Uptake of Fluoride from Water Using Recycled Raw Beef Bone as an Environmently Freindly Waste

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ABSTRACT

Excessive intake of fluoride, mainly through drinking water is a serious health hazard affecting humans worldwide. In this study, the defluoridation capacities of locally available raw waste beef bones have been estimated. Several experimental parameters including contact time, pH, bone dose, fluoride initial concentration, bone grains size, agitation rate, and the effect of co-existence of anions in actual samples of wastewater were studied for fluoride removal from aqueous solutions. Results indicated excellent fluoride removal effeciency up to 99.7% at fluoride initial concentration of 10 mg F/L and 120 min contact time. Maximum fluoride uptake was obtained at neutral pH range 6-7. Fluoride removal kinetic was well described by the pseudo-second order kinetic model. Both, Langmuir and Freundlich isotherm models could fit the experimental data well with correlation coefficient values > 0.99 suggesting favorable conditions of the process. Furthermore, it was found that the co-existing anions had no significant effect on fluoride removal. Ion exchange and fluoride precipitation are the modes of fluoride removal.

KEYWORDS: Beef bone, Fluoride removal, water treatment, Slaughter waste.

اعادة تدوير عظام البقر الخام كمخلفات صديقة للبيئة لازالة الفلورايد من المياه

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الخلاصة

ان زيادة التعرض للفلورايد، بصورة رئيسية عن طريق مياه الشرب تعد مشكلة صحية خطيرة تصيب الانسان في جميع انحاء العالم. من ناحية اخرى كميات كبيرة من العظام تهدر كمخلفات بايولوجية تطرح عادة من مجازر المواشي والدواجن، محلات القصابة و المطاعم والتي تمثل مخلفات متوفرة وليس لها اية قيمة اقتصادية. تم في هذا البحث دراسة قابلية ازالة الفلورايد من المحاليل المائية باستخدام مخلفات عظام البقر الخام المتوفرة محليا. الظروف والعوامل المختبرية المختلفة التي تم دراسة تأثيرها على ازالة الفلورايد من المحاليل المائية تضمنت: فترة التماس، الاس الهيدروجيني، كمية العظام المضافة، التركيز الاولي للفلورايد، الحجم الحبيبي للعظام، سرعة المزج، وتأثير تواجد الايونات السالبة الموجودة في نماذج مياه الصرف. نتائج التجارب المختبرية برهنت كفاءة ممتازة في ازالة الفلورايد تصل الى 99.7 % عند تركيز فلورايد 10 ملغم/ لتر و 120 دقيقة فترة تماس باستخدام مسحوق مخلفات عظام البقر الخام. اوضحت النتائج بأن قابلية ازالة الفلورايد تزداد مع زيادة التركيز الاولي للفلورايد في المحلول. اعلى نسبة ازالة للفلورايد تم الحصول عليها عند وسط متعادل عندما يكون معدل قيمة الدالة الحامضية 6– 7. دراسة حركية عملية ازالة الفلورايد اوضحت ان عملية الازالة تصل حالة التوازن خلال 120 دقيقة وقد وصفت جيدا باستخدام النموذج الحركيPseudo-second order. كذلك البيانات التجريبية تم تمثيلها بالموديلات الرياضية   Langmuir and Freundlich isotherm بشكل جيد بقيم معاملات ارتباط > 0.99 بأفتراض ظروف مناسبة لعملية ازالة الفلورايد. التجارب العملية بينت ان ميكانيكية ازالة الفلورايد تتم بعمليتي الترسيب والتبادل الايوني.

الكلمات الرئيسيه: عظم البقر ، ازالة الفلورايد، معالجة المياه ، مخلفات المجازر

1. INTRODUCTION

Water is one of the major elements essential for sustaining all forms of life. The chemical nature of water is one of the most important criteria that determine its usefulness for a specific need (Jamode et al., 2004). High fluoride levels in drinking water has become one of the most critical health hazards of this century as it induces intense impact on human health including skeletal and dental fluorosis (Sujana et al., 2009). Fluoride is a persistent, non-degradable pollutant. Presence of fluoride in drinking water in exceeding limits at various places all over the world has been reported by various researchers. Fluoride could disperse to the environment through various mediums such as water, food, and several other engineering processes. Fluoride containing wastewater is generated from various industries, for example, semiconductor manufacturing industries, coal power plants, glass and ceramic production units, uranium refinement units, electroplating, rubber, fertilizer manufacturing units contribute a lot towards fluoride pollution (Paudyal et al,. 2011; Swain et al., 2012). The optimum fluoride level in drinking water for general good health, set by WHO, is considered to be between 0.5 and 1.0 mg/L. Concentration higher than this can lead to serious health problems (Biswas et al,. 2009; Karthikeyan et al., 2011; Swain et al., 2012). It is suggested that the solution lies only in prevention; the fluoride should be removed from its source of entry. Due to the public health significance of high fluorides consumption in drinking water, defluoridation is important (Emamjomeh et al., 2011).

