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Fluoride Removal from Aqueous Solutions By Adsorption with Coal Ash

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Abstract

Dynamic adsorption studies were performed to study the suitability of coal ash to remediate fluoride-contaminated water. A series of experiments were conducted with aqueous solutions containing 2.5, 5, 10, 50 and100 mgF/ℓ at 29 ^{o}C in a column packed with 500g of coal ash. The flow rate through the bed was 2 mℓ/hr. The effects of contact time, initial adsorbate concentration and sorbent particle size range on fluoride removal efficiency were studied. Better removal efficiencies were obtained with lower particle size ranges. The Fconcentration in the effluent gradually decreased reaching 0 mgℓ after 96-168 hours depending on the initial adsorbate concentration. The kinetic results showed that defluorination follows first order kinetics. An empirical formula was proposed to describe the relationship between the fluoride removal efficiency and the dependent operating variables with 95% confidence level.

Keywords: Fluoride removal, Adsorption, Coal ash, Statistical analysis

ازالة الفلور من المحاليل المائبة بالأمتزاز باستخدام رماد الفحم

الخلاصة

يهدف البحث الى دراسة جدوى استخدام رماد الفحم لمعالجة الماء الملوث بايونات الفلور. اجريت مجموعة من التجارب باستخدام محاليل مائية للفلور وبالتراكيز (2.5, 5, 10 ,50 و 100 ملغم F^-/ لتر) وبدرجة حرارة 20 درجة مئوية في عمود يحتوي على 500 غم من رماد الفحم. معدل التدفق خلال العمود 2مللتر/ ساعة,تم دراسة تأثير معدل حجم دقائق المادة الممتزة, زمن التماس والتركيز الأبتدائي للفلور على كفاءة عملية الفصل. تم الحصول على نتائج أفضل للكفاءة باستخدام أحجام أصغر للدقائق الممتزة. تراكيز الفلور في المحاليل الناتجة من العملية كانت تقل تدريجيا وبلغت صفر بعد 96-168 ساعة اعتمادا على التراكيز الابتدائية للفلور في محلوله المائي . حركيات عملية أمتزاز الفلور على رماد الفحم يتبع حركيات التفاعل من الدرجة الاولى. تم اقتراح علاقة رياضية تمثل العلاقة بين كفاءة عملية فصل الفلور والمتغيرات المعتمدة للعملية وبدرجة ثقة 95%.

Nomenclature

C : Residual fluoride concentration, *mg/ℓ*

C_o: Initial fluoride concentration, *mg/ℓ*

d_p : Coal ash mean particle diameter, microns

k: First-order rate constant of sorption, hr^{-1}

R: Correlation coefficient

RE% : Overall removal efficiency

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1. Introduction

Fluoride is well recognized as an element of public health concern. Fluoride is present universally in almost every water (higher concentrations are found in ground water), earth crust, many minerals, rocks etc. It is also present in most of everyday needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes, and so on. Though a small amount of it is beneficial for human health for preventing dental carries, it is very harmful when present in excess of 1 mg/ℓ.

World Health Organization (WHO) recommended maximum guideline limit of 1.5 *mg/ℓ*. It has been observed that with the intake of more than 6 *mg/d* of fluoride results in multidimensional health manifestations, the most common are skeletal abnormalities and dental fluorosis. Long term ingestion of excessive fluoride has a chronic effect on kidney.

Various processes tried so far for the removal of excess fluoride from water are adsorption, ion exchange, precipitation, and membrane process. However, most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment. Adsorption techniques have been found to be useful means for the defluoridation of water. Researches were carried on different adsorbents, viz. activated carbon, processed bone char powder, activated alumina, magnesia, activated bauxite, fly ash, granular calcite, alum, lime, etc.

Jamode et al. (2004) studied the suitability of inexpensive leaf adsorbents to effectively remediate fluoride-contaminated water. They found that the efficiency of the sorption of fluoride ion is affected by pH, contact time, adsorbent dose, type and size of adsorbents and initial fluoride ion concentration.

