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Temperature Effects and Thermodynamic Adsorption of Flouride on Activated Coconut Shell Carbon, Activated Montmorillonite Clay and Rice Husk Ash

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Abstract: *The temperature dependency and thermodynamic properties adsorption of fluoride by activated coconut shell carbon, and activated rice husk ash were investigated. The studies were carried out at various temperatures of 303,313,323 & 333K (30℃ to 60℃). The maximum removal percentages were found at the maximum temperature of the study which is 60^{o}C for each adsorbent. Thus, the removal percentage of fluoride increases with the increase in temperature. And the maximum removal percentage were found to be 83.5, 81.7 and 73.1 % for activated coconut shell carbon, activated montmorillonite and activated rice husk ash respectively. The value of the enthalpy change (ΔH) calculated from the slope were -28808.01, -19388.25, and -31335.47 (KJ/mole) for activated coconut shell carbon, activated montmorillonite and activated rice husk ash respectively. The negative values of (ΔH) indicate the exothermic nature of the process. The values of the entropy change, (ΔS) were found to be 123.62, 91.62 and 120.07 (KJ/mole/K) for activated coconut shell carbon, activated montmorillonite and activated rice husk ash respectively. The positive values of entropy change suggest an increased randomness at the solid/liquid interface during the sorption of fluoride into the adsorbents. The average calculated Gibbs free (ΔG) were found to be -67891.92, -48523.4 and -69517.73 (kJ/mole). The negative values of Gibbs free energy suggests the spontaneous and feasibility of the process.*

Keywords: *Adsorption, Enthalpy, Entropy, Free energy, Temperature.*

1. INTRODUCTION

There are two major effects of fluoride on drinking water viz beneficial and harmful effects on human health. Small amount of fluoride in drinking water is essential for bones and the formation of dental enamel in animals and humans [1]. Whereas at higher concentrations, fluoride causes irreversible demineralization of bones and teeth tissues known as dental and skeletal fluorosis [2]. Thus, fluoride (F^-) contamination in drinking water has been recognized as one of the serious problems worldwide [3]. That is why Fluoride has been classified as one of the contaminant of water for human consumption by the World Health Organization (W.H.O), in addition to Arsenic and Nitrate which cause large-scale health problem [4].

Different methods of excess fluoride removal in water have been reported such as coagulation, precipitation [5, 6], reverse osmosis [7], ion exchange [8], and adsorption on to various adsorbents [9]. Among all these techniques, an adsorption method holds a strong potential in fluoride removal due to its key process features such as removal even at low fluoride concentration, high removal capacities, greater accessibility, economical, ease of operation and cost effectiveness [9].

Activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environments; air, gases, potable water and waste water [9]. [10] studies revealed that red soil pots have ability to remove fluoride, it was found that kaolinite clay when activated with acid has good defluoridation capacity. The sorption capacity of the acid activated clay for fluoride ranged between 0.0450 and 0.0557mg/g at different temperatures. Montmorillonite has also been used as adsorbent for removal of fluoride in water, [11] and modification of montmorillonite using lanthanide, magnesium and manganese can increase the adsorption capacity for fluoride removal [12]. [13] conducted a comparative study for the removal of fluoride using activated silica gel (ASiG) and activated rice husk ash (ARHA) as adsorbents through batch studies. The authors reported that both adsorbents were efficient for uptake of fluoride at pH 2.0 and contact time of 100 min. ASiG was found to be more efficient than ARHA with an initial fluoride concentration of 5mg/L with percentage removal efficiency of 88.30 and 96.7% for ARHA and ASiG respectively. Also, [14] conducted study on adsorbents like concrete, ragi seed powder, red soil, horse gram seed powder, orange peel powder, chalk powder, pineapple peel powder and multhani matti. Experimental set up was batch studies. Results indicated fluoride removal efficiency of 86% for chalk powder and pineapple peel powder 79% and 75% for horse gram seed powder. Percentage removal for ragi seed and red mud was found to be 65% and 71% respectively. Removal efficiency was recorded less for multhani mitti and concrete which was 56% and 53%. The aim of this study was to evaluate temperature effects and thermodynamics properties of the adsorption of fluoride on activated coconut shell carbon, activated montmorillonite and activated rice husk ash.

