

Adsorption of fluoride on gas concrete materials

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Abstract

In this study, gas concrete waste materials were used to remove F^- from aqueous solutions. The influence of pH, temperature, agitation rate and gas concrete dosage on F^- removal was investigated by conducting a series of batch adsorption experiments. In addition, the yield and mechanisms of F^- removal were explained on the basis of the results of X-ray spectroscopy and images of scanning electron microscopy (SEM) of the particles before and after adsorption. The values of zeta potential and BET- N_2 specific surface area of gas concrete particles were defined. In this study, F^- removal in excess of 96% was obtained. It was thought that the removal of fluoride by gas concrete took place both adsorption and precipitation of Al^{3+} and Ca^{2+} salts (F^-). As a result of this study, it was concluded that wastes of gas concrete were an efficient adsorbent for the removal of F^- .

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1. Introduction

Fluoride pollution of water can occur due to both natural reasons and human activity. Since fluoride is present in several minerals, it can be leached out by rainwater thereby allowing it to contaminate ground and surface water. On the other hand several fluoride compounds have industrial applications and are used widely and these also contribute to fluoride pollution. Fluoride is frequently encountered in minerals and in geochemical deposits. Because of the erosion and weathering of fluoride-bearing minerals it becomes a surface species. On the other hand, fluorine compounds are industrially important and are extensively used in semiconductors, fertilizers, aluminium industries, and nuclear applications. Toxic wastes containing fluorine/fluoride are generated in all industries using fluorine or its compounds as a raw material. Prominent among these is the aluminium smelter where fluorine gas is released into the atmosphere. Fluoride is an essential constituent for both humans and animals depending on the

total amount ingested or its concentration in drinking water. The presence of fluorine in drinking water, within permissible limits of 0.5–1.0 ppm, is beneficial for the production and maintenance of healthy bones and teeth, while excessive intake of fluoride causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage in severe cases [1–4]. Many countries have regions where the water contains more than 1.5 ppm of fluoride due to its natural presence in the earth's crust, or discharge by agricultural and industrial activities, such as steel, aluminium, glass, electroplating [5–7].

Current methods used to remove fluoride from water can be divided into two categories: precipitation and adsorption. Precipitation of fluoride with calcium and aluminium salts [8,4] has been used to remove fluoride from industrial wastewater. Typically, lime is used as a calcium source, and first reduces the fluoride concentration down to 10–20 ppm. The Ca^{2+} ions released from calcium salts interact with fluoride and form CaF_2 precipitate. Then, aluminium salts are used to reduce the fluoride concentration further to about 2 ppm [9]. The aluminium salts interact with

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fluoride in water and form AlF_n^{3-n} and $\text{Al}(\text{OH})_{3-m}\text{F}_m$, etc. The final concentration of fluoride in the water treated using this method greatly depends on the solubility of precipitated fluorite, as well as calcium and aluminium salts. The solubility of CaF_2 is theoretically 8 ppm fluoride at stoichiometric concentrations of calcium; therefore, even when a large dosage of calcium is used, the concentration of fluoride in water is still greater than 2 ppm [8], and the pH of treated water is at a relatively high value, resulting in a supplementary difficulty of eliminating excess chemicals [10].

Adsorption is another technique, in which fluoride is adsorbed onto a membrane, or a fixed bed packed with resin or other mineral particles. Many techniques have been reported, such as reverse osmosis, electrodialysis, Donnan dialysis, ion exchange, limestone reactor and activated alumina column [5,11]. The efficiency of this technique mainly depends on adsorbents. Among them, ion exchange, electrodialysis and membrane processes are effective and can remove the fluoride to a suitable level, but they are expensive and require frequent regeneration of resin beads or membrane and cleaning of the scaling and fouling [3,5,7,12].