During recent years, several methods including sorption, chemical treatment, ion exchange, membrane separation, electrolytic defluoridation and electro-dialysis have been developed to remove fluoride ions from water. Among these methods, sorption is still one of the most extensively used method for the removal of fluoride ions from aqueous solution due to its low cost and viability (Chakrapani et al., 2010; Karthikeyan et al., 2011; Swain et al., 2012). In recent years considerable attention has been devoted to develop new cost effective natural materials for the removal of fluoride from drinking water and wastewater. However in Iraq, the absence of adequate and effective environmental control systems on some contributing industrial effluents such as those discharged from phosphates fertilizers industry, glass manufacturing industry, and aluminum fabrication industry may cause the release of high concentration of fluoride into the receiving systems. Also, the direct release of wastewaters from dental clinics and complexes to the sewer system without pretreatment may highly contribute to the increase of fluoride concentrations in municipal wastewater. Bones as a type of biomass of no economic value discarded from residential and industrial activities such as meat processing industries could be an attractive raw material to be effectively utilized as char bone for fluoride uptake from water and wastewater. In the past crushed and grounded waste bone materials were used only for fish feeding (Kirchmayr et al., 2003). In the modern slaughter houses, the bone waste materials produced are crushed and used for different purposes. One of the most important applications is as a filter bed for water purifications. This new sustainable approach will assist in reducing the impact of high generation of solid waste mainly bones from slaughter and poultry houses, meat processing industries, restaurants, and butchery stores.

The present study was undertaken to study the feasibility of recycling raw beef bones as a biomass solid waste of no economic value for the removal of hazardous excess fluoride ions from aqueous solutions

2. MATERIALS AND METHODS

2.1 Preparation of granular raw bone material

Beef bones were collected from local slaughter houses, butchers, and restaurants. The bones were manually cleaned from meat, repeatedly washed, and subsequently boiled in distilled water for 4 h in order to remove fats. This process was repeated 4 times. Thereafter, the clean bones were dried at 100°C for 8 h. The dried bones were crushed, milled, and sieved into 4 groups of different particle size ranges which were (> 0.075), (0.075-0.30), (0.3-1.18) and (1.18-2.34) mm for powder, small, medium, and large size-particles, respectively.

2.2 Characterization of bone material

Samples of raw bone waste material were analyzed by X-ray diffraction (XRD), using X-ray Diffractometer with rotation speed of (1000°/min). The changes in the diffracted X-ray intensities are plotted against the rotation angles of the sample; analysis of the peak positions enables qualitative analysis, lattice constant determination and/or stress determination of the sample.

The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) theory, using N_2 as the adsorbate at 77 K (-196∘C). Measurements

were conducted by surface analyzer type Q surf 9600. Before each run, the samples were exposed to a flow of 70% helium and 30% nitrogen for 1 h at 200°C, pore volume measured in the same apparatus using multi-point capability which allows complete analysis of sorption isotherm and total pore volume of the sample.

Detection of the surface functional groups for the bone waste material before and after the uptake of fluoride was carried out by Fourier Transforms Infrared (FT-IR) technique using an EQUINOX FT-IR 55 spectrometer. The bone waste samples were grounded with 200 mg of KBr in a mortar and pressed into 10 mm diameter disks. The scanning range was 4000 - 400 cm^{-1}.

X-Ray Fluorescence analysis was carried out to determine the mineral compositions of the raw bone samples. The system consists of lithium silicon detector; measuring samples as a compressible oven dried- bone powder weighting 2-4 g.

2.3 Fluoride aqueous solution

Fluoride stock solution of 1000 mg F/L was prepared by dissolving the desired amounts of sodium fluoride (NaF) in 1 liter of double distilled water, to obtain the desired concentration of fluoride ion in water. All working solutions of different fluoride concentrations were obtained by successive dilution of the stock solution. Batch mode operation was applied to study the removal of fluoride from aqueous samples.