Tembhurkar and Shilpadongre (2006) investigated the suitability of commercially available activated charcoal to remediate fluoride-contaminated water in batch adsorption. The effects of some of the major parameters of adsorption, viz. pH, dose of adsorbent, rate of stirring, contact time and initial adsorbate concentration on fluoride removal efficiency were studied and optimized. Maximum fluoride removal was observed to be 94% at optimum conditions.

Shihabudheen et al. (2006) investigated the adsorption potential of manganese-oxide-coated alumina (MOCA) for defluoridation of drinking water using batch and continuous mode experiments. The effects of different parameters such as pH, initial fluoride concentration and co-existing ions (usually present in groundwater sample) were studied. Optimum removal of fluoride ions was found to occur in a pH range of 4–7. The results indicated that fluoride adsorption rate and adsorption capacity of MOCA are far superior to that of activated alumina (AA), which was used as the base material for MOCA preparation. The maximum fluoride uptake capacity for MOCA and AA was found to be 2.85 and 1.08mgg^{-1}, respectively. The kinetic results showed that the fluoride sorption to MOCA followed pseudo—second-order kinetics with a

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correlation coefficient greater than 0.98.

Murugan and Subramanian (2006) used tamarind seed, a household waste from the kitchen for the sorptive removal of fluoride from synthetic aqueous solution as well as from field water samples. Batch sorptive defluoridation was conducted under variable experimental conditions such as pH, agitation time, initial fluoride concentration, particle size and sorbent dose. Maximum defluoridation was achieved at pH 7.0. Defluoridation capacity decreases with increase in temperature and particle size. Further, defluoridation follows first order reaction kinetics and Langmuir adsorption isotherm.

Bhargava and Killedar (2008) conducted batch adsorption studies to determine the effects of some parameters such as initial solute concentration and adsorbent dose on fluoride adsorption by fish bone charcoal. They found that the fluoride removal at any given solute concentration and adsorbent dose increased with time. The equilibrium fluoride concentration was found to be a function of the adsorbent dose and the initial fluoride concentration.

Fly ash has been successfully used by several investigators for the removal of metal ions **(Panday et al., 1985)** and radionuclides **(Aptak et al., 1996)** (from aqueous solutions, for treatment of wastewaters to remove organic compounds **[Banerjee et al.(1997), Mott and Weter (1975), Banerjee et al.(1995), and Swamy et al.(1997)]** and color **(Gupta et al.,1988)** as a coal desulfurization agent **(Yaman and Kücükbayrak,1996)** and together with hydrated lime-for SO_2 removal from flue gases **(Fernandez et al.,1997)**. In view of the advantages of fly ash as a low-cost sorbent, it seemed worth-while to study the feasibility of using coal ash in removing fluoride ion from aqueous solutions instead of costly adsorbents such as activated carbon, activated alumina, activated bauxite, etc.

2. Experimental Details

2.1 Materials

All the reagents used for the present study were of AR grade (BDH, Mumbai) and distilled water was used throughout. The stock solution of 100 mg/ℓ fluoride was prepared by dissolving 221 mg anhydrous NaF in 1 liter of distilled water. Thus 1 $m\ell$ of this solution has 0.1 mg of fluoride.

Dried coal ash was treated with 12M HCl at 80 °C for 4 hours, then treated with 5M NaOH to neutralize excess acid. The mixture was then filtered, washed and dried at 110 °C. The dried mass was grinded to two different particle size range (1-100μm) and (125-230μm). The results of its chemical analysis are as follows: SiO_2 24.5%, Al_2O_3 12.1%, Fe_2O_3 1.1%, CaO 36.3%, MgO 12.5%, C 13.5% (class C lignite and sub-bituminous coal (>10% CaO)). Slurry, prepared from 10g of the coal ash and 100 $m\ell$ of water, had a pH of 12.0.

2.2 Experimental Set-up & Measurments

Dynamic adsorption experiments were conducted at room temperature (29 ± 0.5°C) in a column (6cm diameter and 40cm height) packed with 500g of coal ash. Synthetic fluoride solution was drawn into the column at a rate of 2 $m\ell/hr$ from a separating funnel fixed at a height of 0.5m. Effluents were collected at regular intervals of time and analysed, using *FLUORIDE SELECTIVE ELECTRODE - WTW*:

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Measure range 0.2 ppm – saturation – Reference Electrode: Ag/AgCl.