Gas concrete, which is a building material, is included in the light concrete category. It is produced from different mixtures from silica, sand, cement, lime, water, and aluminium cake, which produce gas. One of the main advantages of F^- removal by using gas concrete over the other chemical treatment methods is that it does not produce any chemical sludge. In addition, after gas concrete has been used in building works, its residues can easily be used to remove F^- from wastewaters. In the present study, an attempt was made to investigate the F^- removal potential of gas concrete under different empirical conditions by batch tests.

2. Materials and methods

F^- was removed by using a gas concrete batch reactor from a synthetic wastewater in this study. The grain size of gas concrete used was between 2 and 0.063 mm. Gas concrete samples were washed with distilled water and then dried at 25 °C. The chemical composition of the gas concrete is given in Table 1.

The standard fluoride solutions used in the experiments were prepared from anhydrous NaF. The adsorption studies have been carried out at fluoride concentrations of 120 ppm F^- . A given amount of gas concrete has been placed in 250 ml volumetric flasks and mixed with 50 ml of stock solution.

Table 1
Chemical composition of the gas concrete (wt.%)

| | |
|-------------------------|-----|
| SiO_2 | 65 |
| Al_2O_3 | 22 |
| CaO | 9.6 |
| Others | 3.4 |

The experiments have been carried out at different temperatures (25, 40 and 60 °C) and pH (3.8, 6.9 and 8.9) values. pH adjustments have been done by using solutions of concentrated HCl and NaOH. The mixtures have been filtered prior to each measurement. Fluoride has been measured according to the SPANDS method [13]. The values of zeta potential of the particles were measured by using a microelectrophoresis cell (zeta meter 3.0+). The specific surface area of gas concrete particles was measured by using the BET- N_2 method.

3. Results and discussion

The effect of variation of gas concrete dosage on the removal of fluoride from aqueous solutions is shown in Fig. 1. Gas concrete dosage was varied from 4 to 40 g l^{-1} and initial fluoride concentration was 120 ppm. It was apparent that the equilibrium concentration of F^- decreased with increasing gas concrete dosage for a given initial F^- concentration. This result was anticipated because increasing adsorbent dosage provides greater surface area. From Fig. 1, it is evident that for the removal of 120 ppm fluoride in 50 ml, a minimum gas concrete dosage was 40 g l^{-1} . As a result of adsorption of 60 min, the efficiency of fluoride removal was approximately 86%. The effect of gas concrete dosage on fluoride absorbance per surface area of gas concrete (surface area of gas concrete: 22 $\text{m}^2 \text{g}^{-1}$) is shown in Fig. 1. Because the interaction rate of fluoride on particles of gas concrete decreased with increase of gas concrete dosage, the fluoride ions adsorbed on per surface area of gas concrete decreased with increase of gas concrete dosage as seen in Fig. 1.

3.1. Adsorption time

The effect of the contact time on fluoride adsorption by gas concrete was studied. As it is shown from Figs. 2, 3 and 5, the adsorption occurred in two steps; an initial fast step which lasted for 10–20 min, and a slower second phase which continued until the end of the experimental period. The equilibrium was reached within 60 min. Further increase in contact time did not show an increase in adsorption.

3.2. Effect of agitation speed

Adsorption studies were carried out with a magnetic shaker at pH 8.9. Fluoride solution was 120 ppm. The agitation speed varied from 150 to 235 rpm. The adsorption removal efficiency increased weakly with increasing agitation rate because an agitation rate of 150 rpm was enough to remove fluoride as seen Fig. 2. The result of adsorption of 60 min is that the fluoride removal was constant and 86%. The effect of agitation rate on fluoride adsorbed per surface area of gas concrete was also shown in Fig. 2. The fluoride

