RESEARCH ARTICLE

ADSORPTION STUDIES OF CARBONIZED *SIDA RHOMBIFOLIA* SAMPLE IN DEFLUORIDATION OF POTALE WATER

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ABSTRACT

The present study demonstrates the development and application of plant based carbon sample (oxidised with nitric acid) prepared from *Sida Rhombifolia* adsorbent for the removal of fluoride in aqueous media. Activated carbon characterized texturally and chemically before and after treatment, using surface area determination in the BET model, SEM-EDX and XPS techniques. The adsorption capacity and the kinetics of Fluoride ion removal was determined by batch adsorption technique. The study was carried out to analyze the defluoridation by contact time variation, adsorbate concentration and effect of pH. The analysis of the isotherm equilibrium data using the Langmuir and Freundlich equations by linear methods showed that the data fitted better with Langmuir model ($R^2 > 0.967$) and Pseudo-second-order kinetic model best fit for the current adsorption study. Carbonized *Sida Rhombifolia* oxidized sample (SRC) showed a high affinity for fluoride ions compared with other conventional adsorbents, therefore, it can be considered as a potentially good and low-cost bio-adsorbent for removal of fluoride from water compared to other bio-adsorbent.

Key Words: Activated carbon-Surface characterization-Defluoridation-Isotherm study-Kinetics

1. INTRODUCTION

Adsorption is a widely used as an effective physical method of separation in order to elimination or lowering the concentration of wide range of dissolved pollutants (organics, inorganic) in an effluent. It is big news that activated carbon (AC) is a well-known adsorbent that can be used efficiently for removal of a broad spectrum of pollutants from air, soil and liquids.

Activated carbons are carbonaceous materials that can be distinguished from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces[1]. These materials are characterized by their extraordinary large specific surface areas, well-developed porosity and tunable surface-containing functional groups. For these reasons, activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water and wastewater.

The high cost of commercial activated carbon restricts its application, so, there is need to undertake studies to substitute the costlier commercial activated carbon with the unconventional, low cost and locally available

agricultural waste based adsorbents[5]. India is an agricultural country and generates considerable amount of agricultural wastes. Disposal of agricultural by-products is a major economic and ecological issue these days. The conversion of by-products to adsorbents, such as activated carbon, represents a possible outlet. Agricultural by-products are renewable sources of raw materials for activated carbon production because the development of methods to utilize the waste materials is greatly desired and production of activated carbons from waste is an interesting possibility. Successful studies on these materials could be beneficial to the developing countries and could be easily incorporated in development of appropriate technologies[8]. Activated carbons are produced from different precursors, such as wood, peat, brown coal, lignite, various types of hard coal, polymers, agricultural byproducts, and fruit shells[9]. Plant biomass is one of the most promising materials of activated carbons (Discussed in previous chapter). The plant materials can be classified into four types: agricultural waste, wood, bamboo and lignin. The method of preparation activated carbons includes two steps: carbonization and activation. Chemical activation, physical activation and steam-pyrolysis activation are three common activation methods. The last two methods are clean and environmentally-friendly, chemical activation is mature and widely used. Typically, all organic precursors can be converted into activated carbons; however, in most cases, it requires the usage of an activation agent and only a few are commercially attractive. The properties of the final product depend on the nature of raw material used, the nature of activating agent, and the conditions of activation process.

Activated carbon is widely used for the purpose due to the large surface area available for adsorption as a result of its high degree of micro porosity. The presence of activating agents and carbonization conditions influenced the development of pore structures. These materials are characterized by their extraordinary large specific surface areas, well-developed porosity and tunable surface containing functional groups. The surface oxygen functional groups can be easily introduced to the carbon by different activation methods including dry and wet oxidizing agents like nitric acid (HNO_3). A modified activated carbon containing different functional groups could be used for technological applications. The surface groups can be characterized and identified by more sophisticated techniques such as XPS and TGA-DTA, SEM-EDX etc will contribute significantly to a more precise knowledge about these surface chemical groups.

