*Int. J. Electrochem. Sci.*, 10 **(2015)** 8137 - 8149

**International Journal of ELECTROCHEMICAL SCIENCE**
www.electrochemsci.org

# Equilibrium and Kinetics Studies for the Adsorption of Fluoride onto Commercial Activated Carbons Using Fluoride Ion-Selective Electrode

*Maja Ergović Ravančić*[1] *and Mirna Habuda-Stanić*[2,*]

[1] University of Applied Sciences in Požega, Department of Food Technology, Vukovarska 17, Požega, Croatia
[2] Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 20, Osijek, Croatia
[*]E-mail: mirna.habuda-stanic@ptfos.hr

*Received:* 8 March 2015 / *Accepted:* 11 July 2015 / *Published:* 26 August 2015

---

This paper reports the potentiometric determination of fluoride adsorbed onto four commercials granular activated carbons from aqueous solution under three temperature regime and various conditions: pH (4-9), initial fluoride concentration (2-40 mg/L), dosage of activated carbon (2-20 g/L) and contact time (15-360 min). The maximum fluoride uptakes for all tested activated carbons were obtained when 10 mg/L activated carbons were used at pH 5 and adsorption time 360 min. Obtained dada were fitted using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms showing that Freundlich isotherm model gave the best description of fluoride adsorption onto used activated carbons. The various kinetic models *viz.*, pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich models were used to describe the kinetic of fluoride adsorption at 25, 35°C and 45°C.

---

**Keywords:** potentiometric method, fluoride determination, fluoride removal, activated carbon, isotherms, kinetics

## 1. INTRODUCTION

Fluoride is a necessary element for human metabolism [1] but, due to its electronegativity, exposure to high fluoride concentration over a longer period can caused dental fluorosis, teeth mottling, skeletal damage, cancer and neurological problems [2-7]. Concerning all above mentioned and the fact that the drinking water is one of path through humans are exposed to fluoride, World Health Organization (WHO) set the maximum permissible level (MPL) of fluoride in drinking water at 1.5 mg/L [8].

Water treatment techniques, such as adsorption [4,9–11], coagulation and precipitation [12–14], membrane processes [15–19], electrolytic treatment [20–23], ion-exchange [24,25] are commonly employed for fluoride removal from water, and due to efficiency, selectivity and acceptable running costs, adsorption is often used in practice of fluoride removal [26,27].

Many adsorbents were tested for fluoride removal and demonstrated high capacities for fluoride removal from water including activated carbon [28,29], activated alumina [30,31], hematite [32], metal/metal hydroxide composites [33-36], hydroxyapatite [37], polymeric resins [38], activated rice husk [39], brick powder [40], pumice [41], chitosan [42,43], kaolinite clay [44] and zeolite [45–47].

Due to large active surface and chemical structure, activated carbons are one of the most used commercial adsorbents for removal of various pollutants from drinking water and waste water [48]. Various base materials were used for production of activated carbons and numerous studies reported successful fluoride removal with activated carbon obtained from fruit pits, lignin, nut shells, bones, wood, charcoal, coals, lignite and peat [49].

The aim of this research was to evaluate the performances of water defloridation by four commercially available activated carbons derived from different carbonaceous materials. The batch adsorption experiments were performed using various initial fluoride concentration, temperature regimes and contact time, adsorbent dosage and pH, while kinetic and isotherm studies of fluoride adsorption were used to define the feasibility and to understand the process of fluoride removal via adsorption onto tested activated carbons.

## 2. MATERIALS AND METHODS

### *2.1. Activated carbons*

Four commercials available activated carbons (ACs), activated with steam at high temperature, were used for the adsorption of fluoride: Norit ROW 0,8 Supra (Norit Nederland BV), Norit GAC 1240 (Norit Nederland BV), Cullar D (Culligan International Company) and Hydraffin 30 N (Donau Carbon GmbH & Co.) abbreviated as AC-NR, AC-NG, AC-CD and AC-HN. Characteristics of used commercial activated carbon provided by manufacturers are presented at Table 1.

**Table 1.** Characteristics of used commercial activated carbons.

| | AC-NR<br>*Norit ROW 0.8 Supra* | AC-NG<br>*Norit GAC 1240* | AC-CD<br>*Cullar D* | AC-HN<br>*Hydraffin 30 N* |
|---|---|---|---|---|
| Origin material | peat | coal | bituminous | bituminous |
| Particle size (mm) | 0.8 | 0.6 – 0.7 | 0.42 – 0.84 | 0.6 – 2.36 |
| Total surface area (B.E.T.) ($m^2/g$) | 1300 | 1175 | 1050 | 900 |
| Iodine number | 1175 | 1075 | 750 | 900 |
| Density ($kg/m^3$) | 400 | 480 | 200 - 220 | 440 - 500 |
| Ash content (%) | 7 | 7 | 15 | 12 |
| Water content (%) | 2 | 2 | 3 | 5 |

### *2.2. Fluoride adsorption experiments*

A stock solution containing 100 mg of fluoride per liter was prepared by dissolving 0.221 g of anhydrous sodium fluoride (99.9 % NaF, Merck) in 1 liter of deionized water. The initial stock solution were prepared diluted with deionized water to subsequent concentrations while pH values of aqueous solutions were adjusted at desired initial values using either 0.1 M HCl or 0.1 M NaOH. The pH values were measured by pH meter Seven Easy (Mettler Toledo) with unfilled pH glass electrode. The pH meter was regularly calibrated by pH calibration buffers.

Adsorption experiments were performed in bench scale using 100 ml conical flasks with 100 ml test solution at three different temperatures (25°C, 35°C and 45°C) at temperature-controlled shaker (Kottermann Labortechnik) at 120 rpm. After in advance defined contact time, aqueous solutions were filtered through a 0.45 μm cellulose acetate membrane filters and fluoride concentrations were determined using potentiometric method.

### *2.3. Potentiometric determination of fluoride concentrations*

This study was conducted using direct potentiometric method for determination of fluoride concentrations which allows direct reading of fluoride concentration. The initial and final fluoride concentrations in aqueous solutions were determined using fluoride ion selective electrode (Hach) and total ionic strength adjustment buffer (TISAB) for increasing the ionic strength and ensure that other ions not interfere with the fluoride ions during the measurements.

The specific fluoride uptake $q_e$ (mg/g) by each used activated carbon was determined due to following equation [50]:

$$q_e = \frac{(c_0 - c_e)}{m} \times V \tag{1}$$

where $c_0$ and $c_e$ are the initial and equilibrium fluoride concentrations in aqueous solutions (mg/L), respectively, $V$ is the solution volume (L), and $m$ (g) is the adsorbent mass.