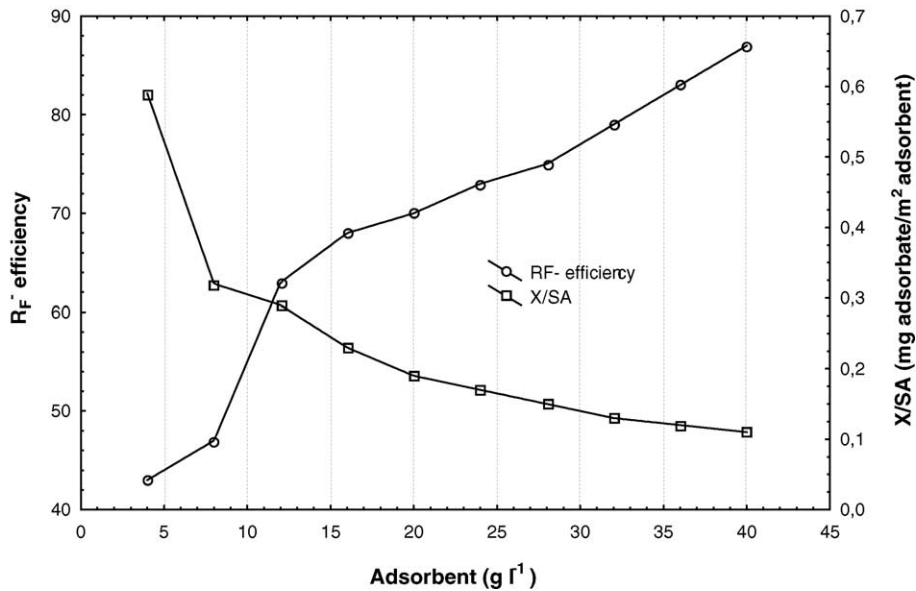


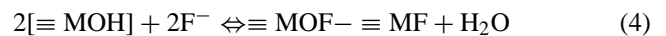
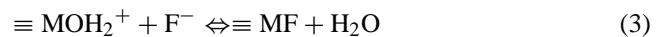
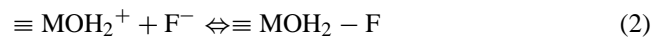
Fig. 1. Effect of adsorbent concentration (C_0 : 120 ppm; surface area of gas concrete: $22 \text{ m}^2 \text{ g}^{-1}$; pH: 8.9; T : 25°C ; agitation rate: 150 rpm).

adsorbed per surface area of gas concrete increased weakly with increasing agitation rate.

3.3. Effect of pH

The extent of adsorption of anions is strongly governed by the pH of the solution. Because anion adsorption is coupled with a release of OH^- ions, the adsorption is favoured at pH 6.9. Gas concrete is a mixed adsorbent with different metal oxides (Ca, Si and Al). In a humid environment, hydroxylated surfaces of these oxides develop charge on the surface. The specific adsorption of fluoride on metal oxides was mod-

elled by assuming ligand exchange reaction as follows (Eqs. (1)–(4)) [14,15]:



where M represents metal ion (Al and Ca). The pH of the aqueous solutions is an important variable, which controls the adsorption between the adsorbent and water interface.

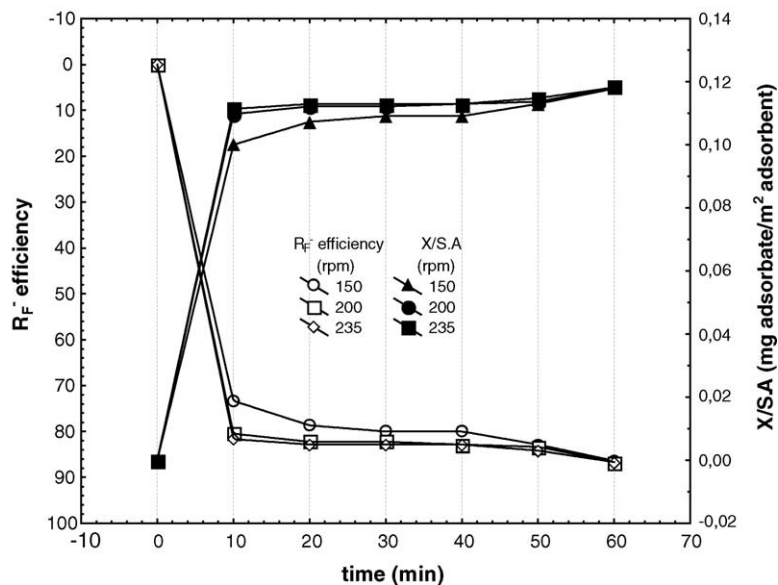


Fig. 2. Effect of agitation rate on adsorption (C_0 : 120 ppm; gas concrete dosage: 40 g l^{-1} ; surface area of gas concrete: $22 \text{ m}^2 \text{ g}^{-1}$; pH: 8.9; T : 25°C).