In order to reduce the production costs, several manufacturers use precursor's like agriwastes and its byproducts. The literature survey clearly indicated the carbons obtained from dried plant biomass carbon (Aerial Parts) of *Sida rhombifolia* (arrowleaf sida) (in the following text this materials is indicated as 'SRC') is not used as adsorbent for defluoridation of water so far. Hence the author has prepared a low cost carbon from the above raw material and has characterized their physical properties. With the aim of defluoridating material development, characteristic properties of the adsorbent viz., Surface functional groups, surface area etc., which are significant in adsorption mechanisms, are determined. This paper deals with the preparation of activated carbons from the raw material *SRC*, surface characterization with sophisticated instrumentation techniques before and after defluoridation and results.

2. MATERIALS AND METHOD

2.1 Raw material for the preparation of adsorbent: *Sida rhombifolia* mass of plant without flowers was collected in bulk amount, cut into small pieces, dried in sunlight until green colour vanished. Then the material was carbonized in muffle furnace (in absence of air) for about 2 hours at 500^oC. After carbonization, carbon obtained was poured in double distilled water, filtered, washed with cold double distilled water several times and dried in an air oven at 110^oC for overnight. Then, the carbon was sieved into desired particle sizes (Average size 75μ approximately). Thus obtained carbon product was treated with 0.5 M Nitric acid oxidation. Then the acid treated product was filtered, thoroughly washed with hot distilled water to remove acidity and then thermally activated at 120^oC for 1 hr in an air oven. After liquid phase oxidation each carbon

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was sieved into a particle size in the range of 70-120 mesh sizes Photographic image of prepared active carbons are shown in Figure 1.

Figure 1: Raw material for the synthesis of SRC activated carbon from *Sida Rhombifolia*

2.2 Chemical characterization: Surface chemical reactions explained by X-ray photoelectron spectroscopy (XPS) and Energy dispersive x-ray difractrometric (EDX) method equipped with SEM.

2.2.1 SEM-EDX: The surfaces of the powder carbonaceous materials have been stubbed using the double-sided adhesive carbon tape. Samples are coated with the help of platinum coater [JOEL Auto fine coater model, JFC –1600 auto fine coater, Coating time is 120 sec with 20mA] and deposited with a thin layer of platinum on the sample. The microphotographs of these samples were recorded using SEM JEOL model, JSM-5600 equipped with EDX Analyzer, an accelerating voltage of 5 kV, at high vacuum mode. The maximum magnification possible in the equipment is 3,00,000 times with a resolution of 3 nm, typically setting at various magnifications for all the samples of study.

2.2.2 X-ray Photoelectron Spectroscopy (XPS): The prepared activated carbon samples were analyzed on KRATOS AXIS 165 under 10^{-9} torr vacuum with dual Al-Mg-anodes using Mg Kα radiation. Pass energy of 80eV was used in recording the spectra. X-ray excitation source Mg K (1253.06 eV) and hemi spherical electron analyzer. The samples were dried at 283 k for 24 h before the analysis. Survey and high resolution narrow scans were recorded for C1s, O 1s, and F 1s photoelectron peaks. The atomic concentrations were calculated from the photoelectron peak areas, using Shirley background subtraction20 and sensitivity factors were taken

from PHI21. The obtained XPS spectra were fitted using a nonlinear square method with the convolution of Lorentzian and Gaussian functions after the polynomial background subtraction from the raw data.

2.2.3 Surface area: The BET surface area and pore structure characteristics of the carbon samples were determined by Nitrogen adsorption at 77 K, using Quanta chrome NOVA 2200e, surface area and pore size analyzer. Prior to adsorption measurements, respective carbon samples were degassed at 150˚C for a period of 4 hrs, in nitrogen atmosphere[18]. The S_{BET} values of the samples were calculated by the Brunauer, Emmett, and Teller (BET) method using adsorption isotherms in the range 0.05 ≤ relative pressure (P/Po) ≤ 0.30.

2.2.4 The total pore volume was estimated by BJH Method, from the amount of nitrogen adsorbed at P/P^o 0.95. The micropores volume and average pore width was determined by Dubinin- Radushkevich (DR) equation from the value of nitrogen (77K) adsorption isotherm. The DA plot method was used for the determination of pore diameter. The volume of Mesopores was calculated by subtracting the volume.

