicates the presence of new shiny bulky particles and layer over the surface of metal loaded adsorbent which are absent from the native adsorbent before metal loading (Fig. 1(b)).

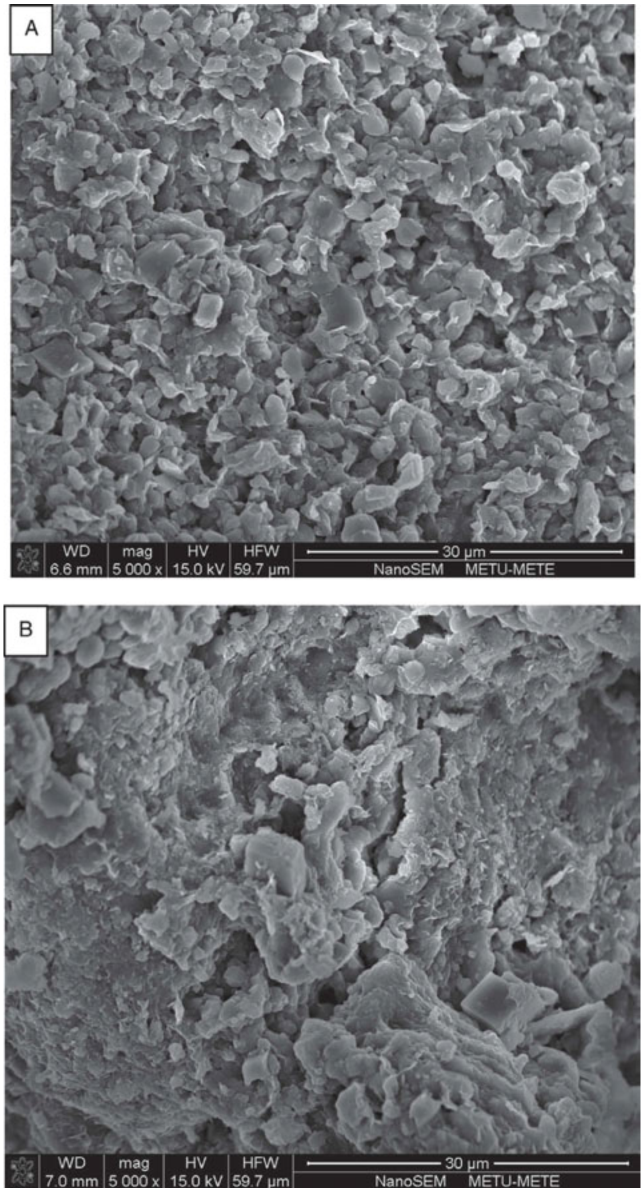

Fig. 1. SEM photographs of native adsorbent (a) and nickel loaded adsorbent (b).

3.2. Calibration curve

Calibration is fundamental for achieving consistency of measurement. Often calibration involves establishing the relationship between an instrument response and one or more reference values. Linear regression is one of the most frequently used analyses in calibration. Once the relationship between the input value and the response value assumed to be represented by a straight

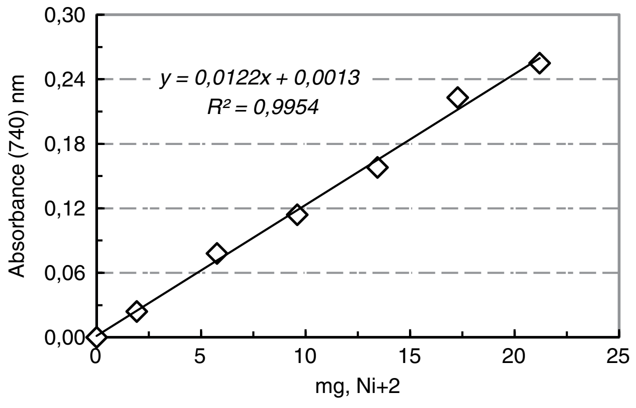

Fig. 2. Calibration curve of nickel adsorption.

line is established, the calibration curve is used in the evaluation of accuracy of the result. From the calibration curve, it was observed that there is an approximate linear relationship between absorbance and nickel concentration in the aqueous solutions (Fig. 2). It is observed that the regression coefficient (R^2) is quite high, and its value is 0.9954.