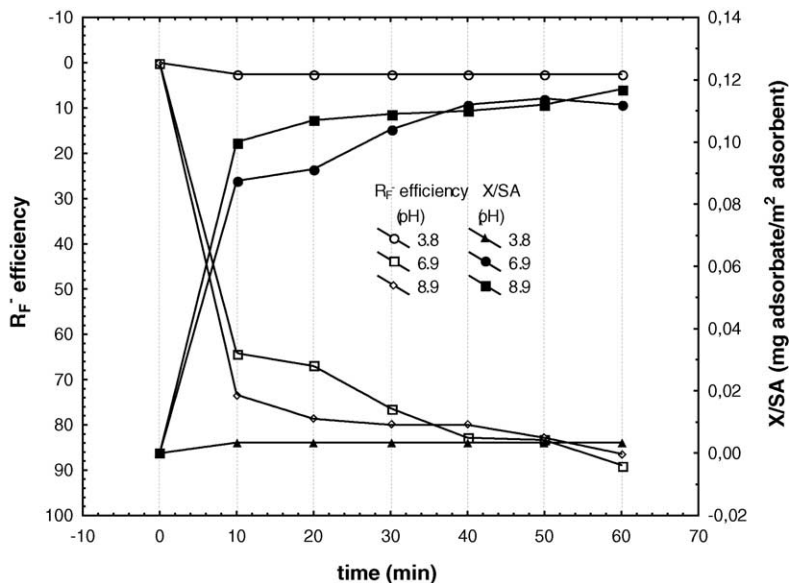


Fig. 3. Effect of pH on adsorption (C_0 : 120 ppm; gas concrete dosage: 40 g l⁻¹; surface area of gas concrete: 22 m² g⁻¹; T: 25 °C; agitation rate: 150 rpm).

The adsorption of fluoride on gas concrete was studied at different pH values (3.9, 6.9, and 8.9). The results are presented in Fig. 3, which reveals that the adsorption of fluoride is approximately maximum at pH 6.9 and 8.9. At a pH above 6.9, fluoride removal was not changed because of stronger competition with hydroxide ions on adsorbent surface. Adsorption is also not favoured in the acidic range; this may be as a result of the formation of weakly ionised hydrofluoric acid. The removal of fluoride was not realised at pH 3.9 [16]. At result of adsorption of 60 min, the fluo-

ride removal efficiency at pH 6.9 and 8.9 was approximately 86%.

The effect of pH for fluoride adsorbed on per surface area of gas concrete was also shown in Fig. 3. The fluoride adsorbed on per surface area of gas concrete at pH 3.9 was much more less, but it was maximum at pH 6.9 and 8.9. It is thought that the removal of fluoride by gas concrete at the values of pH 6.9 and 8.9 has taken place both adsorption and precipitation of Al³⁺ and Ca²⁺ salts (F⁻). The predominant product on the surface of gas concrete materials is AlF₃ be-