2.2.5 Fluoride Adsorption Study: In the present study, the prepared SRC sample utilized for the removal of fluoride from its aqueous solution. The sorption isotherm and kinetics experiments were performed by batch adsorption experiments and were carried out by mixing 0.5 g (obtained by the study of effect of adsorbent dose) of sorbent with 100 mL of water containing sodium fluoride at 10 mg/L as initial fluoride concentration. The mixture was agitated in a thermostatic shaker at a speed of 250 rpm at room temperature. The defluoridation studies were conducted for the optimization of various experimental conditions like contact time, initial fluoride concentration, and fluoride uptake with fixed dosage by varying pH. All of the experiments were carried out at 30˚C ± 1˚C temperature. Fluoride ion concentration was measured with an automatic ion analyzer using the equipment model Orion™ 2109XP Fluoride Analyzer and the pH of the solution was measured by Elico model selective equipment. All other water quality

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parameters were analyzed by using standard methods.

The percentage removal of F⁻ ion and amount adsorbed (in mg/g) were calculated using the following relationships:

$$\% \, Removal = \frac{C_i - C_f}{C_i} \times 100$$

$$q_e = \frac{[(C_i - C_f)V]}{m}$$

where, q_e (g/g) is the solid phase concentration, C_i (g/L) is the initial concentration of fluoride in solution, C_f (g/L) is the final concentration of fluoride in treated solution; V (L) is the volume of the solution, and m (g) is the weight of the adsorbent sample. Blanks without F- ions were used for each series of experiments as controls. All the experiments were performed in triplicate. The linear regression computer program with one independent variable was used for slope and statistical analyses of the data.

3.0 Results and Discussion

3.1 Surface and elemental analysis (EDX): SEM-EDX pictures in Figure 2 (a & b) (before and after defluoridation) of AC's provide information about the distribution of fluoride ion complexes. These pictures present results from the characterization of porous texture and surface chemical elements localizations for the material used. For the elemental microanalysis of SRC sample was analyzed by EDX. These spectra show the presence of C, O, Cl, N and Ca (table 1) and after adsorption F is appeared on adsorbent sample.
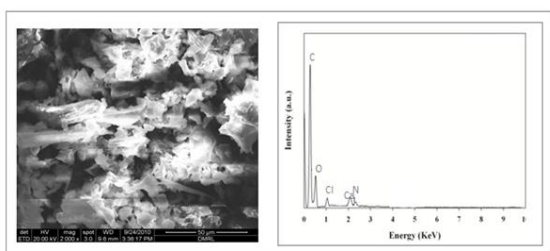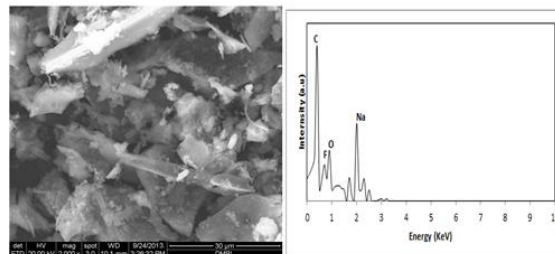

Figure 2(a): SEM-EDX analysis of SRC sample before defluoridation

Table 1 (a): EDX Analysis of SRC sample after Defluoridation

Element	Weight%	Atomic %
C K	80.5	83.5
O K	16.62	14.25
Cl K	0.62	0.24
Ca K	0.89	0.22
N K	1.37	1.64
Total	100	100

Figure 2(b): SEM-EDX analysis of SRC sample After defluoridation

Table 1 (b): EDX Analysis of SRC sample after Defluoridation

Element	Weight%	Atomic %
C K	81.31	78.8
O K	14.68	17.21
Na K	0.56	0.28
F K	1.24	1.05