3.3. Effect of contact time

Fig. 3 shows the effect of contact time on the adsorption process. It can be observed that the removal of nickel increases with time in the first 15 min with apoCA and without apoCA. Basically, the removal of nickel is rapid at this time but it gradually decreases with time until it reaches equilibrium. This indicates that the concentration of nickel in the solution decreased rapidly within 15 min and the removal was virtually completed within 60 and 90 min with apoCA and without apoCA, respectively. From Fig. 3, the plot reveals that the amount of nickel removal is higher at the beginning. This is probably due to larger surface area of the silica fume being available at beginning for the adsorption of nickel ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [56]. Special emphasis is paid to the selective adsorption of apoCA on tailor-made strongly hydrophobic support surfaces. This adsorption procedure is based on the assumption that the large hydrophobic area that surrounds the active site of apoCA is the one mainly involved in their adsorption on strongly hydrophobic silica fume solid surface. The rapid removal of the adsorbate has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy [57].

3.4. Effect of pH

The pH of the solution is an important factor in the adsorption process in terms of affects surface charge of the adsorbent, the degree of ionization and specification of adsorbate [58]. In order to establish the effect of pH on the adsorption of nickel ions, the batch equilibrium studies at different pH values have been carried out in the range of 3–9. The effect of initial pH on the adsorption process is presented in Fig. 4. It is shown that the absorption amount of nickel increase with increasing pH and maximum adsorption of nickel ions are obtained at pH 5 which is the initial pH of the solution with and without apoCA. This is due to the surface complexation reactions, which are mostly influenced by the electrostatic force of attraction between nickel and the surface of the adsorbent. The acidity of the medium can affect the metal ions' uptake amount of the silica fume adsorbent because hydrogen ions in the solution could compete with nickel for active sites on the adsorbents surface [4,8,59].

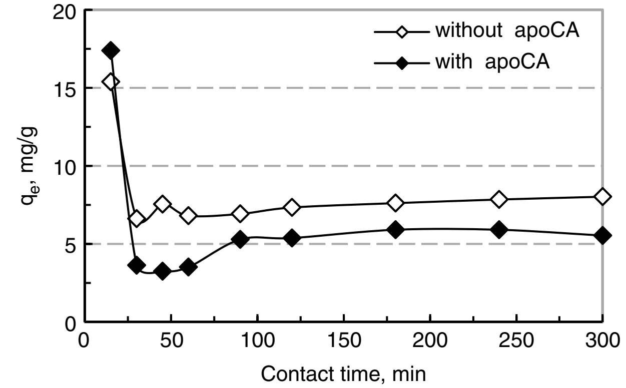

Fig. 3. Removal of nickel as a function of equilibrium time (pH: 5.0, initial nickel concentration: 3 mmol dm^{-3}, silica fume dose: 1g (50 ml)$^{-1}$, agitation speed: 500 rpm and temperature: 25 ± 1°C).

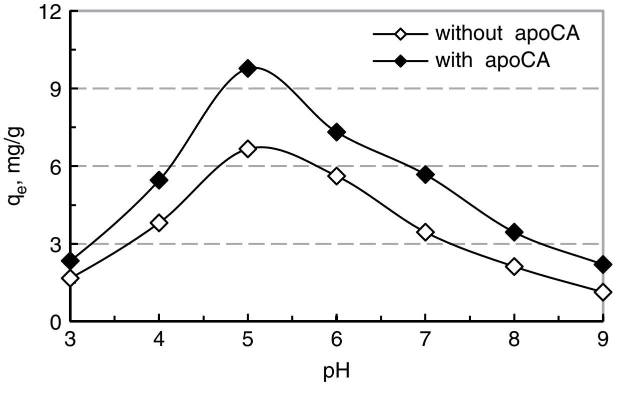

Fig. 4. Effect of nickel as a function of pH (initial nickel concentration: 3 mmol dm^{-3}, silica fume dose: 1 g (50 ml)$^{-1}$, agitation speed: 500 rpm and temperature: 25 ± 1°C).