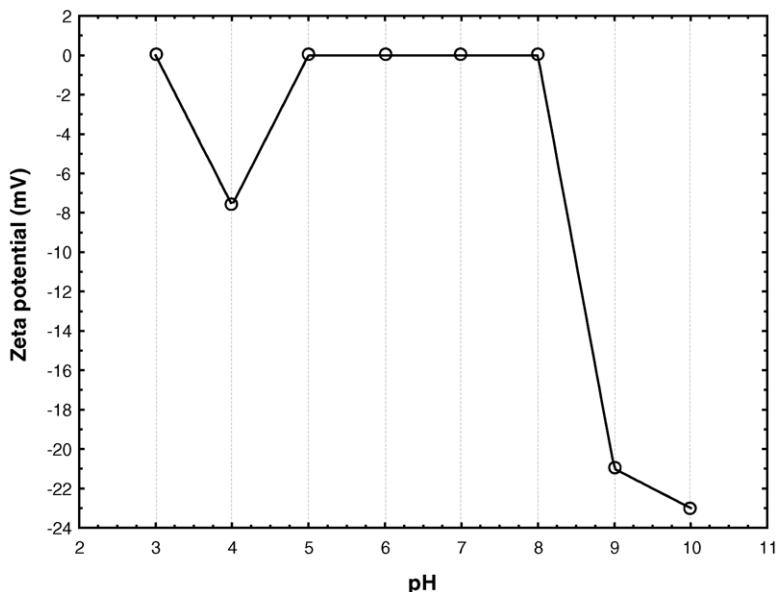


Fig. 4. Relation between zeta potentials and pH.

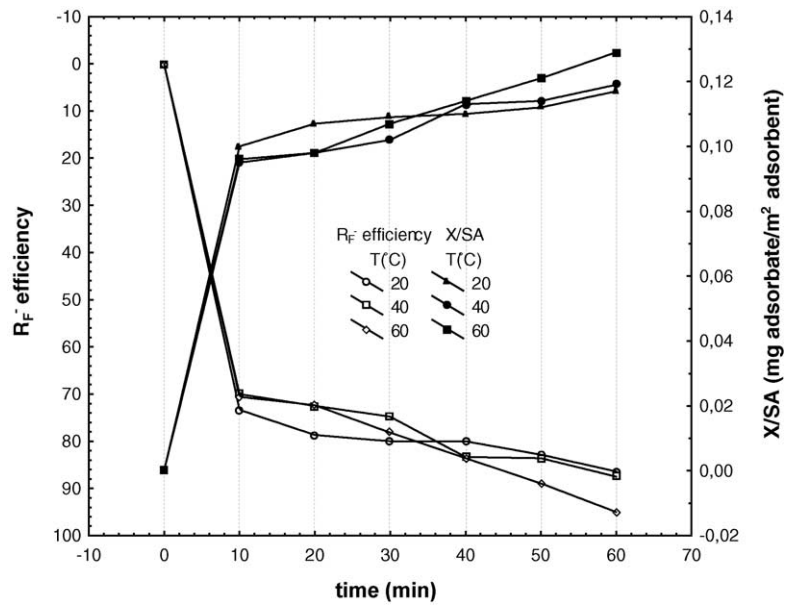


Fig. 5. Effect of temperature on adsorption (C_0 : 120 ppm; gas concrete dosage: 40 g l^{-1} ; surface area of gas concrete: $22 \text{ m}^2 \text{ g}^{-1}$; agitation rate: 150 rpm).

cause the solubility value (7.08×10^3) for AlF_3 is lower than that of CaF_2 (2.57×10^{10}).

From Fig. 4, it can be seen that at pH 4, 9 and 10, particles have negative zeta potential values, but at pH 5–9 values, the zeta potentials of particles are zero. This clearly shows that the removal of F^- takes place the physical interactions between the surface of adsorbent particles and adsorbate.

3.4. Effect of temperature

The effect of temperature on the removal of fluoride was investigated as a function of contact time. The results were graphed in Fig. 5. From this figure, it has been determined that the contact time of 60 min is sufficient to remove a considerable amount of fluoride at 25, 40 and 60 °C temperatures