2.4 Experimental procedure

Fluoride uptake experiments were carried out by agitating 100 mL of the prepared fluoride solutions of various initial concentrations contained in 250 mL-plastic Erlenmeyer flasks at room temperature. After proper pre-determined time intervals, samples of supernatant were filtered and the filtrates were analyzed to determine the residual fluoride concentration. All experiments were carried out in replicate. In order to investigate the effect of pH on fluoride removal, the pH was adjusted to different values over a range of 3-11 by the addition of either 1M   NaOH   or   1M   HCl. Additional sets of experiments were carried out to investigate the effects of particle size of bone granules. Also, the effects of the initial concentration of fluoride (5, 10, 25, and 35 mg F/L) as well as the agitation rate on the removal effeciency were considered in this study.

3 RESULTS AND DISSCUSION

3.1 Chemical composition and characterization

The elemental chemical analysis of bone samples revealed that the bone char was mainly composed of Ca and P as well as traces of Na, Mg, Al, Fe, and Zn. Results of (XRF) analysis after fluoride removal revealed that the concentration of the main components; calcium and phosphorus were reduced indicating the involvement of these elements in the fluoride uptake process.

Surface area values determined by Brunauer-Emmett-Teller (BET) method revealed that the surface area values decreased with increasing the particle size as given in Table 1.

Table 1 Surface area and pore volume of beef bone

Particle size range, (mm)	Size	Surface area, (m^2/g)	Pore volume, (m^3/g)
< 0.075	Powder	6.30	0.0080
0.075-0.30	Small	3.60	0.0044
0.30-1.18	Medium	1.60	0.0014
1.18-2.34	Small	1.18	0.0014

XRD patterns of the raw waste bone (RWB) samples indicate the presence of calcium hydroxyapatite, $[Ca_{l0} (PO_4)_6 (OH)_2]$ (HAP) as the major component of the raw beef bone samples.

For the Fourier infrared spectroscopy (FT-IR), the characteristics bands of the natural raw bones before and after the fluoride uptake at pH 7 were used to assess the changes in the functional groups of the biomass material. The spectra (Fig.1) were plotted using the same scale on the transmittance axis for all sorbents before and after fluoride uptake. The broad band from 3600 to 2600 cm^{-1} indicates the presence of OH^- groups. The sorption around 3565 cm^{-1} was OH^- associated by hydrogen bond stretch, which is the typical band for natural hydroxylapatite (HAP) (Mikhaylova et al., 2006). The peaks at about 1028, 958, 603, and 559 cm^{-1} arise from different vibrations of PO_4^{-3} group. Peaks at about 1456 and 1419 cm^{-1} and near 871 could be attributed to CO_3^{-2} group. However, the change of PO_4^{-3} and CO_3^- peaks were observed indicating the involvement of these groups in the fluoride removal process.
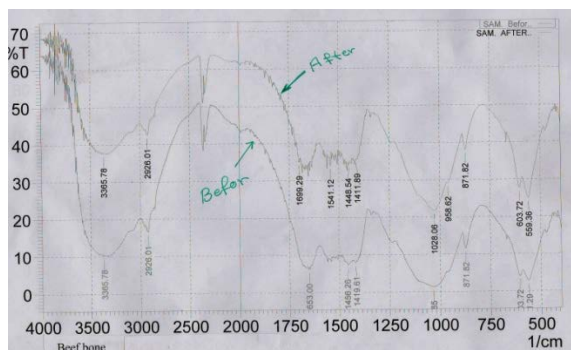
Fig. 1 FT-IR spectra

3.2 Fluoride removal

In order to determine the optimum conditions for maximum uptake of fluoride by raw beef bone, the effect of several key parameters including bone dose, particle size, fluoride initial concentration, contact time, agitation rate, and pH were carefully considered in this study as follows:

Effect of granular bone dose
Six different dosages (1, 5, 10, 15, 20, and 25g/ L) of bone granules were applied for the removal of fluoride ions from aqueous samples keeping the initial concentration of fluoride at 10 mg F/L, agitation rate 200 rpm, large particle size, pH 7.0-7.2, and contact time of 120 min. The effect of bone doses on the fluoride uptake is depicted in Fig.2. The plot indicates that the removal efficiency of fluoride increased rapidly with increasing the bone dosage from 1 to 15 g/L. A marginal increase in fluoride removal was observed for further increase in bone dose. The increase of fluoride removal capacity could be attributed to the fact that by increasing the bone dose, more sorbent surfaces or more active sites were available for the fluoride uptake. These results are in a good agreement with the trend of fluoride removal by bone char reported by Abe et al. (2004) and fluoride removal by natural clay suggested by Ramdani et al. (2010).