The following isotherm models: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) were used for description of adsorption process while four kinetic models (pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich model) were used for determination of the behavior of fluoride ions during the adsorption onto tested activated carbons.

To assure the quality of the obtained results, each experiment was carried out in duplicate and average values only are reported.

## 3. RESULTS AND DISCUSSION

### *3.1. Effect of initial fluoride concentration*

The driving force for the fluoride mass transfer from the aqueous solution to solid phase, i.e. adsorbent, is correlated to the initial fluoride concentration. The effect of the initial fluoride concentration (from 2 to 40 mg/L) on the adsorption capacities of four different activated carbons was evaluated at pH 7±0.3 under three temperature regimes (25°C, 35°C and 45°C). The fluoride uptake was tested using an adsorbent dosage of 10 g/L during 120 min. Obtained results are presented in Figs. 1a-d where it can be observed that the adsorption capacities increased with increasing the initial fluoride concentrations for all four activated carbons. In all experiments the highest adsorption capacities were noted at 45°C when adsorption performances of four activated carbons were tested by solutions with initial fluoride concentration of 40 mg/L. The similar effect of temperature onto fluoride adsorption were observed at tested activated carbon, AC-NG and AC-HN, when increasing from 25°C to 45°C increased capacities from 0.143 mg/g to 0.714 mg/g for AC-NG i.e. from 0.286 mg/g to 0.662 mg/g for AC-HN.

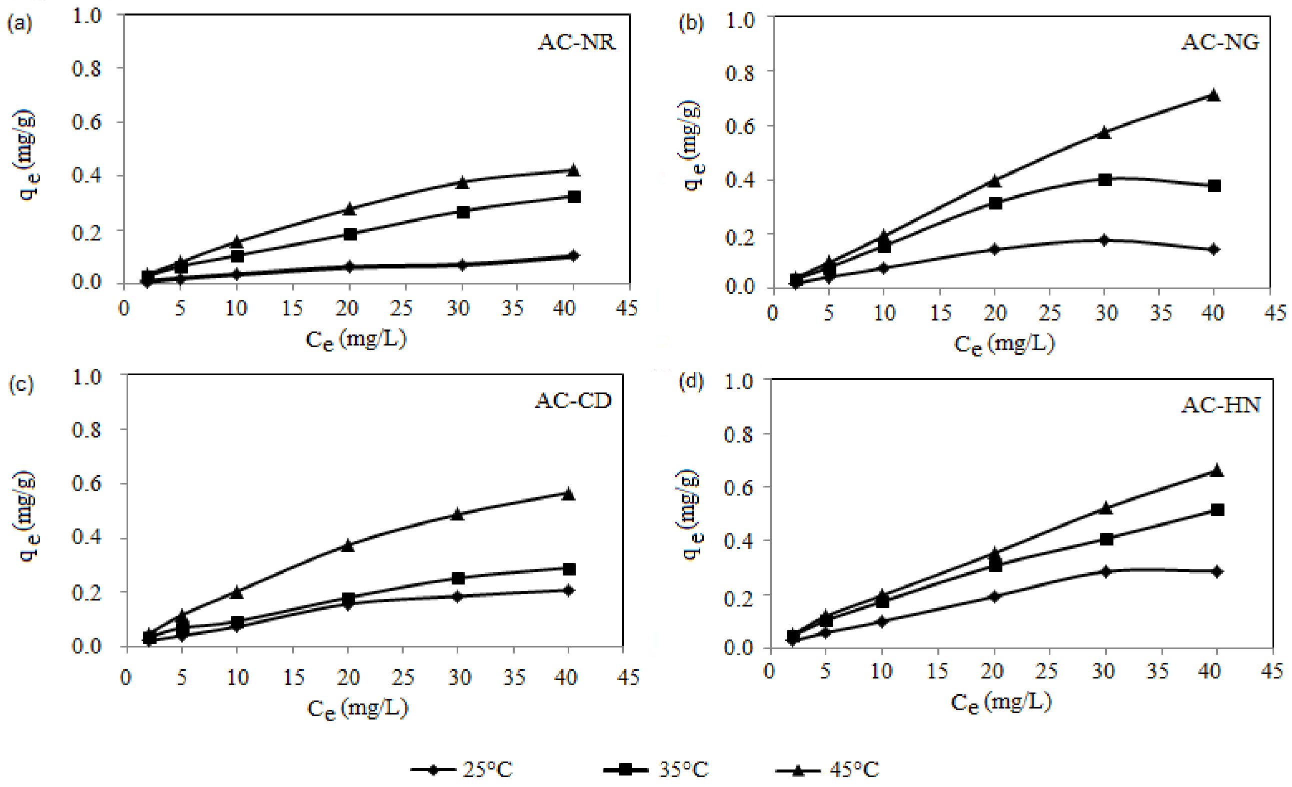

**Figure 1.** Effect of initial fluoride concentration and temperature onto fluoride adsorption capacities (mg/g) of (**a**) AC-NR; (**b**) AC-NG, (**c**) AC-CD and (**d**) AC-HN.

### *3.2. Effect of pH*

Since the pH of aqueous solution is one of the key parameter of the fluoride adsorption, the effect of pH was studied at six pH value, viz., 4, 5, 6, 7, 8 and 9 under 25°C, 35°C and 45°C, while other important parameters were kept constant (initial fluoride concentration 5 mg/L, adsorbent dose 10 g/L, contact time 120 min). Figs. 2a-d presents the effect of initial pH value of aqueous solution on the capacity of the adsorbents. For all used activated carbons maximum adsorption capacities were noted at pH 5 at 45°C (AC-NR 0.422 mg/g; AC-NG 0.714 mg/g; AC-CD 0.567 mg/g AC-HN 0.662

mg/g), while the increase of the pH over 5 decreased the adsorption capacities of four tested activated carbons which is in accordance with the results of adsorption studies reported many authors [49] which explaining it with protonated active sites responsible for anion adsorption at the surface of activated carbons.

Authors also quoted that the decreasing of the fluoride amount adsorbed onto activated carbons under pH less than 5, is the result of the formation of neutral hydrogen fluoride, which is much less adsorbable than ionized $F^-$. At higher pH values (above 7) deprotonation of active sites at surface of activated carbons occurs which significantly reduce the amount fluoride binding onto adsorbent surface, and therefore causing the reduction of fluoride uptake by activated carbons at the alkaline pH range [49,51].