3.2 X- ray Photoelectron Spectroscopy (XPS): XPS is an important surface sensitive tool for the characterization of surface properties of activated carbons which gives vital information from the outer most 3-4nm surface layers of carbon surfaces. This technique was employed with an aim to study the changes on the surface of the activated samples. The XPS survey spectra of the investigated activated carbons indicate the presence of three distinct peaks at 285 eV, 400 eV and 532 eV which can be attributed due to carbon, nitrogen and oxygen, respectively. The C 1s signal of all the samples consists of a major peak at 284.6 eV, which corresponds to a non-functionalized carbon that is the contributions of C as Csp^2 and Csp^3, belonging to the carbon skeleton of the material and the contributions of aliphatic Csp^3 that corresponds to hydrocarbons. The results could be resolved into five individual component peaks representing graphite carbon BE = 284.608 eV, carbon present in alcohol or ether groups 286.513 eV, carbonyl groups BE = 287.294 eV, carbonyl or ester groups BE = 289.410 eV and shake up satellite peaks due to Π-Π∗ transitions in aromatic rings BE = 291.493 eV. The high resolution survey scan for SRC before and after defluoridation shown in Figure 3
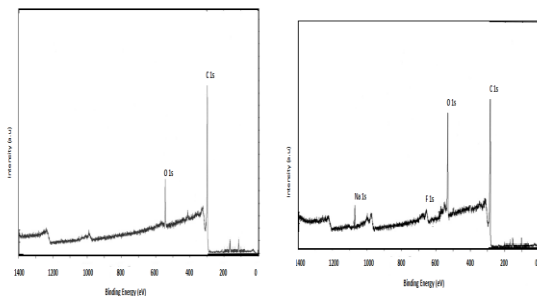
Figure 3: Survey scan of SRC before (left) and after defluoridation (right) in defluoridation process

The surface area and pore volume of activated carbon prepared under optimum conditions were 997 m^2/g during before defluoridation and it was reduces to 758.24 m^2/g after defluoridation indicating the occupying the surface area of adsorbent particle by adsorbate ions (Fluoride). Average pore radius was 9.24 A°. Due to the larger the specific surface area of the adsorbent, the better its adsorption performance as obtained literature[11].

3.4 Effect of contact Time

Contact time plays a very important role in adsorption dynamics. The effect of contact time on adsorption of fluoride onto SRC is shown in Figure 4. Batch adsorption studies using the concentrations 1.5 to 10 mg/L of fluoride solution with 4.0 g/L of the adsorbent were carried out at $30^oC\pm1$ as a function of time to evaluate the de-fluoridation and adsorption rate constants. The adsorption of fluoride increases with time and gradually attains equilibrium after 35 minutes. From Figure 4, the time to reach equilibrium conditions appears to be independent of initial fluoride concentrations. Therefore, 40 minutes was fixed as minimum contact time for the maximum de-fluoridation of the sorbents.
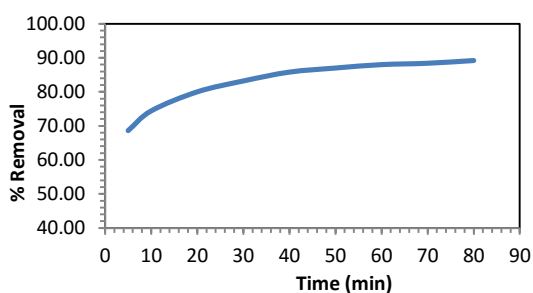

Figure 4: The effect of contact time on adsorption of fluoride onto SRC

Under shaken conditions, the sorption rapidly occurs normally by the diffusion process from the bulk to the surface and the adsorption of fluoride and was controlled by the adsorbent structure and chemical properties [1]. Adsorption of fluoride and was controlled by the adsorbent structure and chemical properties [1]. The F uptake capacity was very slow under static conditions because all the adsorbent sites were vacant. The solute concentration gradient was high and as a result, there was no relative movement between adsorbents and solutions. Later, the F uptake rate by adsorbent was decreased significantly due to the decrease in number of adsorption sites as well as fluoride concentration which supports the possible monolayer formation of fluoride ion on the outer surface [2].