Effect of particle size of bone granules
Experiments were conducted to evaluate the influence of raw bones particle size for the removal of fluoride at 10 mg F/L initial concentration, 15 g/L of bone dose, pH 7.0-7.2, and agitation rate 200 rpm. The uptake of fluoride ions at different particle sizes of bone granules increased with decreasing the particle size (Table 2). This observation is well

expected and acceptable since the surface area and the number of active pores of the bone particles increase with decreasing the particle size. Also, fluoride uptake by the bone materials depends on pore size distribution and subsequently on the number of pores in the bone structure. The access to all pores is facilitated in the smaller size particles (Gupta et al., 2010).
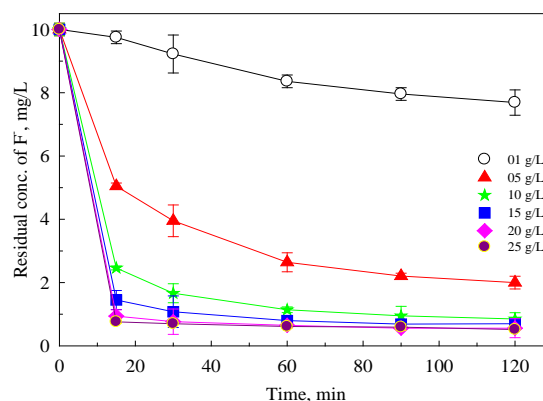

Fig. 2 Effect of bone doses on fluoride removal

These observations could be due to the fact that the smaller particles of RWBs becomes less stuffiness in their formation which allow more solute (fluoride ions) to cross through, resulted in more removal capacity for the same period of contact time.

Table 2 Removal capacities of fluoride (q_e mg F/g) at equilibrium using 10 mg F/L initial concentration, pH 7.0-7.2, agitation rate 200 rpm, bone dose of 15 g/L.

Size	Removal capacity of fluoride (q_e mg F/g)
Powder	0.661
Small	0.660
Medium	0.616
Large	0.567

Effect of fluoride initial concentration
Experiments were carried out to study the effect of various initial concentrations of fluoride on its removal capacity by bone particles. The experiments were conducted using 5, 10, 25, and 35 mg F/L initial concentrations of fluoride, 15g/L of bone particles, agitation rate 200 rpm, contact time 120 min, and pH 7.0-7.2. Fig. 3 presents the plot of fluoride initial concentrations versus the fluoride removal capacity by the bone material at equilibrium. It is well observed that by increasing the initial fluoride

concentration from 5 to 35 mg F/L, the uptake capacity increased from 0.33 to 2.21 mg F/g. This could be attributed to the fact that at higher concentration gradient between the bulk of aqueous solution and the sorbent material, the driving forces increased.
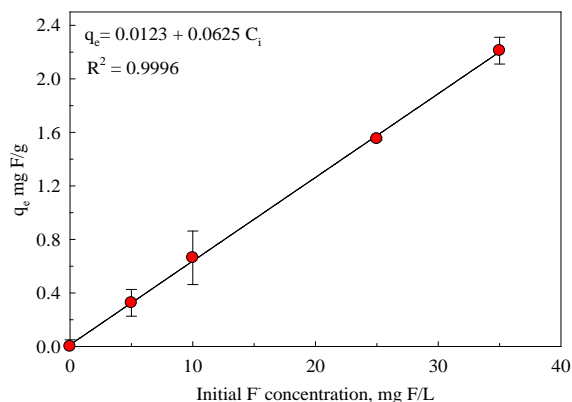

Fig.3 Effect of initial concentration of fluoride

Effect of contact time

In this study, a preliminary set of experiments were carried out for equilibration times ranging from 15 min to 240 min to assess the time required for achieving equilibrium. The result of this preliminary set of experiments revealed that fluoride uptake by raw bones is a relatively fast process. A biphasic profile for fluoride removal consist of two portions; a fast uptake rate within 15 min followed by a slow removal rate until complete equilibrium at 120 min as shown in Fig. 4. The effect of contact time on the removal of fluoride by bone waste material was investigated using 5, 10, 25, and 35 mg F/L initial concentration of fluoride, pH range 7-7.5, agitation rate 200 rpm, 15 g/L of bone particles, and particle size of 0.30-1.18mm.