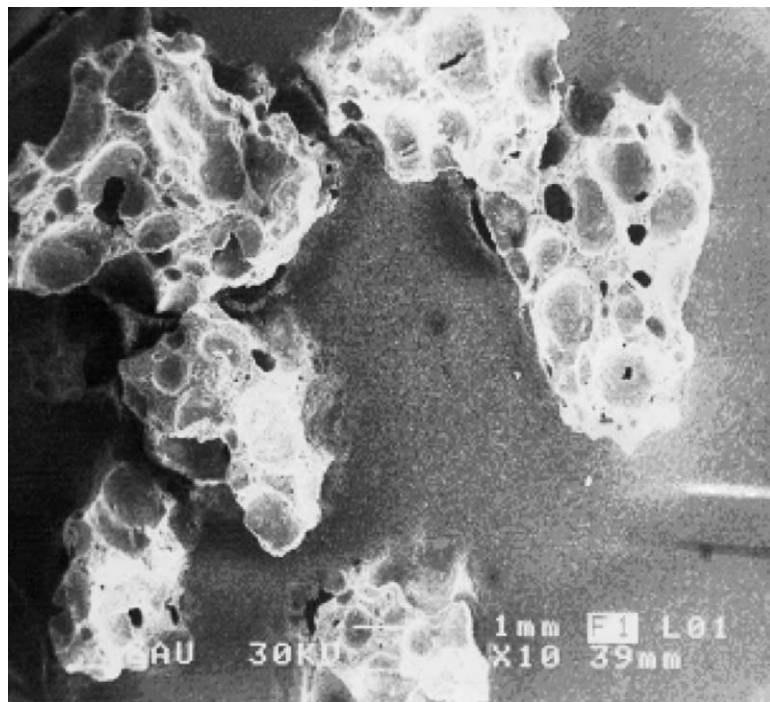


Fig. 6. SEM micrograph of the particles of gas concrete before adsorption (C_0 : 0 ppm; pH: 8.9; T : 25 °C; agitation rate: 150 rpm).

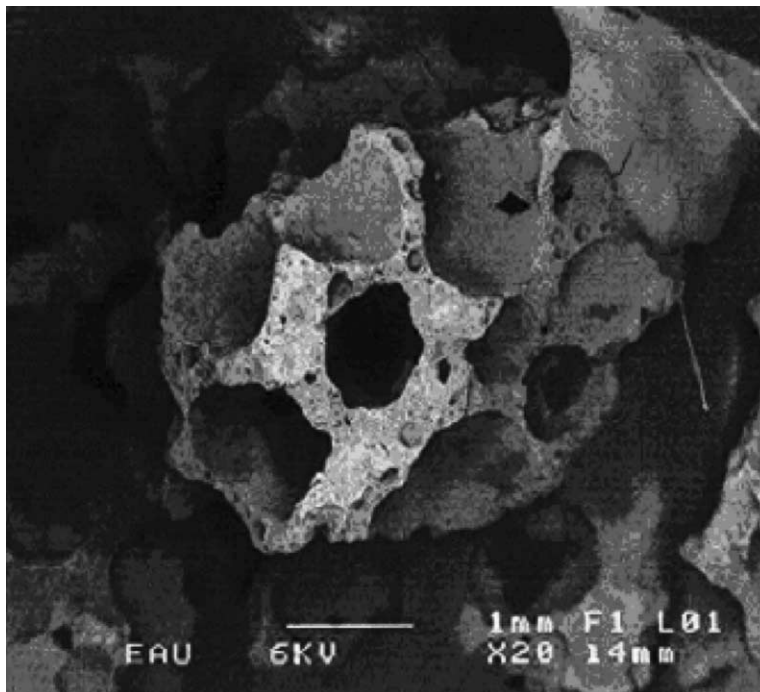


Fig. 7. SEM micrograph of the particles of gas concrete after adsorption (C_0 : 120 ppm; pH: 8.9; T : 25 °C; agitation rate: 150 rpm).

from aqueous solutions. The kinetic energy of fluoride ions increased with increasing temperature of solution. The collision frequency between adsorbent and adsorbate increased, then adsorbate electrostatically adsorbed on the surface of the adsorbent particles. Fig. 5 also shows that the removal of fluoride weakly depends on temperature. At result of an adsorption of fluoride of 60 min, the efficiency of fluoride removal for fluoride dosage of 120 ppm at 40 and 60 °C temperatures was approximately 96%. The effect of temperature on fluoride adsorbed per surface area of gas concrete material was also shown in Fig. 5. The fluoride adsorbed on per surface area of gas concrete weakly increased at high temperature ranges as seen in Fig. 5.