2. MATERIALS AND METHODS

2.1. List of Apparatus/Reagents

The apparatus used in this experiment were; weighing balance, filter paper(what man No-1), pipette(10ml), aluminium foil, pH meter, mortar and pestle, muffle furnace, hot plate (electric tung), measuring cylinder, oven, micrometer sieves, beakers, standard volumetric flasks, tap water, deionized water, test tubes, spatula, stirrer, hammer, masking tape, UV-spectrophotometer(model JENWAY 6300).

The reagents used were as follows: Hydrochloric acid (HCl), Acetic acid (CH_3COOH), SPADNS Reagent (2-parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfanate), TISAB (Total Ionic Strength Adjustment Buffer), Sodium hydroxide(NaOH), Fluoride ion of known concentration, Phosphoric acid (H_3PO_4), Sulphuric acid (H_2SO_4), Sodium fluoride (NaF), Zirconyl chloride octahydrate, Sodium chloride (NaCl), Sodium citrate, concentrated acetic acid.

2.2. Preparation of Solution

2.2.1. Fluoride Standard

1000 mg/L stock solution was prepared by dissolving 2.21g of NaF in 1L of deionized water.

2.2.2. Preparation of SPADNS Reagents

A weighed amount of 0.192g of SPADNS was dissolved in 100ml deionized water. Also 0.0266g of zirconyl chloride octahydrate was dissolved in 25ml of deionized water and 20ml of HCl was added to the solution and the deionized water was added up to 100ml marked. The SPADNS reagent was obtained by mixing SPADNS and zirconyl chloride in equal volumes called SPADNS reagent which is stable for more than two years if stored away from light.

2.2.3. Preparation of TISAB

Exactly 5.8g of chloride chloride and 1.2g of sodium citrate were mixed and 50ml deionized water was added and shaken, 5.7ml of concentrated acetic acid was also added. The pH of the solution was then adjusted using pH meter by adding a solution of 5.0mol/L NaOH (4.0g in 10ml) to give pH of 5.0-5.5 which is the ideal range for a working electrode sensitive to fluoride.

2.2.4. Preparation of Phosphuric Acid (H_3PO_4)

Preparation of 50% H_3PO_4 was done by taking 50ml of Phosphoric acid and adding 50ml of deionized water in 100ml volumetric flask.

2.2.5. Preparation of 1M Hydrochloric Acid (HCl)

This was prepared by taking 30.9ml of concentrated HCl into 1000ml volumetric flask and filled to the marked with distilled water.

2.3. Collection and Preparation of Adsorbent

2.3.1. Sampling Collection

The montmorillonite (clay) and rice husk were collected from Talasse town in Balanga L.G.A of Gombe state, while the coconut shell was obtained from Gombe main market in Gombe town of Gombe state.

2.3.2. Chemical Activation and Carbonization of Coconut Shell

The coconut shells was cut into smaller sizes using hammer and then washed several times with tap water to remove soil and dirt, it was then dried in an oven at 110^{o}C until constant weight was obtained for several hours.

The modified method of [15] was adopted. 70g of coconut shell was weight and soaked into phosphoric acid (H_3PO_4) in a beaker and heated for one hour (1 hour). It was then aged for 24 hours (one day) wrapped with aluminium foil in order to soaks the acid very well. After then, it was washed several times using tap water and distilled water to remove the acid and then oven dried for six hours at 110^{o}C.

The 70g activated coconut shell was placed in motar and wrapped with aluminium foil and then carbonized at 500^{o}C for three hours [16, 17]. It was carbonized in a murfle furnance model (M104) twice under same condition. Then the charcoal was ground and sieved using 105 mesh sizes and kept for analysis.

2.3.3. Preparation of Montmorillonite (Clay)

The montmorillonite (clay) was washed several times with tap water and then distilled water, it was also dried in an oven at 120^{o}C for several hours until a constant weight was obtained and then air dried for another two hours.