Silica fume is a metal oxide adsorbent containing different metal oxides in the structure. Hydroxylated surfaces of these oxides developed charge on the surface of the water. It can be due to the interaction between nickel ion and metal oxide. The removal of nickel pollutant from aqueous solution by adsorption is highly dependent on pH of the media which affects the surface charge of the solid particles and degree of ionization and speciation of adsorbate [60]. It is thought that apoCA provides the keeping of more nickel ions both by connecting nickel to its active center and by creating a bridge between nickel ions and silica fume surface [52].

3.5. Effect of temperature

The temperature has a pronounced effect on the adsorption capacity of the adsorbent. The effect of temperature influencing the adsorption has been studied in the range of 20–80°C. The effect of temperature on the adsorption capacity of silica fume is shown in Fig. 5. It is observed that the degree of adsorption increases with increasing temperature and maximum adsorption of nickel ions are obtained at 25°C which is the temperature of the solution with apoCA and without apoCA. An increase in temperature involves an increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions. These result in the enhancement in the sorptive capacity of the adsorbent [61]. The temperature dependence of the adsorption process is associated with changes in several thermodynamic parameters [62].

3.6. Effect of adsorbent dosage

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent has been studied on nickel removal and the results have been illustrated in Fig. 6. When the adsorbent dosage is higher, there is a very fast adsorption onto the adsorbent surface, which results in a lower adsorbate concentration in the solution. However, the adsorption sites on the adsorbent surface remain unsaturated when the adsorbate concentration in the solution drops to a lower value. Thus, the amount of nickel adsorbed onto per unit weight of adsorbent gets reduced with the adsorbent dosage increasing with apoCA and without apoCA [4,63–65].

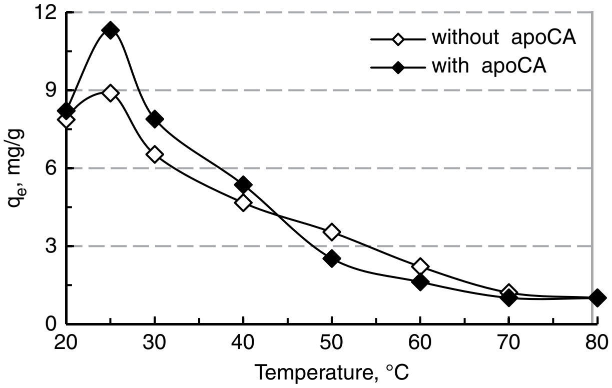

Fig. 5. Effect of nickel as a function of temperature (pH: 5.0, initial nickel concentration: 3 mmol dm^{-3}, silica fume dose: 1 g (50 ml)$^{-1}$, agitation speed: 500 rpm, contact time 60 min).

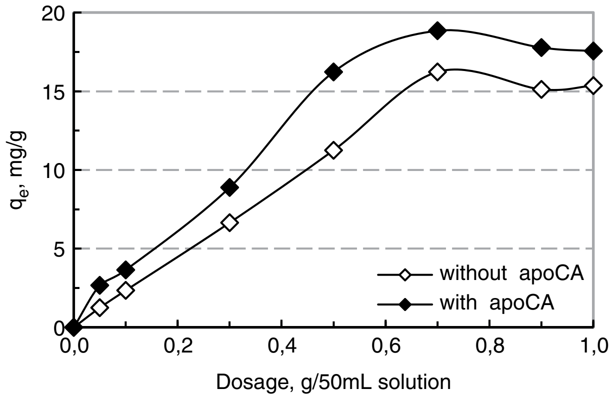

Fig. 6. Effect of silica fume dosage on adsorption of nickel (pH: 5.0, initial nickel concentration: 3 mmol dm^{-3}, agitation speed: 500 rpm, contact time 60 min).