3.5 Effect of initial concentration

The initial Fluoride ion concentration provides an important driving force to overcome resistant encountered when molecules are transferred between aqueous and solid phases [3]. Figure 5 shows that the capacity of the adsorbent material gets exhausted with increase in initial Fluoride ion concentration; this may be probably as a result of the fact that for a fixed adsorbent dose, the total available adsorption sites remain invariable for all the concentrations checked. With increasing concentration, the available adsorption sites become fewer and hence the percent removal of Fluoride ion is dependent upon the initial concentration [4].
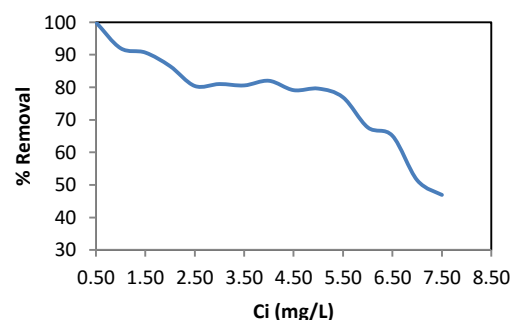

Figure 5: Variation of percent removal of fluoride with increasing the initial concentration

The effect of initial Fluoride ion concentration in the range of 0.5 to 8.0 mg/L Fluoride ion on adsorption efficiency onto SRC was investigated for adsorbents

at optimum conditions and is shown in Figure 5. It is observed from the figure that the percentage Fluoride ion removal decreased with the increase in initial concentration of Fluoride ion. For SRC adsorbent, the initial rate of adsorption is rapid in the first 15 minutes of contact time and it is greater for higher initial F- concentrations. Though the percent adsorption decreased with increase in initial Fluoride ion concentration, the actual amount of Fluoride ion adsorbed per unit mass of adsorbent increased with increase in Fluoride ion concentration in test solution.

There is a strong linear relationship between the equilibrium loading capacity and initial F- concentrations with correlation coefficients greater than 0.9 for SRC adsorbents. This result may indicate that there is a possibility to treat polluted water samples with relatively higher F- concentration, especially by making use of SRC and as adsorbent.

3.6 Effect of pH

To study the influence of solution pH on fluoride removal, the test solutions containing 5 mg/L of fluoride were adjusted to pH values of 4, 5, 6, 7, 8, and 10 using 1 N HCl and 1 N NaOH. Then, 4g/L of SRC sample was added to the test solutions separately and shaken for 30 min. Residual fluoride ion concentration was analyzed in each experiment.

The pH of the medium is one of the important parameters which significantly affects the fluoride adsorption. As can be seen in Fig. 6, the removal of fluoride decreases with increasing pH of the solution. An examination of the figure indicates that maximum fluoride removal had occurred in strongly acidic medium (pH 5-6) and fluoride adsorption decreases with increase in pH. However, at neutral pH (pH 6.5) fluoride removal is considerably high, of the order of 81%. In the alkaline range, the fluoride adsorption remains slow. The same trend has been observed for both the adsorbents at their corresponding optimized conditions of adsorbent dose and contact times. In the acidic medium, the surface of the adsorbent is highly protonated, and hence, more fluoride ions can be attracted toward the surface. That is, higher fluoride sorption rate in acidic medium is attributed to strong coulombic force of attraction between positively charged surface and negatively charged fluoride ion. The repulsion between negatively charged surface (deprotonated) and fluoride ions leads to comparatively low fluoride adsorption in alkaline medium. Similar mechanism for the effect of pH on fluoride adsorption has been indicated in the literature [5-7]. A pH of 6.5, which gives maximum fluoride removal, was taken as an optimal pH for application to real water samples.
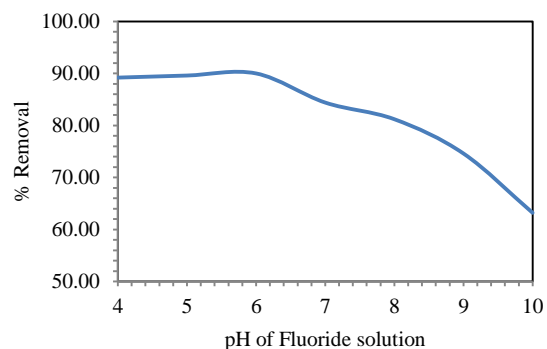

Figure 6: Variation of percent removal of fluoride with increasing the initial pH of adsorbate solution

4.0 Adsorption isotherms

Adsorption isotherms are essential for the description of how fluoride ion concentration will interact with prepared carbons and are useful to optimise the use of activated carbon as an adsorbent and as it provide an approximate estimation of the sorption capacity of the adsorbents.