The clay was then ground and 150g of it was weight and refluxed in 500mL 1MHCl at 120^{o}C for one hour thirty minutes ($1^1/_2$ hours), it was then air dried for two days, ground and sieved using 105 mesh size and kept for analysis [18].

2.3.4. Preparation of Rice Husk Ash (WRHA)

Rice husk was collected from a rice mill in Talasse Balanga L G A in Gombe state. The rice husk obtained was thoroughly washed with tap water and then distilled water about five times to removes adhering soil and dirt and then dried in an oven at 80^{o}C over night. 150g of cleaned rice husk was refluxed with 1MHCl at 90^{o}C for one hour. After the reaction, acid was completely removed from the rice husk by washing it distilled water several times. It was then dried over night in an oven at 110^{o}C temperature.

The treated rice husk was calcined in a muffle furnance using motar wrapped with aluminium foil paper at 650^{o}C for six hours; silica with higher degree of purity was obtained in the form of White Rice Husk Ash (WHRA) [19]

2.4. Spectrophotometric Determination of Fluoride Using SPADNS Reagent (Indicator)

1000mg/L stock solution was prepared by weighing 2.21g of NaF dissolved in one litre (1L) deionized water. Various concentrations of 0, 1,2,3,4 and 5mg/L were serially prepared for the standard curve respectively. For each test tube, 1ml of SPADNS reagent was added and the corresponding absorbance for each concentration was obtained and recorded using UV-Spectrophotometer at a wave length of 570nm. The same procedure was followed for adsorption fluoride using activated coconut shell, montmorillonite and rice husk ash using UV-Spectrophotometer. (Model JENWAY 6300).

For each adsorbent, five (5) different weights of the adsorbent; 0.5, 1.0, 1.5, 2.0 and 2.5g was measured into five different conical flasks. For each flask, 25ml of the flouride solution (i.e 5mg/L) was added and agitated for 60min. (1 hour).After the required contact time, it was allowed to stand for two minutes for settling the adsorbent, it was then filtered using No 1 whatman filter paper. The filtrate was then analysed for residual fluoride concentration by SPADNS method.

The percentage removal of fluoride ion and amount adsorbed (mg/g) were calculated using the following equations

$$\% \text{ Removal} = \frac{Ci - Ce}{Ci} \times 100 \quad (1)$$

$$\text{Amount adsorbed } (q_e) = \frac{(Ci - Ce)}{m} v \quad (2)$$

Where;

C_i=initial concentration of the fluoride solution (mg/L)

C_e=equilibrium concentration of the fluoride solution (mg/L)

M=mass of the adsorbent (g)

V=volume of the fluoride test solution (L).

3. Results and Discussion

3.1. Effect of Temperature for Activated Coconut Shell Carbon

The effect of temperature was studied by conducting the experiment at different temperatures of 303,313,323 and 333K (30^{o}C to 60^{o}C) and optimum conditions; 5mg/L of fluoride ion concentration, contact time of 50 minutes, fixed pH of 7, dosage of 1.5g/L, and results obtained, Table 1, was plotted as percentage removal of the fluoride ion versus temperature as shown in figure 1.

It is observed that with an increase in the temperature from 303 to 333K (30^{o}C to 60^{o}C), the percentage removal of fluoride ion increases from 63.5% to 83.5%. As the temperature increases, the thickness of the outer surface of the activated carbon adsorbent decreases and the kinetic energy of the fluoride ion decreases across the external boundary layer and internal pores of the activated carbon adsorbent.