2.3 Experimental procedure

1. The required concentrations of fluoride in water fed on the column were prepared from the stock solution by dilution. They are; 2.5, 5, 10, 50 and 100 mg/ℓ.
2. The bed was washed with demineralized water until colorless effluent was coming out.
3. A fluoride solution (250 $m\ell$) was first poured onto the column to moisten the coal ash.
4. Then a 250- $m\ell$ of the solution was placed in the top separating funnel and the draining rate was adjusted to 2.0 $m\ell/hr$.
5. The fluoride level in the effluent was determined every 24 hour, potentiometrically, by using a fluoride ion-selective electrode.
6. The removal efficiency was calculated as:

$$RE\% = \frac{C_o - C}{C_o} \times 100 \quad \ldots.(1)$$

Where C_o is the initial fluoride concentration in the aqueous solution and C is the residual fluoride concentration in the effluent treated wastewater.

7. Each experiment with a solution of a given concentration was run in duplicate with fresh coal ash.

3. Kinetic Analysis

Theoretically, adsorption kinetics of fluoride onto solid particles is controlled by different mechanisms. These mechanisms involve diffusion or transport of fluoride from bulk solution to exterior surface of the adsorbent particle, adsorption of fluoride ions onto particle surfaces, movement of solute within the pores of particles, attachment of solute at sites on the interior surface of the adsorbent particles via sorption, complexation or intraparticle precipitation phenomena. The rate of sorption onto a solid surface depends upon a number of parameters such as structural properties of the sorbent, initial concentrations of the solute, and the interaction between the solute and the active sites of the sorbent **(Oliveira et al., 2005)**. Therefore, kinetic data analysis for fluoride sorption onto coal ash was studied with the following models;

$$\frac{dC}{dt} = -kC(t)^n \quad \ldots\ldots..(2)$$

Where, C(t) is the concentration of residual fluoride up to time t; k is the defluoridation rate constant; and n is a constant characterizing the order character of the process. On solving equation (2) for n=1 then;

$$\ln\frac{C}{C_o} = -kt \quad \ldots\ldots (3)$$

The plot of $\ln(C/C_o)$ vs. t yields the value of the kinetic rate constant.

4. Results and Discussion

Knowledge of the optimal conditions would herald a better design and modeling processes. Thus, the effect of some major parameters like contact time, particle size of adsorbent and concentration of fluoride ions of the uptake on adsorbent materials was investigated.

The effect of contact time on the removal efficiency was studied by varying it from 24 to 168 hours. Figure (1) shows the progression of adsorption reaction and the percentage removal of fluoride for different contact times. It was found that the removal of fluoride ions increases with the increase in contact time. The changes in the extent of removal might be due to the fact that initially all sorbent sites were vacant. Later, the fluoride uptake by

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adsorbent decreases, due to the decrease in the number of adsorption sites.

Figure (2) shows that, the percentage removal of fluoride ion decreases with increasing the concentration of the initial fluoride ion concentration. Complete retention of the fluoride by coal ash occurs after 96 hours for the lower F concentrations (2.5 *mg/ℓ*) and after 144,168 hours for the higher F concentrations (50 and 100 *mg/ℓ*) respectively.

The explanation for the high sorption capacity of coal ash with respect to the fluoride ion seems quite straightforward if one considers its high CaO content (36.2%) on the one hand, and a slow flow rate of the solution through the column (48 *mℓ*/24*hr*) on the other. The hydration of the oxide is responsible for the high pH of the water slurry of coal ash (pH exceeding 12). The resulting calcium hydroxide reacts with the fluoride to afford a sparingly soluble calcium fluoride. Strong sorptive capacity of residual carbon is also likely to contribute to this process. The residual carbon samples have microporous surface area of 100 - 200 m^2g^{-1} carbonaceous material which is much larger than that of bulk coal ash (1to 6 m^2g^{-1}). Moreover large pores of the carbon are capable of accommodating oxygen molecules with the diameter of 300 pm, and can also provide good access to much smaller fluoride ion with the diameter of 172 pm.