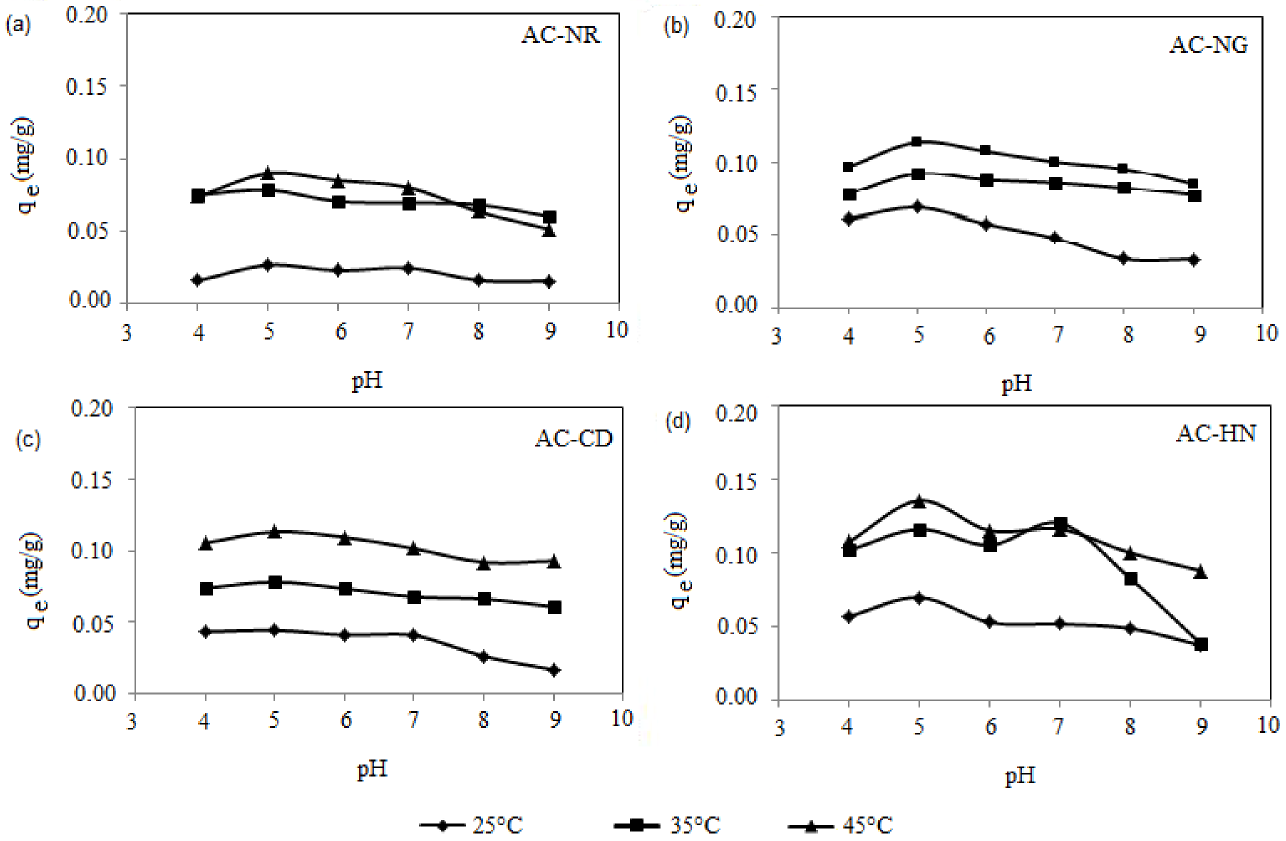

**Figure 2.** Effect of pH and temperature onto fluoride adsorption capacities (mg/g) of (**a**) AC-NR; (**b**) AC-NG; (**c**) AC-CD and (**d**) AC-HN.

### *3.3. Effect of adsorbent dosage*

The effect of AC dosages on the fluoride removal were examined using various adsorbent dosages (from 2 to 20 g/L) at 25°C, 35°C and 45°C. Obtained results are shown in Figs. 3a-d.

As shown in Fig. 3 the higher amount of fluoride was uptake when bituminous AC-HN dosages increased from 2 to 20 g/L at all temperatures (from 0.011 to 0.088 mg/L at 25°C; from 0.028 to 0.121 mg/L at 35°C and from 0.037 to 0.139 mg/L at 45°C) while when other three ACs were tested, the significant increasing of adsorption capacities were obtained when the adsorbent mass was increased up to 10 g/L suggesting that the adsorption process reached a dynamic equilibrium due to enough active adsorption sites for binding of fluoride ions at higher adsorbent dosages.