Effect of pH

The pH of aqueous solutions is a primary parameter that affects and controls the sorption capacity of a sorbent for ions sequestering from aqueous solution due to its influence on the surface properties of the sorbent and the ionic forms of the pollutants in the solutions (Garg et al., 2007). The effect of pH on fluoride removal was studied at a pH range of 3-11, keeping the initial fluoride concentration at 10 mg F/L, raw bone particles dose of 15 g/L, agitation speed 200 rpm, and contact time 120 min. As shown

in Fig. 5, the equilibrium fluoride removal increased with increasing pH towards neutral conditions and decreased with increasing pH up to 11.
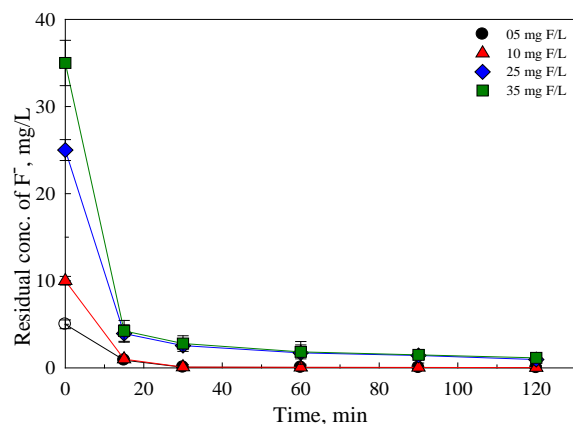

Fig. 4 Effect of contact time on fluoride removal

The main reason for the progressive decrease of fluoride removal at lower pH could be due to the fact that the phosphate ions in the bone structure are more easily ceded to the fluoride ion. This result indicated that the phosphate ions are more dissociated in a lower pH solution (Abe et al., 2004). Bever &Peschen (1991) as cited by Abe et al. (2004) suggested that the solubility of calcium phosphate and calcium fluoride are 2.5 and 1.7 mg/ 100 ml, respectively. Hence, the calcium fluoride is more stable than calcium phosphate. Also, solubility of calcium phosphate increases with decreasing pH in the solution. Additionally, the formation of weakly ionized HF at pH values below 4 could be another reason for the reduction of fluoride removal at low pH (Loganathan et al., 2013). On the other hand, the progressive decrease of fluoride removal capacities was observed at pH above neutral (6-7) which could be attributed to the formation of hydroxyl groups that compete with fluoride ions for uptake by bone materials and co-precipitate. At high pH the bone particles surface becomes negatively charged causing stronger repulsion forces between F$^-$ and negative surfaces.

Effect of agitation rate

A set of experiments were carried out to investigate the effect of three different agitation rates; 100, 150, and 200 rpm on the removal of fluoride by raw bone waste material. The effect of agitation rate on the removal of fluoride was investigated using 10 mg F/L initial concentration of fluoride, 15 g/L of bone

particles, contact time of 120 min, and pH range of (7-7.5) as shown in Fig. 6. Results revealed that the fluoride uptake capacity increased with increasing the mixing rate. This increase could be related to the boundary layer thickness, in which by increasing the stirring rate, a good degree of mixing could be achieved and the boundary layer thickness around the bone particles could be reduced.

3.3 Suggested mechanisms for F⁻ removal

In this study, the suggested dominant mechanisms of fluoride removal may include sum of two main mechanisms including ion-exchange associated with chemical precipitation.
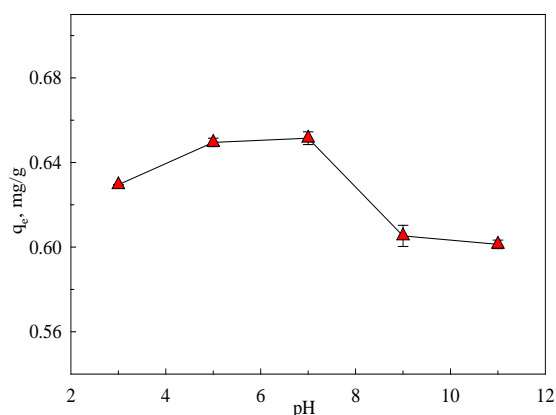

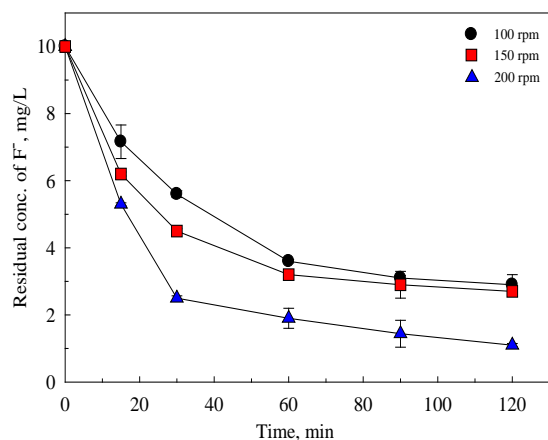**Fig. 5** Effect of pH on fluoride removal