The polluted river water solution was also treated using activated silica fume solution containing an adsorbent dosage of 1 g (50 ml)$^{-1}$ with apoCA and without apoCA. The nickel concentration in the aqueous solution taken from samples of polluted river water solution treated with silica fume indicated that silica fume enhanced adsorption capacity. Without the addition of the silica fume, the leachate nickel concentration was approximately 1.396 and 3.184 mg ml^{-1} for polluted river water and $NiCl_2$ solutions, respectively. The addition of silica fume strongly inhibited the leaching of nickel in both solutions. When the silica fume was added to the aqueous solutions contaminated with nickel, the concentration of nickel in the leachate drastically reduced without apoCA and with apoCA, whereas the adsorption capacity increased. The nickel concentration in the samples of silica fume treated leachates solutions decreased from 1.262 to 0.436 and 0.260 and from 11.742 to 4.115 and 2.436 without apoCA and with apoCA for the polluted river water and $NiCl_2$ solutions, respectively. In each sample of silica fume treated aqueous solution with apoCA and without apoCA, it was observed that the adsorption in the nickel ions was obtained using silica fume. The nickel concentration in the silica fume treated aqueous solutions was decreased using silica fume as shown in the Fig. 7.

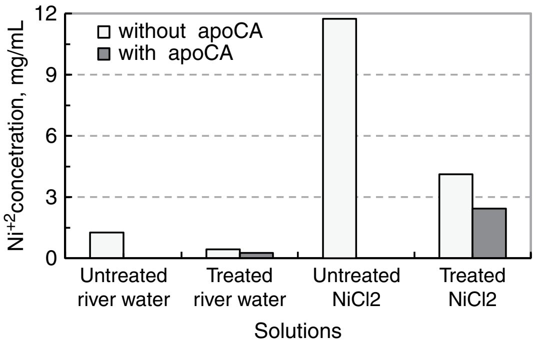

Fig. 7. Variation of nickel concentration after silica fume treating with river water and $NiCl_2$.

The increase in the adsorption capacity of silica fume treated aqueous solutions was attributed to the pH values and active components of silica fume with apoCA and without apoCA. The samples of polluted river water treated with silica fume with apoCA and without apoCA reached their minimum point values in the nickel concentration. Because of its fine particles, large surface area, and the high SiO_2 content, silica fume is a very reactive pozzolan. The nickel ions might absorb on silica fume because of its high content of silica and large surface area.

The silica fume particles have adsorbed nickel ions with apoCA more than witout apoCA. This can be explaned apoCA is acted as an excellent chelating agent. A chelate is a complex resulting from the combination of a metal ion and a multidentate ligand such that the ligand forms two or more bonds with the metal, resulting in a ring structure that includes the metal ion. apoCA itself possesses the coordinating functions of three carboxylic and one hydroxyl group due to protein structure. All these groups are known to participate in the binding of metal ions. apoCA as an anhydride will react with the hydroxyl functional groups of corn starch or fiber (as well as the nucleophilic NH_2, SH, and OH groups of protein to generate ester or amide derivatives). This derivatization of apoCA with biobased materials results in a water insoluble chelate with carboxylic acid and hydroxyl group [31,65–68].

3.7. Adsorption isotherms

The adsorption data obtained for equilibrium conditions have been analyzed by using the linear forms of the Freundlich and Langmuir isotherms. Langmuir and Freundlich models are the simplest and most commonly used isotherms to represent the adsorption of components from a liquid phase onto a solid phase. The graphical comparison of the experimental value with the calculated value from the Freundlich and Langmuir isotherms for nickel adsorption by silica fume adsorbent with apoCA and without apoCA are shown in Fig. 8. It is obvious that the adsorption capacities calculated from the Langmuir isotherms are much closer to the experimental values of adsorption capacity than that of Freundlich isotherms. The constants of Freundlich and Langmuir isotherms and correlation coefficients calculated from the adsorption data are given in Table 3. The high correlation coefficients showed that both models are suitable for describing the adsorption equilibrium of nickel ions. The adsorption capacity of silica fume for the uptakes of nickel is 9.5168 and 8.6893 mg g^{-1} with apoCA and without apoCA, respectively [4,58,65,68].