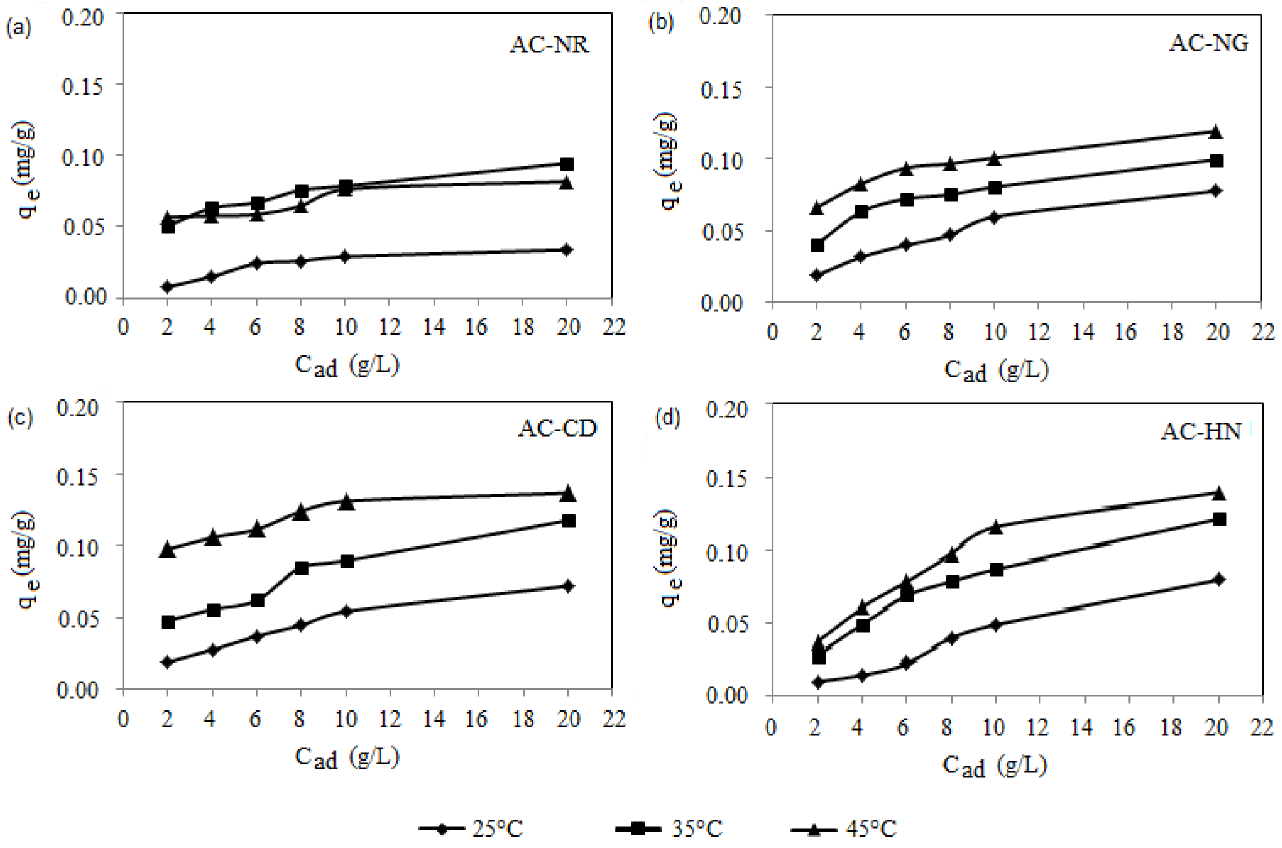

**Figure 3.** Effect of adsorbent dose and temperature on fluoride adsorption capacities (mg/g) of (**a**) AC-NR; (**b**) AC-NG; (**c**) AC-CD and (**d**) AC-HN.

### *3.4. Effect of contact time*

In order to define the effect of contact time on the fluoride adsorption onto ACs, batch adsorption tests were carried out at six time intervals using an initial fluoride concentration of 5 mg/L with 10 g/L of activated carbons, at pH 7±0.3 and under temperatures of 25°C, 35°C and 45°C and obtained results are presented in Figs. 4a-d.

As shown in Figs. 4a-d, fluoride uptakes increased with contact time at all tested temperature regimes, but after short period of rapid increasing of amount of adsorbed fluorides, adsorption process and fluoride uptake approached to almost constant values referring to achievement of equilibrium (the point when the curves appear nearly asymptotic to the time axis) which can be explained with the vacancy of all active sites on the adsorbents surfaces at the beginning of adsorption processes and its rapid decrease in near equilibrium phase when occupied most of the activated sites. For all tested activated carbons, the equilibrium time were obtained after 120 min of adsorption. Malakootian et al. [41] explained achievement of equilibrium with formation of monolayer of fluoride ions at the outer surface, as well as with its diffusion into inner surface.

Comparing the effect of temperature increasing with adsorbent dosage increasing, it can be observed in Fig. 1 that the stronger impact of temperature rinsing onto fluoride removal was observed when fluoride was removed by coal's activated carbon (AC-CD) while the weakest temperature influence was observed when peat-based activated carbon was used (AC-NR).

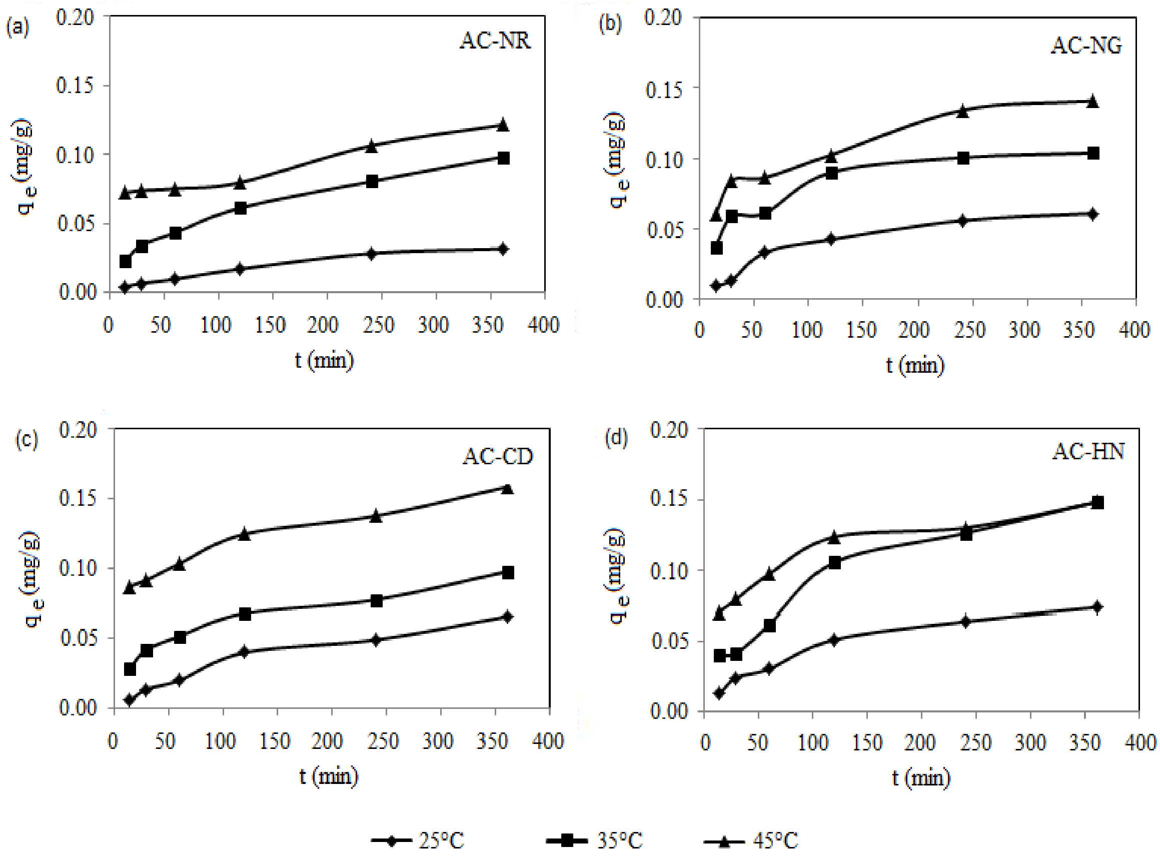

**Figure 4.** Effect of contact time and temperature on fluoride adsorption capacities (mg/g) of (**a**) AC-NR; (**b**) AC-NG; (**c**) AC-CD and (**d**) AC-HN.

### *3.5. Adsorption isotherms*

There are a several isotherm models which are usually employed for the characterization of the adsorption process and estimation of the adsorbent application's feasibility for the pollutant removal from aqueous solutions and the description of correlation among the pollutant concentration and it's binding onto the adsorbent surface at constant temperature [52]. Four of isotherm models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), are used for description of fluoride adsorption onto tested activated carbons at temperature regimes of 25°C, 35°C and 45°. Due to obtained results i.e. values of correlation coefficients ($R^2$) presented at Table 2, the validity of isotherm models is in the following order: Freundlich > Temkin > Langmuir > Dubinin-Radushkevich.