4.1 Freundlich isotherm

The linearised Freundlich adsorption isotherm, which is of the from (8)

$\log (q_e) = \log K_f + (1/n) \log C_e$

Where, K_f and $1/n$ are the Freundlich constants, qe is the amount of fluoride adsorbed per unit weight of the adsorbent (in mg/g), and if $1/n < 1$ bond energies with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$, all surface sites are equivalent, related to sorption capacity and sorption intensity respectively.

4.2 Langmuir isotherm

The linear form of the Langmuir isotherm can be expressed as,

qe = a b Ce / (1 + b Ce),

where qe is the amount adsorbed (mg/g) and Ce is the equilibrium concentration of adsorbate (mg/L), a and b are the Langmuir constants related to capacity and energy of adsorption, respectively.

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Linear plots of Friundlich and Langmuir Plots at different fluoride concentrations are applied to confirm the applicability of suitable isotherm model for the removal of fluoride ions are shown in Figure 7(a&b) and the isotherm parameters along with the correlation coefficients (r-values) for adsorbents are presented in Table 3. The observed linear relationships as evidenced by r-values close to unity (0.96) confirm that Langmuir isotherm is more applicable.
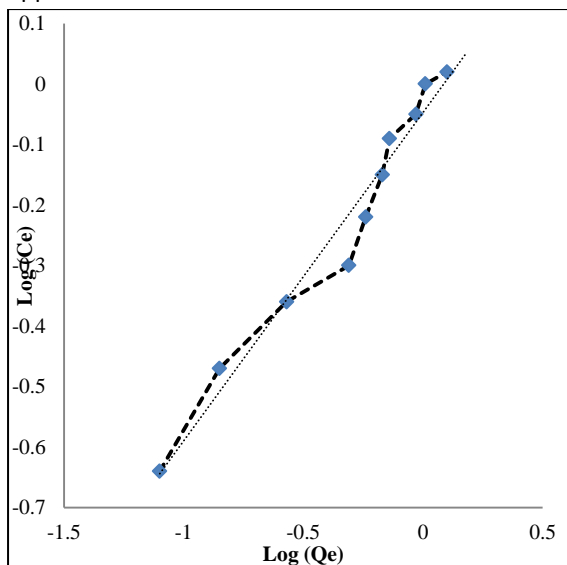

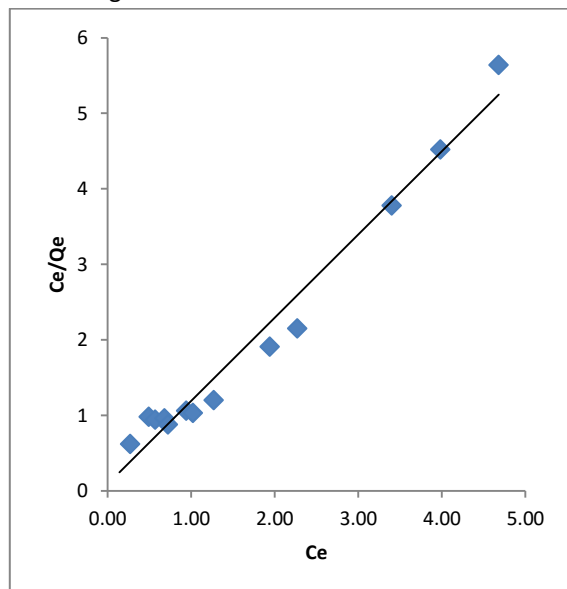Figure 7a: Freundlich Isotherm model

Figure7b: Langmuir isotherm for the removal fluoride by adsorption on SRC

The applicability of Langmuir isotherm model indicates the formation of monolayer coverage of adsorbate on outer surface of the adsorbent.