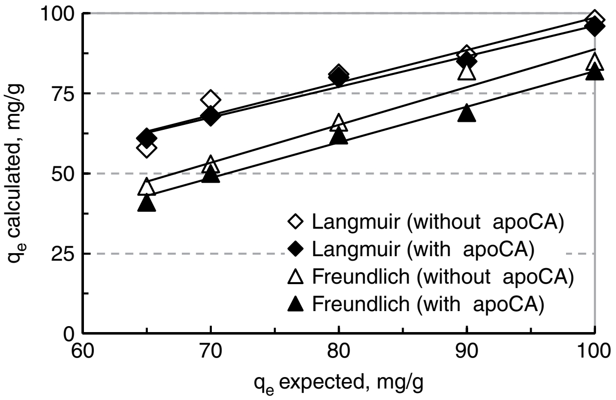

Fig. 8. Comparison of Langmuir and Freundlich models with an experimental for nickel adsorption by silica fume with apoCA and without apoCA.

Table 4 shows a comparison between the results of this work and other studies found from literature. The values of nickel specific uptake found this work were significantly higher, with two exceptions [69,70], than reported elsewhere. The comparison of adsorption capacities of silica fume used in this study with those obtained in the literature shows that silica fume with apoCA and without apoCA is the most effective for the removal of nickel from aqueous solutions.

Table 3
Values of adsorption isotherm parameters for adsorption of nickel without apoCA and with apoCA

Adsorption isotherms	without apoCA	with apoCA
Langmuir constant		
q_u (mg g^{-1})	8.6893	9.5168
K_L (l mg^{-1})	0.3321	0.3638
R^2	0.9905	0.9942
Freundlich constant		
K_F	2.2881	2.5060
n	0.6494	0.7112
R^2	0.9955	0.9925

Table 4
Comparison of adsorption capacity of various adsorbents for nickel

Adsorbent	Adsorption capacity, mg g^{-1}	Reference
Fly ash	0.03	[38]
Bagasse	0.007	[38]
Tea factory waste	18.42	[69]
Baker's yeast	11.40	[70]
Sheep manure waste	7.20	[71]
Sphagnum moss peat	9.18	[72]
Silica fume	8.69	This study
Silica fume with apoCA	9.52	This study

4. Conclusions

In this study, silica fume was converted into an adsorbent, and the suitability of the activated silica fume for adsorption of nickel from the polluted river water solutions was investigated by adsorption experiments with apoCA and without apoCA. The following conclusions were drawn:

- The SEM photographs showed that the surface of metal loaded adsorbent which are absent from the native adsorbent before metal loading.
- From the calibration curve, it was observed that the regression coefficient is quite high, and its value is 0.9954.
- The degree of adsorption increases with increasing temperature and maximum adsorption of nickel ions are obtained at 25°C which is the temperature of the solution.
- When the silica fume was added to the solution with nickel, the concentration of nickel in the leachate drastically decreased.
- The nickel concentration in samples of silica fume treated to polluted river water and $NiCl_2$ solution decreased from 1.262 to 0.436 and 0.260 and from 11.742 to 4.115 and 2.436 without/with apoCA for the polluted river water and $NiCl_2$ solutions, respectively.
- The nickel concentration in the samples of silica fume treated leachates solutions decreased. It was determined that the adsorption of nickel ions increased with the addition of apoCA as compared with those of without apoCA.
- The adsorption capacities calculated from the Langmuir isotherms are much closer to the experimental values of adsorption capacity than that of Freundlich isotherms. The high correlation coefficients showed that both models are suitable for describing the adsorption equilibrium of nickel ions.
- The investigation showed that silica fume is a very valuable material for removal of nickel ions from the aqueous solutions including heavy metals with apoCA and without apoCA. Thus, it could favor chemical immobilization and could reduce the solubility of the heavy metal contaminated water.
- In addition, the use of silica fume for the removal of the nickel ions from the aqueous solutions with heavy metals can potentially reduce the remediation costs.

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