Table1. *Showing the result effect of temperature for activated coconut shell carbon*

Temp (^{0}C)	Absorbent (g)	Time (min)	C_i (mg/L)	C_e (mg/L)	$C_i - C_e$ (mg/L)	% Removal
30	1.5	50	5	1.826	3.174	63.5
40	1.5	50	5	1.304	3.696	73.9
50	1.5	50	5	1.043	3.957	79.1
60	1.5	50	5	0.826	4.177	83.5

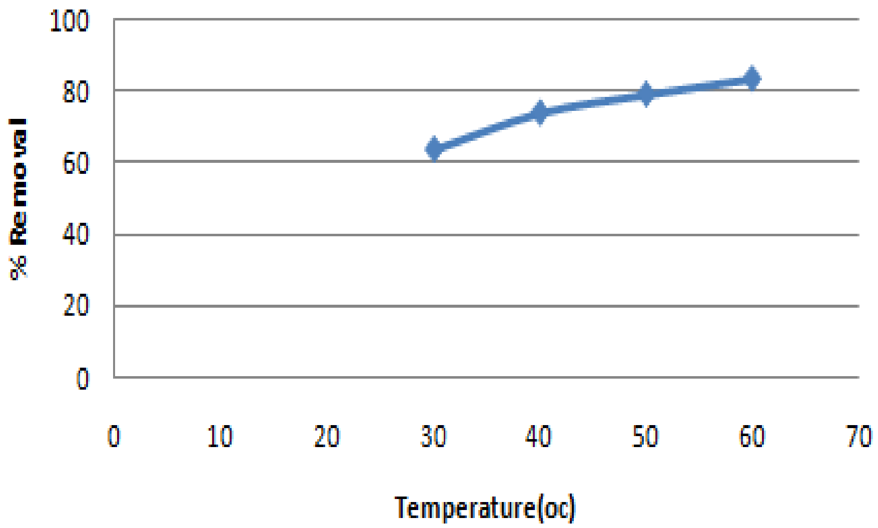

Figure1. *Temperature effect for activated coconut shell carbon*

3.2. Effect of Temperature for Activated Montmorillonite

The temperature dependence of fluoride adsorption by montmorillonite was studied over a range of 30^{o}C to 60^{o}C and at optimum conditions; contacts time of 50 minutes, 5 mg/L of fluoride initial concentration and 2g of adsorbent. The percentage of adsorption of fluoride ions at 50 minutes was found to be 69.6, 73.1, 79.1 and 81.7% at 30, 40, 50 and 60^{o}C respectively, Table 2. The plot of temperature against fluoride adsorbed by the material at four different temperatures is given in fig 2. The increase in the percentage of fluoride adsorption at higher temperatures confirms the endothermic nature of the process.

Table2. *Showing the effect of temperature for activated montmorillonite clay*

Tem (^{0}C)	Absorbent (g)	Time (min)	C_i (mg/L)	C_e (mg/L)	$C_i - C_e$ (mg/L)	% Removal
30	2	50	5	1.522	3.478	69.6
40	2	50	5	1.347	3.653	73.1
50	2	50	5	1.043	3.957	79.1
60	2	50	5	0.913	4.087	81.7

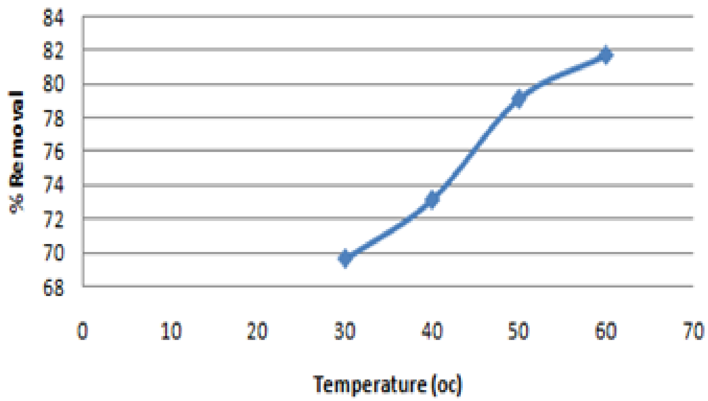

Figure2. *Effect of temperature for activated montmorillonite*

3.3. Effect of Temperature for Activated Rice Husk Ash

The effect of solution temperature was studied by conducting the experiment at different temperatures of 303,313,323 & 333K (30℃ *to* 60℃) at optimum conditions; 5mg/L of fluoride ion concentration, contact time of 50 minutes, dosage of 2.5g/L and pH of 2. And the results obtained were plotted as percentage removal of the fluoride ion against temperature as shown in figure 3. The percentage of fluoride adsorbed at 50 minutes was found to be 50.4, 55.7, 69.6 and 73.1% at the temperature of 30, 40, 50 and 60℃ respectively, Table 3. The increase in the percentage of fluoride adsorption at higher temperatures confirms the endothermic nature of the process [20].