**Table 2.** Isotherm models for adsorption of fluoride onto AC-NR, AC-NG, AC-CD and AC-HN.

| **Isotherm** | **Parameter** | **25°C** | | | | **35°C** | | | | **45°C** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | AC-NR | AC-NG | AC-CD | AC-HN | AC-NR | AC-NG | AC-CD | AC-HN | AC-NR | AC-NG | AC-CD | AC-HN |
| **Langmuir** | $q_m$ (mg/ g) | 0.184 | 0.242 | 0.424 | 0.706 | 0.616 | 0.847 | 0.492 | 1.010 | 0.959 | 1.392 | 1.122 | 1.632 |
| | $K_L$ (L/ mg) | 0.026 | 0.054 | 0.027 | 0.020 | 0.028 | 0.028 | 0.036 | 0.027 | 0.023 | 0.005 | 0.030 | 0.018 |
| | $R^2$ | 0.883 | 0.854 | 0.879 | 0.858 | 0.933 | 0.806 | 0.844 | 0.952 | 0.979 | 0.709 | 0.992 | 0.857 |
| | | | | | | | | | | | | | |
| **Freundlich** | $n$ | 1.319 | 1.399 | 1.305 | 1.210 | 1.302 | 1.205 | 1.482 | 1.280 | 1.217 | 1.078 | 1.273 | 1.209 |
| | $K_F$ (mg/g)(L/mg)$^{1/n}$ | 0.006 | 0.014 | 0.014 | 0.017 | 0.021 | 0.025 | 0.025 | 0.033 | 0.025 | 0.027 | 0.038 | 0.036 |
| | $R^2$ | 0.994 | 0.953 | 0.987 | 0.992 | 0.991 | 0.975 | 0.989 | 0.998 | 0.994 | 0.990 | 0.994 | 0.998 |
| | | | | | | | | | | | | | |
| **Temkin** | $A_T$ (L/ g) | 0.520 | 0.659 | 0.548 | 0.518 | 0.576 | 0.582 | 0.634 | 0.600 | 0.560 | 0.482 | 0.633 | 0.568 |
| | $B_T$ | 0.029 | 0.052 | 0.065 | 0.012 | 0.095 | 0.131 | 0.082 | 0.019 | 0.131 | 0.212 | 0.169 | 0.024 |
| | $R^2$ | 0.906 | 0.896 | 0.931 | 0.915 | 0.929 | 0.931 | 0.900 | 0.919 | 0.946 | 0.834 | 0.945 | 0.891 |
| | | | | | | | | | | | | | |
| **Dubinin-Radushkevich** | $q_m$ (mg/ g) | 0.179 | 0.119 | 0.131 | 0.179 | 0.196 | 0.265 | 0.176 | 0.298 | 0.261 | 0.353 | 0.350 | 0.362 |
| | $K_{DR}$ (mol$^2$/kJ) | $2 \cdot 10^{-6}$ | $2 \cdot 10^{-6}$ | $2 \cdot 10^{-6}$ | $2 \cdot 10^{-6}$ | $1 \cdot 10^{-6}$ | $1 \cdot 10^{-6}$ | $1 \cdot 10^{-6}$ | $1 \cdot 10^{-6}$ | $1 \cdot 10^{-6}$ | $1 \cdot 10^{-6}$ | $1 \cdot 10^{-6}$ | $1 \cdot 10^{-6}$ |
| | $R^2$ | 0.732 | 0.784 | 0.694 | 0.731 | 0.769 | 0.762 | 0.678 | 0.755 | 0.764 | 0.707 | 0.776 | 0.746 |

Freundlich adsorption isotherm mathematically describes adsorption process as ions binding onto a heterogeneous adsorbent's surface suggesting a multilayer adsorption, exponentially distribution of active sites onto adsorbent surface and its energy adsorbent surface. The Freundlich isotherm was commonly presented as follows [53]:

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (2)$$

or linearized as:

$$\ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \qquad (3)$$

where $q_e$ is the milligrams of fluoride adsorbed per grams of the adsorbent at equilibrium (mg/g) and $C_e$ is the equilibrium concentration of fluoride solution (mg/L). The Freundlich adsorption constants $K_F$ and $n$ (as $1/n$) presents the adsorption capacity (mg/g) and intensity of the adsorption or surface heterogeneity. The value of $1/n$ is also related with a measure of the relative magnitude and diversity of energies related with an adsorption process and adsorption process is favorable when the value of $1/n$ lies between 0.1 and 1 i.e. when the value of $n$ is in the range between 1 and 10. In all conducted experiments $n$ is in the range between 1.078 and 1.399 which suggesting that the fluoride adsorption is favorable.

The $K_F$ present the adsorption capacity of adsorbent due to Freundlich isotherm model and from data presented at Table 2 it can be observed that adsorption capacities for tested ACs increases with increasing of the temperatures. All results of adsorption experiments fitted well with Freundlich isotherm model since the correlation coefficients ($R^2$) were between 0.953 and 0.998. The adsorption capacities due to Freundlich isotherm model of tested ACs were in followed order: AC-NH > AC-CD > AC-NG > AC-NR at 25°C, AC-HN > AC-CD > AC-NG > AC-NR at 35°C and AC-CD > AC-HN > AC-NG > AC-NR at 45°C.

Fig. 5 presents the Freundlich isotherms for four tested activated carbons i.e. amount of fluoride adsorbed onto various activated carbons as a function of equilibrium concentration in the aqueous solution at 25°C, 35°C and 45°C. Among tested activated carbons, the highest adsorption capacity for fluoride ions, expressed Freundlich constant at 25°C and 35°C had AC-HN ($K_F$=0.017;

$K_F$=0.033), while at 45°C the highest $K_F$ was obtained when AC-CD was used ($K_F$=0.038). The strongest positive effect of temperature onto adsorption capacity was noted when AC-NR was used for fluoride adsorption since increase of temperature increased $K_F$ almost four times i.e. from 0.006 at 25°C to 0.025 at 45°C (Fig. 5a). Although AC-HN shown the highest adsorption capacities at 25°C and 35°C, increase of temperature from 25°C to 45°C increased its $K_F$ only from 0.017 to 0.036 (Fig.5d).