Inspection of the results presented in figure (3) show that the sorbent particle size range influenced the reduction of fluoride. The removal efficiency measured with 5 *mg/L* initial fluoride concentration after 24 hours contact time decreases with increasing sorbent particle size (best removals at small particle size ranges). In experiments performed under gravitational flow operation increases in sorbent particle size ranges allow larger flows, but at the same time it significantly decreases the effectiveness of the sorbent bed for the removal of fluoride.

Figures (4 and 5) show a plot for $\ln(C/C_0)$ vs. time for initial fluoride concentrations of 5 and 100 *mg/ℓ* respectively. The linear behavior, confirm that the deflorination of aqueous solution by adsorption on coal ash follows a first order reaction kinetics. These findings are in agreement with the results obtained by Murugan and Subramanian (2006).

A relationship for the estimation of the rate constant as a function of the initial fluoride concentration was proposed as;

$$k = a \ln C_o + b \qquad \ldots\ldots(4)$$

Where, a & b are constants, k is the rate constant (h^{-1}) and C_o is the initial fluoride concentration in*mg/ℓ*.

An empirical formula for the defluorination efficiency, using coal ash, in terms of fluoride initial concentration and sorbent particle size was developed as follows:

$$RE = aC_o^{\ b} dp^c \qquad \ldots\ldots. (5)$$

Where, RE is the overall removal efficiency, a, b and c are constants; C_o is the fluoride initial concentration and dp is the mean diameter of sorbent particles.

STATISTICA software 9.0 is applied to evaluate the empirical constants of equations (4 & 5). An implicit nonlinear numerical method (Quasi-Newton) is applied as regression method. Initial values and step sizes are automatically allocated by the software. In this regression, second order (partial) derivatives of the loss

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function are used to determine iteration steps. Determination constant coefficient, R, is used to quantify the accuracy of regression.

Figure (6) shows the relationship between the rate constant and the initial fluoride concentration. The empirical formula that represents the relation is found to be;

$$k = 1.255\times10^{-3}\ln C_o + 0.00295 \quad \text{.....(6)}$$

The determination coefficient, R= 0.946

Figure (7) is 3D surface plot for the effect of fluoride initial concentration and sorbent particle diameter on the overall removal efficiency. The equation representing the system is given as:

$$RE = 92C_o^{0..308}dp^{-0.365} \quad \text{..... (7)}$$

The determination coefficient, R = 0.9698.

Estimated results based on the proposed correlation for different operating conditions are compared with the experimental data, as shown in Figure (8).

5. Conclusions

Based on these studies, it is concluded that coal ash can be fruitfully utilized for the removal of fluoride from its aqueous solutions. A double mechanism is likely to operate in the retention of fluoride by coal ash: chemical binding by calcium hydroxide and physical sorption by residual carbon particles. The percentage of fluoride removal was found to be a function of contact time and initial solute concentration. The removal increased with time and with the increase of initial solute concentration. The removal kinetic follows a first order reaction rate. An equation for the estimation of the value of reaction rate constant as a function of the initial fluoride concentration was proposed. The developed empirical formula, for the removal efficiency represented the present experimental data with 95% confidence level with a correlation coefficient of 0.9698.

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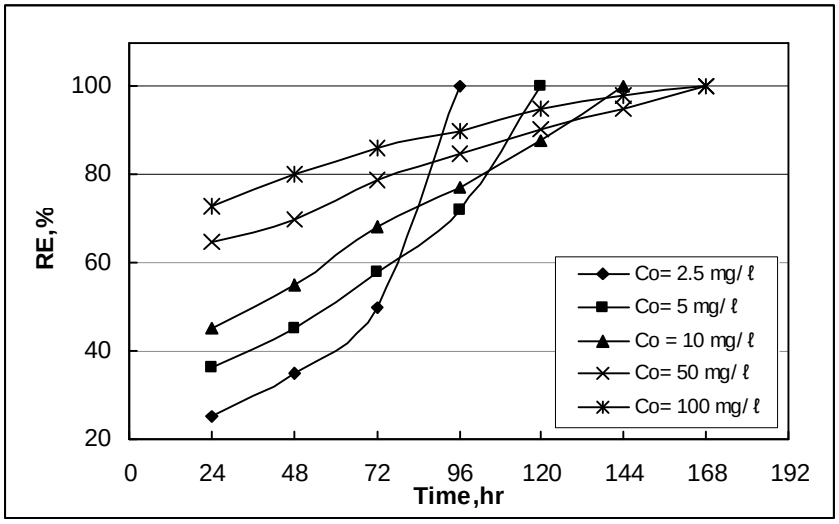