Further, the essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and describe the type of isotherm defined by;

$R_L = 1/ (1 + b\, C_i)$

Where, C_i is the initial concentration of fluoride (in mg/L) and 'b' is the Langmuir constant (in g/L). The separation factor R_L indicates the isotherm's shape and the nature of the adsorption process as unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irrereversible ($R_L = 0$). In the present study the values of RL (Table 3) being 0.28 for the adsorbent SRC indicating that the sorption process is favorable for all this low-cost adsorbent. Where *b* and C_i are terms appearing in Langmuir isotherm.

Table 2	Adsorption isotherm parameters	
Isotherm	Isotherm Parameter	Values
Freundlich isotherm	Intercept (K_f)	0.04
	Slope (1/n)	0.543
	Correlation coeff.(r)	0.947
	R^2	0.89681
Langmuir isotherm	Correlation coeff. (r)	0.969
	R^2	0.93896
	'a' (mg/g)	1.72
	'b' (g/L)	0.19
	R_L	0.51

5.0 KINETIC STUDY OF ADSORPTION PROCESS

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption(9).

5.1 Pseudo-second-order kinetic model

The pseudo second-order adsorption kinetic rate equation is expressed as (10):

$$\frac{t}{qt} = \frac{1}{K_2 q^2{}_e} + \frac{1}{qe}\,(t)$$

The plot of (t/qt) and t of Eq. (3.32) should give a linear relationship from which *qe (1/slope)* and k_2 *(slope^2/Intercept)* can be determined from the slope and intercept of the plot, respectively. Available studies have shown that the pseudo-second order rate equation is a reasonably good fit of data over the entire fractional approach to equilibrium and therefore has been employed extensively in the study of adsorption kinetics.

However, it is not uncommon to observe multi linearity on the *t/qe* Vs *t* plot. The trend is usually such that the rate constant decreases with time or

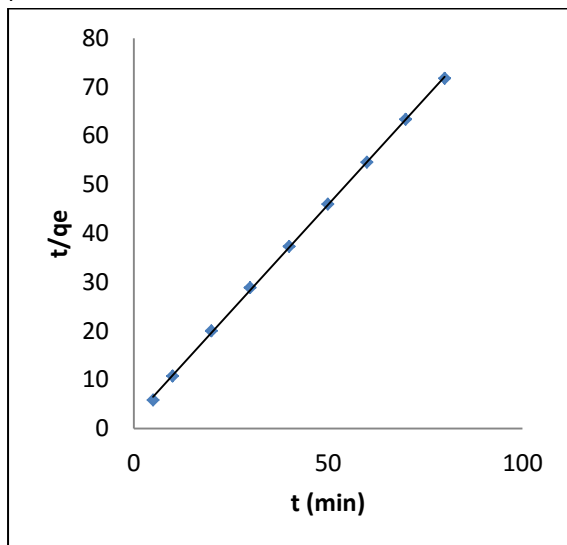more specifically decreases with increasing solid phase concentration.

Figure 8: Pseudo-second-order kinetics for the adsorption of fluoride onto SRC

In the present kinetic study (Figure8) the R^2 value for the adsorbent SRC having 0.999 close to unity hence pseudo-second order kinetic equation is fit for the current adsorption study.

Conclusion

It can be concluded that SRC sample has good properties for the sorption of fluoride ions from aqueous solutions. The equilibrium time for removal of fluoride concentration is determined to be 35 min. The fluoride saturation capacity of SRC is 1.38 mg F^-/g at room temperature. The best fitting adsorption isotherm is Langmuir model (R^2 > 0.998), which indicates that fluoride bio-adsorption onto SRC is characterized by physisorption on heterogeneous surfaces. The particle size is an important parameter that affects the sorption for fluoride on SRC since the sorption of these ions increases as the particle size decreases. Finally, this low-cost material can be employed as an adsorbent for fluoride removal from groundwater, in particular in domestic systems where fluoride related problems exist.

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