Fig. 6 Effect of agitation rate on fluoride removal

This assumption is based on the fact that the structural inorganic part of bones consists essentially

of hydroxyapatite (HAP) $[Ca_{10}(PO_4)_6(OH)_2]$. In this structure, OH^- and F^- are inter-changeable and the hydroxides are replaced by fluoride, forming an insoluble fluorapatite (FAP) $[Ca_{10}(PO_4)_6F_2]$ according to the following equation (Kaseva, 2006):

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \leftrightarrow Ca_{10}(PO_4)_6F_2 \downarrow + 2OH^- \qquad (1)$$
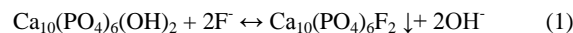
A slight increase of the solution pH was observed after treating the fluoride bearing aqueous solution with RWB due to the elution of hydroxyl-groups (OH^-) in the treated solution, indicating the formation of fluorapatite (FAP) and occurrence of precipitation. Also, bone contains calcium phosphate in different forms mainly including Dicalcium phosphate anhydrate (Ca_2HPO_4), Dicalcium phosphate dehydrate $(Ca_2HPO_4.2H_2O)$, Tricalcium phosphate $[Ca_2(PO_4)_3]$, Tetra calcium phosphate $[Ca_2(PO_4)_2O]$ which have a great affinity for fluoride to react with Ca^{+2} to form insoluble CaF_2 and release the phosphate ions in the solution according to the following equation:

$$Ca^{+2} + F^- \rightarrow CaF_2 \downarrow \qquad (2)$$

The average concentration of PO_4^{-3} in aqueous samples due to the elution process is 3.747 ± 0.50 mg P/L. Kawasaki et al. (2009), used cow, big, chicken, and fish bone char as adsorbent for fluoride removal and found that fluoride ion exchanges not only with hydroxide ion but also with phosphate ion in bone char and the amount of phosphate ion eluted from the bone char with fluoride sorption depending on the source species of animal biomass. As cited by Loganathan et al. (2013), Weiner (2008) reported that H-bonding is a strong dipole-dipole attractive force between bonding of the strong electropositive H atom in a molecule in a sorbent or sorbate and a strong electronegative atom such as fluorine or oxygen in another molecule.

3.4 Effect of other anions in actual aqueous samples

A set of experiments were carried out using actual domestic wastewater samples in order to investigate the effect of co- existing anions such as chloride, sulfate, and phosphate ions on the effeciency of fluoride uptake by raw beef bone. Average concentration of fluoride in the actual wastewater samples was found to be 6.5 ± 1.5 mg F/L. Other constituents in the samples of Al-Rustamia treated effluent including but not limited to BOD, COD, TSS, pH, and TDS were also measured (data not shown), they were within the expected concentration

ranges in wastewater. The concentrations of conventional anions in wastewater samples including SO_4^{-2}, Cl^-, and PO_4^{-3} were also determined as the co-existing anions which may compete with the fluoride ions for available sorption sites. The average concentrations of SO_4^{-2}, Cl^-, and PO_4^{-3} were found to be 200 ± 3.4, 20 ± 3.2, and 12 ± 0.8 mg/L, respectively

However, characteristics of Al-Rustamia wastewater samples in regard with fluoride concentration revealed that the average concentration of F^- ions in the influent is higher than the typical allowable concentration. In fact, none of the conventional treatment units including primary settling and secondary bio- treatment is convenient for fluoride removal. Therefore, reduction in fluoride concentration is unexpected in the treated effluent. Results revealed that the removal efficiencies of defluoridation process by beef bone granules are 98.5 ± 0.8 and 99.0 ± 0.2 at initial concentrations of 5 and 6.5 mg F/L for the synthetic and actual samples, respectively. It is obvious that there was no significant influence of competing anions (SO_4^{-2}, Cl^-, and PO_4^{-3}) on F^- removal capacity, which could be attributed to the availability of plenty of exchangeable and sorption sites on this natural material. However, Loganathan et al., (2013) reported that the extent of the competition depends on the relative concentrations of the ions and their affinity for the sorbent. Meenakshi & Viswanathan (2007) suggested that increased concentrations of Cl^-, SO_4^{-2}, NO_3^-, Br^-, and HCO_3^- decreased F^- uptake by anion exchange resin which adsorbs anions by an ion exchange mechanism, whereas these anions had no effect on fluoride sorption by a chelating resin which adsorbed F^- selectively by a H-bonding mechanism. Raichur & Basu (2001) found that F^- removal by a mixture of naturally occurring rare earth oxides was not significantly affected by the presence of SO_4^{-2} and NO_3^- in water at a concentration equal to that of F^- ions. Solangi et al., (2010) studied the removal of fluoride ions by a thio-urea incorporated amberlite resin in the presence of PO_4^{-3}, Cl^-, SO_4^{-2}, Br^-, NO_3^-, NO_2^-, HCO_3^-, and CO_3^- at 5 times the molar concentration of F^- and observed that Br^-, PO_4^{-3} and NO_2^- had little interference with F^-, but the other anions had no interference. Loganathan et al., (2013) concluded that the non-specifically adsorbing anions (e.g. Cl^-, NO_3^-) don't compete with F^- for sorption by specific adsorption. Only anions that are sorbed by specific sorption (e.g. selenate, arsenate, phosphate) compete with F^- for sorption.