Figure (1) The change of fluoride removal efficiency with time for different fluoride initial concentration

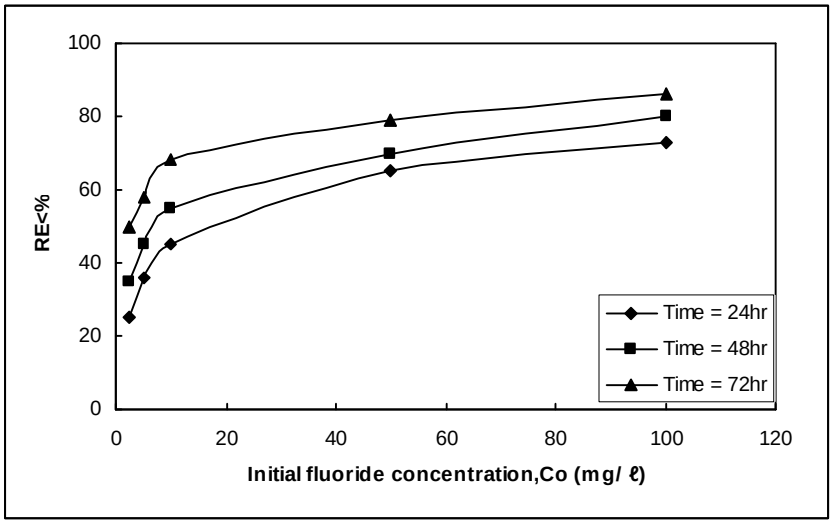


Figure (2) The effect of fluoride initial concentration on the removal efficiency for different contact times

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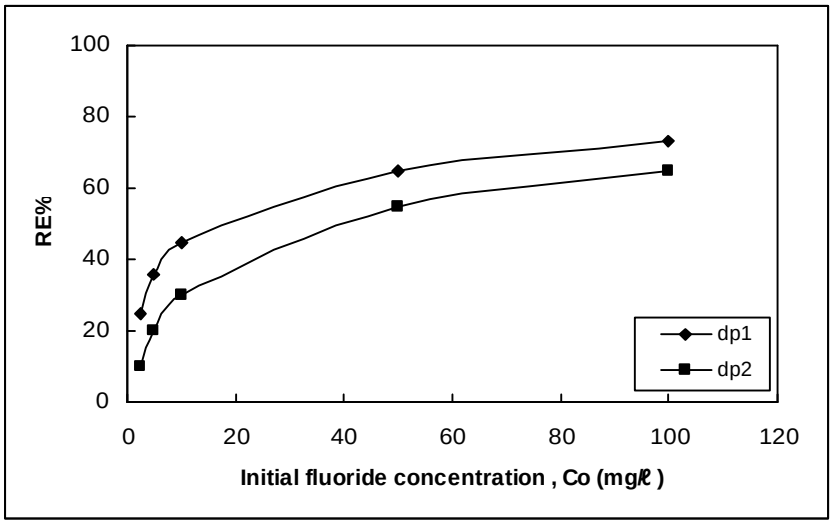


Figure (3) The change of fluoride removal efficiency with fluoride initial concentration for different sorbent particle size ranges (dp_1=1-100μm, dp_2=125-230μm)