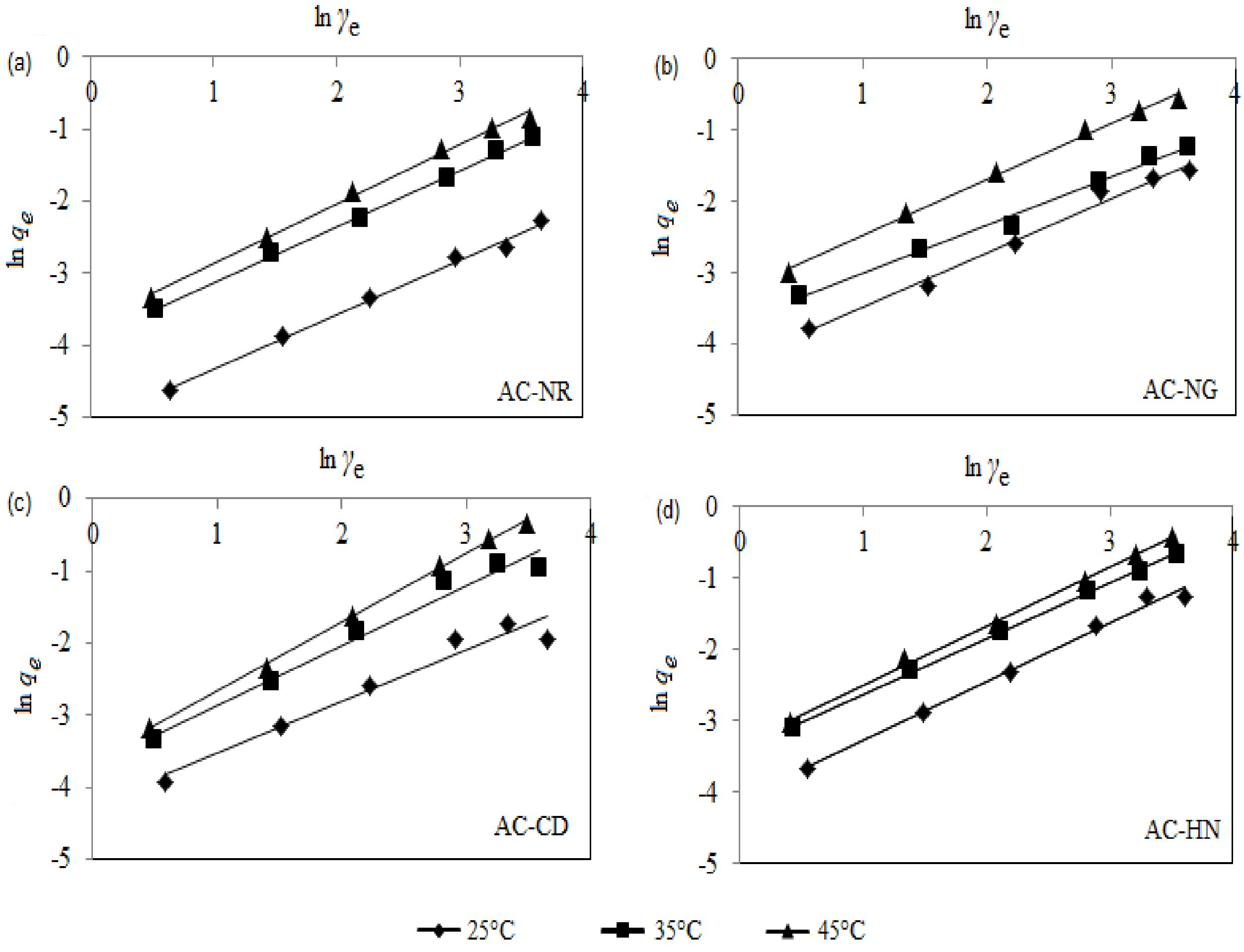

**Figure 5.** Freundlich isotherms for fluoride adsorption onto (a) AC-NR; (b) AC-NG; (c) AC-CD and (d) AC-HN.

### *3.6. Kinetic models*

The diffusion processes and fluoride uptake onto AC-NR, AC-NG, AC-CD and AC-HN at 25, 35°C and 45°C were studied using solution with initial fluoride concentration of 5 mg/L, adsorbent dose 10 g/L and pH 7±0.3. Obtained experimental data were submitted to four kinetic models: pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich model, and values of characteristic parameters and values of correlation coefficient ($R^2$) obtained from the slope and intercept of linear plots are shown at Table 3.

**Table 3.** Kinetic models for adsorption of fluoride onto AC-NR, AC-HG, AC-CD and AC-HN

| **Kinetic model** | **Parameter** | **25°** | | | | **35°C** | | | | **45°C** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | AC-NR | AC-NG | AC-CD | AC-HN | AC-NR | AC-NG | AC-CD | AC-HN | AC-NR | AC-NG | AC-CD | AC-HN |
| **Pseudo-first order** | $q_{m1}$ (mg/g) | 0.035 | 0.059 | 0.062 | 0.070 | 0.079 | 0.078 | 0.072 | 0.077 | 0.102 | 0.097 | 0.076 | 0.125 |
| | $k_1$ (g/mg min) | 0.009 | 0.010 | 0.006 | 0.008 | 0.006 | 0.011 | 0.006 | 0.007 | 0.005 | 0.011 | 0.006 | 0.006 |
| | $R^2$ | 0.972 | 0.991 | 0.961 | 0.968 | 0.998 | 0.986 | 0.934 | 0.975 | 0.892 | 0.951 | 0.979 | 0.903 |
| | | | | | | | | | | | | | |
| **Pseudo-second order** | $q_{m2}$ (mg/g) | 0.049 | 0.084 | 0.104 | 0.099 | 0.115 | 0.115 | 0.113 | 0.156 | 0.127 | 0.153 | 0.164 | 0.180 |
| | $k_2$ (g/mg min) | 0.104 | 0.095 | 0.032 | 0.064 | 0.106 | 0.181 | 0.126 | 0.077 | 0.231 | 0.243 | 0.217 | 0.211 |
| | $R^2$ | 0.948 | 0.974 | 0.908 | 0.886 | 0.976 | 0.996 | 0.953 | 0.973 | 0.974 | 0.989 | 0.990 | 0.993 |
| | | | | | | | | | | | | | |
| **Intra-particle diffusion** | $k_i$ (mg/g min) | 0.002 | 0.003 | 0.003 | 0.004 | 0.003 | 0.004 | 0.004 | 0.005 | 0.005 | 0.005 | 0.005 | 0.007 |
| | C | 0.003 | 0.002 | 0.009 | 0.002 | 0.006 | 0.003 | 0.012 | 0.007 | 0.053 | 0.005 | 0.068 | 0.056 |
| | $R^2$ | 0.987 | 0.943 | 0.982 | 0.943 | 0.997 | 0.899 | 0.957 | 0.969 | 0.914 | 0.959 | 0.989 | 0.951 |
| | | | | | | | | | | | | | |
| **Elovich** | α (mg/g min) | 0.576 | 0.559 | 0.511 | 0.557 | 0.602 | 0.609 | 0.661 | 0.549 | 0.692 | 0.808 | 0.797 | 0.996 |
| | β (g/mg) | 111.1 | 57.47 | 54.05 | 50.51 | 67.57 | 46.30 | 47.85 | 40.32 | 43.48 | 40.00 | 44.84 | 27.40 |
| | $R^2$ | 0.936 | 0.960 | 0.960 | 0.918 | 0.965 | 0.960 | 0.911 | 0.945 | 0.772 | 0.952 | 0.949 | 0.975 |

Values of correlation coefficient ($R^2$) indicated that all four kinetics models fitted obtained data very well (correlation coefficient for pseudo-first-order ranged from 0.892 to 0.998; for pseudo-second-order from 0.886 to 0.996; for intra-particle diffusion from 0.899 to 0.997 and for Elovich model from 0.772 to 0.975), but, in general, the highest values of $R^2$ suggest that intra-particle diffusion kinetic model is most suitable for description of fluoride adsorption onto used activated carbons.