3.5 Sorption isotherms of Fluoride

The sorption isotherms indicate how the sorption molecules distribute between the liquid phase and solid phase at equilibrium. In this study, the experimental data were fitted to the typical Freundlich and Langmuir models. The linear form of Freundlich and Langmuir models are represented by Eqs. 3 and 4, respectively:

$$\text{Ln } (q_e) = \log K + (1/n) \ln C_e \quad (3)$$

$$C_e / (q_e) = (1/b\, q_m) + (1/\, q_m)\, C_e \quad (4)$$

Where q_e (mg F/g) is the amount of F^- adsorbed per unit weight of bone at equilibrium, C_e is the residual concentration of fluoride in the aqueous solution at equilibrium (mg F/L), q_m is the amount of F^- adsorbed per unit of adsorbent for a monolayer surface (mg F/g), K and n are Freundlich constants, b is the Langmuir constant (L/mg). The estimated parameters for Freundlich and Langmuir sorption isotherms are given in Table 3.

Table 3 Estimated parameters for Freundlich and Langmuir sorption isotherms

Estimated parameters					
Freundlich isotherm			Langmuir isotherm		
K	n	R^2	q_m	b	R^2
0.074	1.092	0.9982	1.435	0.054	0.9939

3.6 Kinetic study

Kinetic models were applied in this study to test the experimental data in order to describe the behavior of sorption process for further scale-up. The kinetic models are pseudo-first order, pseudo-second order, and intra-particle diffusion model. Pseudo-first order is generally applicable over the first 20-30 min of the sorption process (Ncibi et al., 2008). The linear form of this kinetic model can be described as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

The pseudo-second order predicts the behavior of the chemical sorption over the entire time of sorption; this model is based on the adsorption capacity of the adsorbent (Ncibi et al., 2008). The linearized form of pseudo-second order is:

$$t/q_t = (1/k_2 q_e^2) + (t/q_e)$$

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The intra-particle diffusion model describes the transfer of fluoride ions from the bulk solution to the interior surface of the sorbent as follows:

$$q_t = k_p (t)^{0.5}$$

Pseudo-first order model
Straight-line plots of $\ln (q_e-q_t)$ versus time were used to determine the rate constants k_1 for different fluoride concentrations as shown in Fig. 7. Although these plots show good linearity, the values of theoretical removal capacities ($q_{e, Tho}$) are different from the experimental ones ($q_{e, ex}$) as given in Table 4.
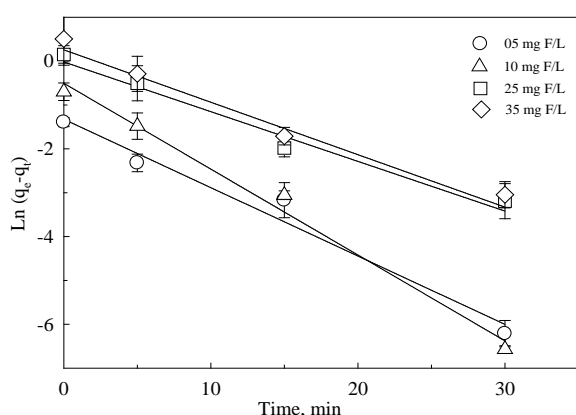
Pseudo-second order model
The plot of t/q_t versus time must give a straight line if pseudo- second order kinetic model is applicable and q_e and k_2 can be determined from the slope and intercept of the plot as presented in Fig. 8. Better linearity than pseudo-first order was obtained for these plots as shown in Table 4 with correlation coefficients slightly higher than those of pseudo-first order model. Also, in this model, the values of $q_{e, Tho}$ are in a good agreement with the experimental values of $q_{e, ex}$. Accordingly, the pseudo-second order model could be considered as the best model that can be used for predicting the kinetic of fluoride sorption process in this study.
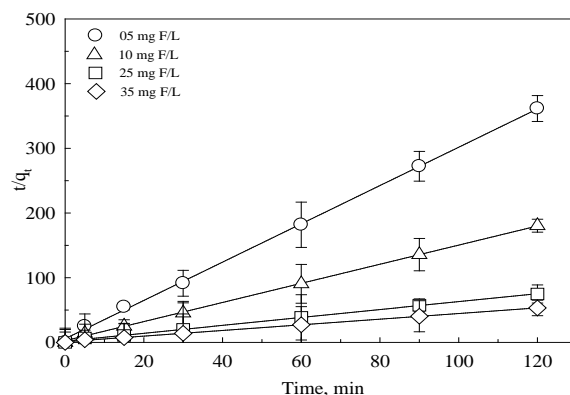