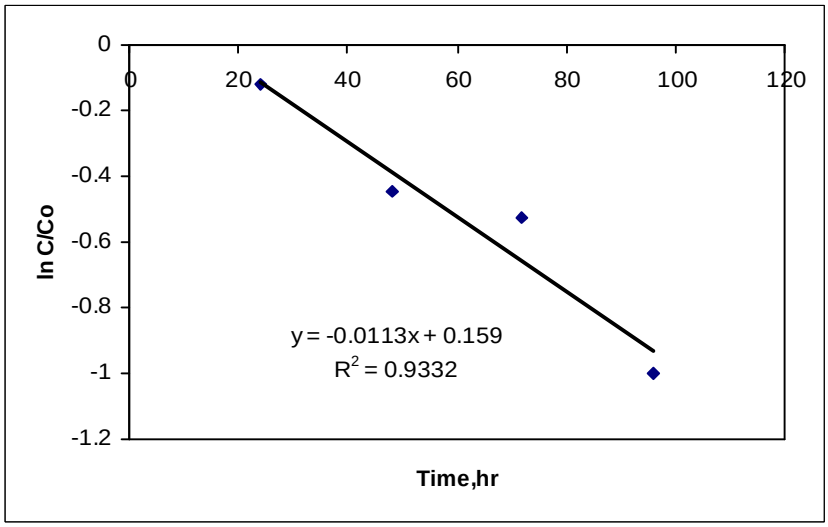


Figure (4) Kinetics analysis of the defluorination process, C_o=5 *mg*/ℓ.

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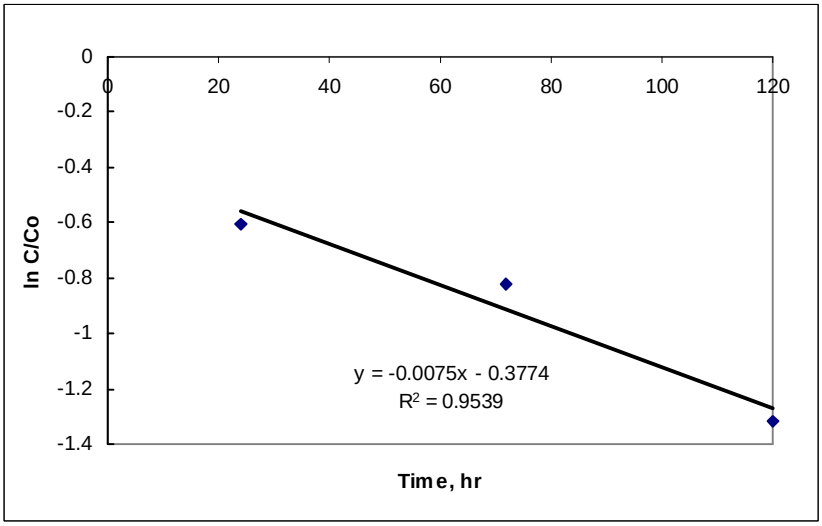


Figure (5) Kinetics analysis of the defluorination process, C_o=100 *mg*/ℓ.

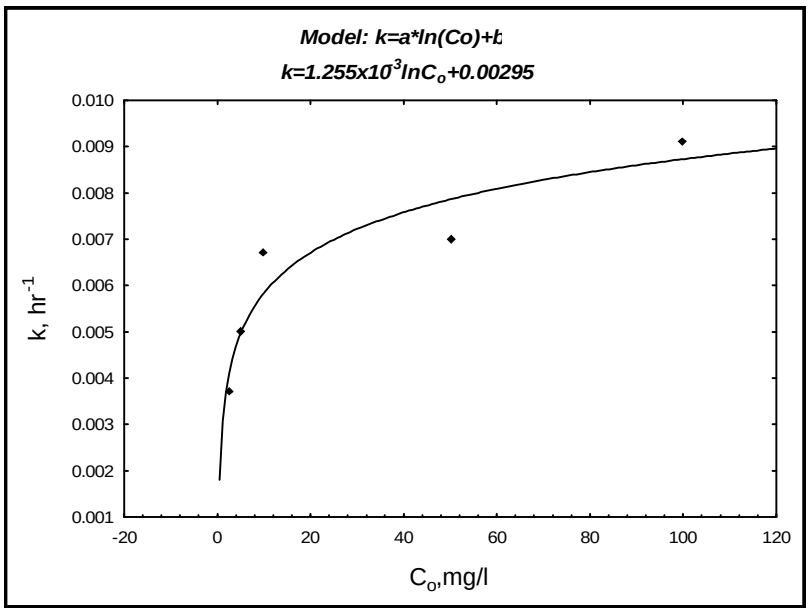


Figure (6) The relation ship between the rate constant and the initial fluoride concentration