Due to intra-particle diffusion model the adsorbate moves from the solution phase to the surface of the adsorbent particles via several steps and the overall adsorption process may be controlled by one or more steps (e.g., film or external diffusion, pore diffusion surface diffusion and adsorption on the pore surface, or a combination or more than one step).

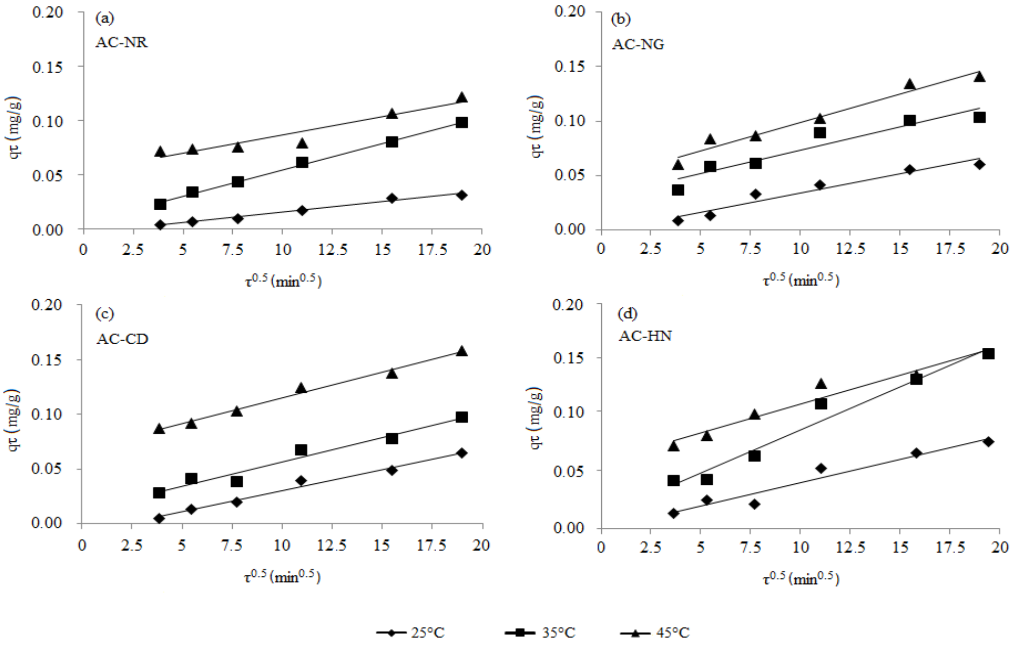

**Figure 6**. Intra-particle diffusion kinetic models of fluoride adsorption onto (a) AC-NR; (b) AC-NG; (c) AC-CD and (d) AC-HN.

The possibility of intra-particle diffusion was explored using the intra-particle diffusion model [53]:

$$q_t = k_{id} t^{1/2} + C \qquad (4)$$

where $k_{id}$ is the intra-particle (pore) diffusion rate constant (mg/g min) and $C$ is the intercept that gives an idea about the thickness of the boundary layer. The larger the value of $C$, the greater the boundary-layer effect.

From Table 3 it can be observed that the increasing of temperature increased the values of intra-particle diffusion rate constant during all conducted experiments. The highest value of $k_{id}$ of 0.007 mg/g min was detected when AC-HN was used at 45°C, and the lowest $k_{id}$ of 0.002 mg/g min was detected when AC-NR was tested at 25°C. Fig. 6 present intra-particle diffusion kinetic models of fluoride adsorption onto four tested activated carbons.

## 4. CONCLUSIONS

The results indicate that fluoride uptake from water by commercial activated carbons (AC-NR, AC-NG, AC-CD and AC-HN) depended on the pH, contact time, initial fluoride concentration, dosage of the adsorbents and temperature. The highest fluoride removals were obtained at 45°C and at pH 5 in all experimental conditions while the progressive increase of adsorbent dosage did increased fluoride uptake only up to 10 mg/L. Initial fluoride concentration also shown strong effect on fluoride adsorption and higher adsorption capacities were obtained when fluoride solutions with 40 mg/L were used (maximum at 45°C as follows: AC-NR 0.422 mg/g; AC-NG 0.714 mg/g; AC-CD 0.567 mg/g AC-HN 0.662 mg/g).

Fluoride adsorption followed Freundlich isotherm model better than Langmuir, Temkin and Dubinin-Radushkevich isotherm models. The validity of isotherm models based on the coefficient correlation values were in the following order: Freundlich > Temkin > Langmuir > Dubinin-Radushkevich. Among tested activated carbons the higher adsorption capacity for fluoride uptake at 25° and 35°C demonstrate AC-HN (0.017 and 0.033 mg/g), while at 45°C the higher adsorption capacity shown AC-CD (0.038 mg/g).

Kinetic study results indicate that the adsorption process followed intra-particle diffusion kinetic model. In all experiments temperature increasing elevated the value of intra-particle diffusion rate constants. The highest value of $k_{id}$ of 0.007 mg/g min was noted at 45°C when AC-HN was tested. Results from this study demonstrated potential utility of tested activated carbons as a viable technology for fluoride removal from drinking water.