Fig. 7 First order plots for F⁻ removal by raw beef bone

Fig. 8 Second order plots for F⁻ removal by raw beef bone

Intra-particle diffusion model
Demir et al. (2002) suggested that for intra-particle diffusion model, a plot of q_t versus $t^{0.5}$ should be linear if intra-particle diffusion is involved in the sorption process; and if this line passes through the origin, intra-particle diffusion is the rate controlling step. If the plot does not pass through the origin, it is indicative of some degree of boundary layer control and further shows that the intra-particle diffusion is not the only rate limiting step and other kinetic models may control the rate of adsorption, all of which may be functioning simultaneously. Based on this fact, the plot of q_t versus $t^{0.5}$ in this study gave straight lines as shown in Fig. 9 indicating that the sorption process was controlled by intra-particle diffusion. However, the straight lines do not pass through the origin which means that both the surface sorption and intra-particle diffusion are involved in the complex sorption process of fluoride to the raw beef bone material.
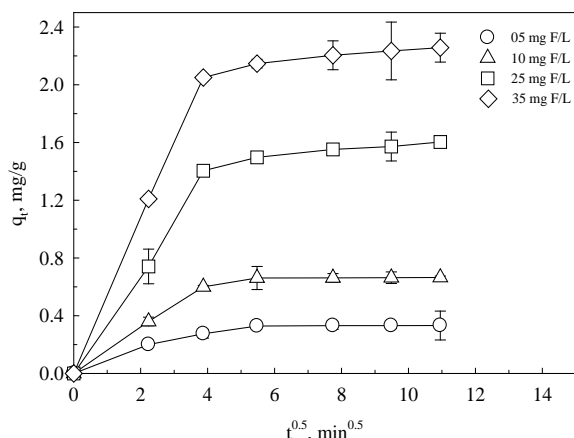
Table 4 Kinetic parameters for the applied kinetic models using raw beef bone

Fluoride concentration (mg F/L)	Pseudo-first order model			
	k_1, (min⁻¹)	$q_{e,Tho}$ (mg/g)	R^2	q_{ex} (mg/g)
35	0.1195	0.391	0.9398	1.658
05	0.1133	0.980	0.9553	1.164
10	0.1957	0.603	0.9891	0.497
05	0.1559	0.265	0.9740	0.248
	Pseudo-second order model			
	k_2, (g mg⁻¹ min⁻¹)	$q_{e,Tho}$ (mg/g)	R^2	
35	0.278	1.718	0.9992	
05	0.286	1.224	0.9985	
10	1.140	0.507	0.9991	
05	8.604	0.249	0.9991	

Fig. 9 Intra-particle diffusion model for F⁻ removal by raw beef bone

4. CONCLUSION

This study examined the potential of fluoride removal from aqueous solution using raw waste beef bone Characterizations of the bone material indicated the presence of calcium hydroxyapatite, $[Ca_{l0} (PO_4)_6 (OH)_2]$ (HAP) as the major component of the beef bone. This study has demonstrated that the beef bone waste materials can be used efficiently for fluoride removal from aqueous solutions. Maximum removal effeciency of fluoride using powder bone dose 15 g/L was 99.7 at pH 7.0, fluoride initial concentration 10 mg F/L, and agitation rate of 200 rpm. The extent of fluoride removal was dependent on initial fluoride concentrations, pH, contact time, bone dose, and agitation rate. Maximum fluoride uptake was obtained at neutral pH range of 6-7. Results revealed that the fluoride removal capacity of the powder sized particles (< 0.075 mm) was found to be the highest among the four tested ranges of particle size. Both, Langmuir and Freundlich isotherm models could fit the experimental data well with correlation coefficient values > 0.99 suggesting favorable conditions of the process. Fluoride removal kinetic indicated the equilibrium of fluoride uptake was within 120 min, and it is well described by the pseudo-second order kinetic model.

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