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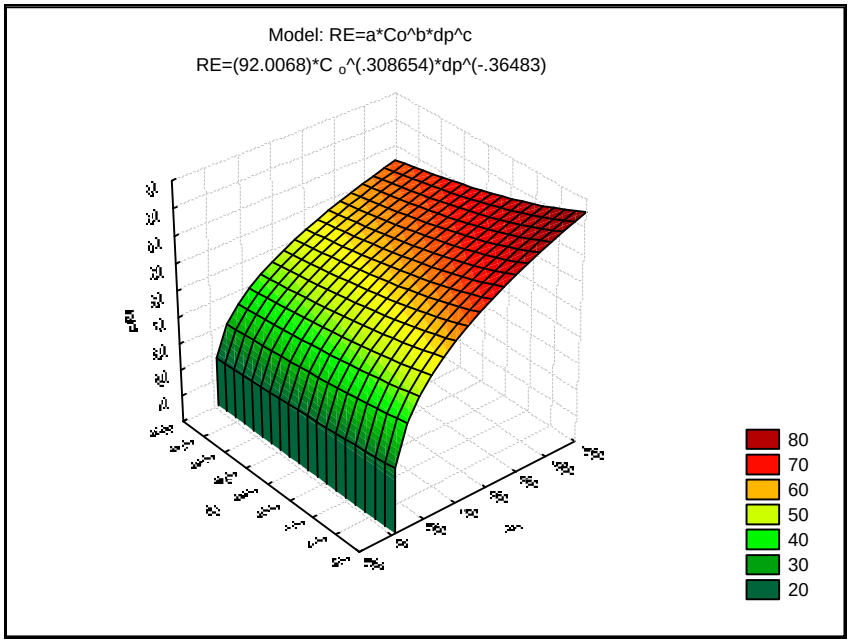


Figure (7) 3-D Surface plot representing the relation ship between the overall removal efficiency, fluoride initial concentration and coal ash mean particle mean diameter

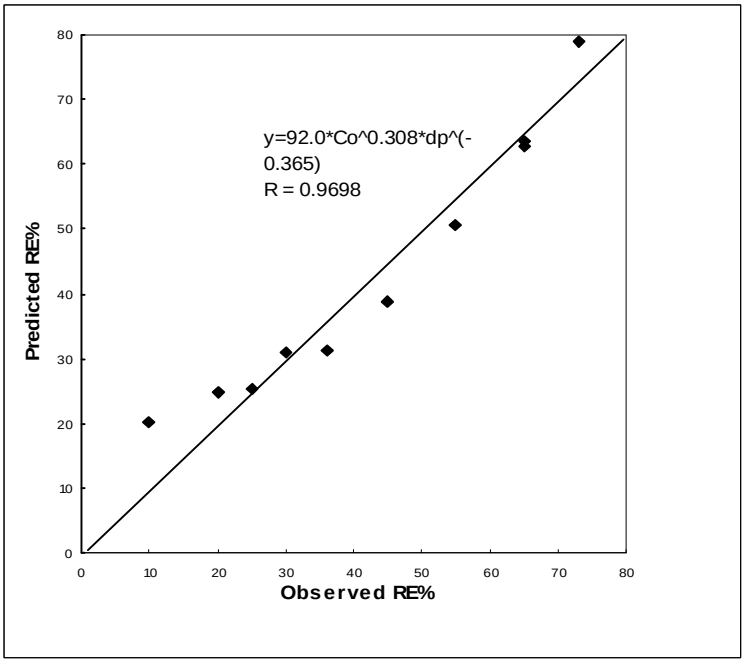


Figure (8) Predicted vs. observed removal efficiency

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