In order to see the surfaces of particles after and before adsorption, scanning electron microscopy (SEM) images for

the samples of the raw and treated adsorbents were obtained. These micrographs are presented in Figs. 6 and 7. A representative experiment under the given conditions such as 25 °C, pH 8.9, a contact time of 1 h, an agitation rate of 150 rpm (min^{-1}), and an initial fluoride concentration of 120 ppm was carried out to obtain the micrograph in Fig. 7. It is thought that the removal of fluoride by gas concrete has taken place both adsorption and precipitation of Al^{3+} and Ca^{2+} salts (F^-).

As it is seen from Fig. 6, before the fluoride adsorption on gas concrete materials, the pores of the particles of the adsorbent are open. According to the SEM spectra, there is an electrostatic (columbic) attraction between adsorbate and the surface of the adsorbent particles. This interaction between adsorbate and the adsorbent particles has increased with the formation of AlF_3 as it is seen in Fig. 7. According to the

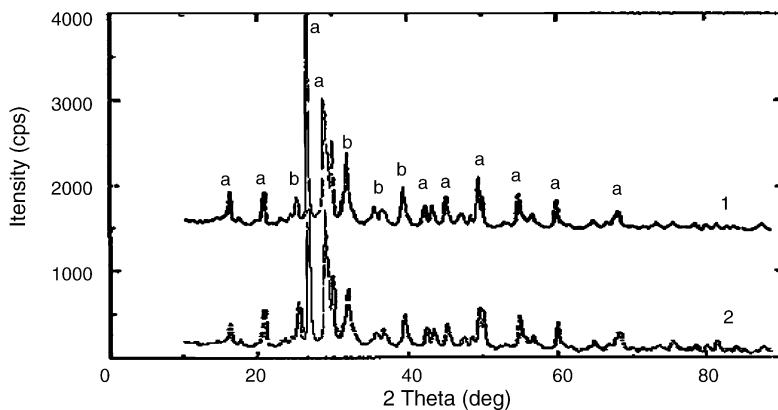


Fig. 8. X-ray diffraction diagram of the gas concrete before and after adsorption (C_0 : 120 ppm; pH: 8.9; T : 25 °C; agitation rate: 150 rpm; values of a , b , c are SiO_2 , Al_2O_3 and CaO , respectively).

micrograph obtained after adsorption, it is thought that the pores of the particles of the adsorbent have been covered with AlF_3 . In this experiment, almost 86% of the fluoride in the aqueous solution has been removed.

Fig. 8 shows X-ray spectroscopy of gas concrete. The gas concrete has specific chemical composition intensities at different 2θ ($^\circ$). X-ray spectroscopy of gas concrete before adsorption of fluoride on gas concrete is seen from Fig. 8 [1]. Fig. 8 also shows that the fluoride adsorbed electrostatically on gas concrete modified the peaks of chemical composition intensities on gas concrete. A considerable shifting of peaks was observed from 20 to 80 2θ ($^\circ$) as seen in Fig. 8 [2]. According to the X-ray spectra, there is an electrostatic (columbic) attraction between fluoride and gas concrete particles. This interaction between fluoride and gas concrete particles increased at pH 6.9 and 8.9. Thus, the absorption spectra of chemical compositions on gas concrete changed as seen Fig. 8 [2]. The results of X-ray analysis in Fig. 8 clearly reveals the presence of fluoride on the structure of adsorbent after adsorption process.

4. Conclusion

The results of this study indicate that gas concrete is an effective adsorbent for removal of fluoride from aqueous solutions. Fluoride removal up to 96% was obtained. It was found that the amount of fluoride adsorbed on gas concrete efficiently depends on pH, and weakly agitation rate and temperature of the solution. It is thought that gas concrete can

be regenerated because of no removal of fluoride at lower pH values (1–3.9).

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