## References

1. Y. Tang, X. Guan, J. Wang, N. Gao, M.R. McPhail and C.C. Chusuei, *J. Hazard. Mater.* 171 (2009) 774
2. L. Valdez-Jiménez,C. Soria Fregonzo, M.L. Miranda Beltran, O. Gutierrez Coronado and M.I. Perez Vega, *Neurologia* 26 (2011) 297

3. T. Wajima, Y. Umeta, S. Narita and K. Sugawara, *Desalination* 249 (2009) 323
4. X. Fan, D.J. Parker and D.J. Smith, *Water Res.*37 (2003) 4929
5. Y. Li, P. Zhang, Q. Du, X. Peng, T. Liu, Z. Wang, Y. Xia, W. Zhang, K. Wang, H. Zhu and D. Wu, *J. Colloid Interf. Sci.* 363 (2011) 348
6. P.T.C. Harrison, *J. Fluorine Chem.* 126 (2005) 1448
7. Meenakshi and R.C. Maheshwari, *J. Hazard. Mater.* 137 (2006) 456
8. World Health Organization, *International Standard for drinking water*, 3rd ed., WHO; Geneva (2008)
9. W.X. Gong, J.H. Qu, R.P. Liu and H.C. Lan, *Chem. Eng. J.* 189–190 (2012) 126
10. M. Islam, P.C. Mishra and R. Patel, *Chem. Eng. J.* 166 (2011) 978.
11. I. Abe, S. Iwasaki, T. Tokimoto, N. Kawasaki, T. Nakamura and S.Tanada, *J. Colloid Interf. Sci.* 275 (2004) 35
12. S. Saha, *Water Res.* 27 (1993) 1347
13. M.G. Sujana, R.S. Thakur, S.N. Das and S.B. Rao, *Asian J. Chem.* 4(1997) 561
14. V. Khatibikamal, A. Torabian, F. Janpoor and G. Hoshyaripour, *J. Hazard. Mater.* 179 (2010) 276
15. P.I. Ndiaye, P. Moulin, L. Dominguez, J.C. Millet and F. Charbit, *Desalination* 173 (2005) 25
16. A.J. Karabelas, S.G. Yiantsios, Z. Metaxiotou, N. Andritsos, A. Akiskalos, G. Vlachopoulos and S. Stavroulias, *Desalination* 138 (2001) 93
17. P. Sehn, *Desalination* 223 (2008) 73
18. A. Lhassani, M. Rumeau, D. Benjelloun and M. Pontie, *Water Res.* 35 (2001) 3260
19. K. Hu and J.M. Dickson, *J. Membrane Sci.* 279 (2006) 529
20. S.X. Feng, P.G. Chen and C.G. Hua, *Chem. Eng. Sci.* 58 (2003) 987
21. N. Kabay, O. Arar and F. Acar, *Desalination* 223 (2008) 63
22. E. Erdem, T. Ali and C. Yunus, *Sep. Purif. Technol.* 64 (2008**)** 147
23. C.Y. Hu, S.L. Lo and W.H. Kuan, *Water Res.* 39 (2005) 895
24. N.I. Chubar, V.F. Samanidou, V.S. Kouts, G.G. Gallios, V.A. Kanibolotsky, V.V. Strelko and I.Z. Zhuravlev, *J. Colloid Interf. Sci.* 291 (2005) 67
25. L. Ruixia, G. Jinlong and T. Hongxiao, *J. Colloid Interf. Sci.* 248 (2002) 268
26. K. Babaeivelni and A.P. Khodadoust, *J. Colloid. Interf. Sci.* 394 (2013) 419
27. P. Loganathan, S. Vigneswaran, J. Kandasamy and R. Naidu, *J. Hazard. Mater.* 248-249 (2013) 1
28. G. Alagumuthu, V. Veeraputhirin and R. Venkataraman, *Arch. App. Sci. Research.* 2(4) 2010, 170
29. A.A.M. Dalifullah, S.M. Yakout and S.A. Elreefy, *J. Hazard. Mater.* 147 (2007) 633
30. S.S. Tripathy and A.M. Raichur, *J. Hazard. Mater.* 153 (2008) 1043
31. S.M. Maliyekkal, S. Shukla, L. Philip and I.M. Nambi, *Chem. Eng. J.* 140 (2008) 183
32. A. Teutli-Sequeira, M. Solache-Ríos and P. Balderas-Hernández, *Water Air Soil Poll.* 223 (2011) 319
33. H.-X. Wu, T.-J. Wang, L. Chen, Y. Jin, Y. Zhang and X.-M. Dou, *Ind. Eng. Chem. Res.* 48 (2009) 4530
34. J. Wang, D. Kang, X. Yu, M. Ge and Y. Chen, *Chem. Eng. J.* 264 (2015) 506
35. Y. Jia, B.-S. Zhu, Z. Jin, B. Sun, T. Luo, X.-Y. Yu, L.-T. Kong and J.-H. Liu, *J. Colloid Interf. Sci.* 440 (2015) 60
36. X. Zhao, L. Zhang, P. Xiong, W. Ma, N. Qian and W. Lu, *Micropor. Mesopor. Mat.* 201 (2015) 91
37. C. Sairam Sundaram, N. Viswanathan and S. Meenakshi, *Bioresourse Technol.* 99 (2008) 8226
38. N. Viswanathan and S. Meenakshi, *J. Fluorine Chem.* 129 (2008) 645
39. C.M. Vivek Vardhan and J. Karthikeyan, *Int. Water Tech. J.* 1 (2011) 120
40. A.K. Yadav, C.P. Kaushik, A.K. Haritash, A. Kansal and N. Rani, *J. Hazard. Mater.* 128 (2006) 289
41. M. Malakootian, M. Moosazadeh, N. Yousefi and A. Fatehizadeh, *African J. Envir. Sci. Tech.* 5 (2011) 299

42. N. Viswanathan and S. Meenakshi, *J. Hazard. Mater.* 176 (2010) 459
43. S. Jagtap, D. Thakre, S. Wanjari, S. Kamble, N. Labhsetwar and S. Rayalu, *J. Colloid Interf. Sci.* 332 (2009) 280
44. P.K. Gogoi and R. Baruah, *Indian J. Chem. Tech.* 15 (2008) 500
45. M.S. Onyango, Y. Kojima, O. Aoyi, E.C. Bernardo and H. Matsuda, *J. Colloid Interf. Sci.* 279 (2004) 341
46. Y. Sun, Q. Fang, J. Dong, X. Cheng and J. Xu, *Desalination* 227 (2011) 121
47. S. Wang and P. Peng, *Chem. Eng. J.* 156 (2010) 11
48. K.A. Emmanuel, K.A. Ramaraju, G. Rambabu and A. Veerabhadra Rao, *Rasayan J. Chem.* 1 (2008) 802
49. M. Habuda-Stanić, M. Ergović Ravančić and A. Flanagan, *Materials* 7(9) (2014) 6317
50. H. Paudyal, B. Pangeni, K.N. Ghimire, K. Inoue, K. Ohto, H. Kawakita and S. Alam, *Chem. Eng. J.* 195–196 (2012) 289
51. Y. Hanumantharao, M. Kishore and K. Ravindhranath, *Int. J. Plant Animal Envir. Sci.* 1 (2011) 209
52. X. Xu, Q.L.H. Cui, J. Pang, L. Sun, H. An and J. Zhai, *Desalination* 272 (2011) 233
53. V. Sivasankar, T. Ramachandramoorthy and A. Chandramohan, *J. Hazard. Mater.* 177 (2010) 719