Table2. *Showing the effect of temperature for activated*

Temp (^{0}C)	**Absorbent (g)**	**Time (min)**	**C_i (mg/L)**	**C_e (mg/L)**	**$C_i - C_e$ (mg/L)**	**% Removal**
30	2.5	50	5	2.478	2.522	50.4
40	2.5	50	5	2.217	2.783	55.7
50	2.5	50	5	1.522	3.478	69.6
60	2.5	50	5	1.347	3.653	73.1

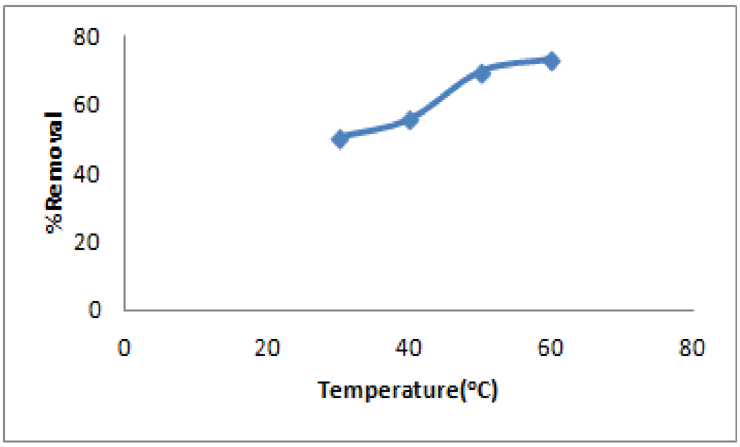

Figure3. *Effect of temperature for activated rice husk ash*

3.4. Thermodynamic Evaluation of the Adsorption Process

Thermodynamic parameters of the adsorption process such as change in free energy ΔG (kJ/mole), change in enthalpy, ΔH(kJ/mole) and change in entropy, ΔH(kJ/mole/K) were determined at different temperatures by using the equation below;

$\Delta G = -RT\ln k_d$

$\Delta G = \Delta H - T\Delta S$

$\ln kd = \Delta H/R - \Delta H/RT$

Where T –temperature in Kelvin degrees

R –Universal gas constant (8.314J/mole/K)

ΔS – standard entropy (KJ/mole/K)

ΔH – standard enthalpy (KJ/mole)

The plot of Inkd versus 1/T gives a linear graph with the slope and intercept equal to - ΔH/R and ΔH/R respectively. The results for the thermodynamic parameters of the adsorption process such as change in free energy ΔG (kJ/mole), change in enthalpy, ΔH(kJ/mole) and change in entropy, ΔH(kJ/mole/K) were presented in Table 4. The value of the enthalpy change (ΔH) calculated from the slope were -28808.01, -19388.25, and -31335.47 (KJ/mole) for activated coconut shell carbon, activated montmorillonite and activated rice husk ash respectively. The negative values of (ΔH) indicate the exothermic nature of the process. The values of the entropy change were found to be 123.62, 91.62 and 120.07 (KJ/mole/K) for activated coconut shell carbon, activated montmorillonite and activated rice husk ash respectively. The positive values of entropy change suggest an increased randomness at the solid/liquid interface during the sorption of fluoride into the adsorbents, Amrani and Tazrouti, 2009. The calculated Gibbs free energy values for activated coconut shell carbon were found to be -65355.87, -67501.07, -68737.27, and -69973.47 (kJ/mole) at the temperatures of 303,313,323 & 333K (30℃ *to* 60℃) respectively. For activated montmorillonite, temperatures of 303,313,323 & 333K (30℃ *to* 60℃) the calculated Gibbs free energy were found to be -47149.11, -48065.25, 48981.51, and 49597.71 (kJ/mole) respectively. And for activated rice husk ash, the calculated Gibbs free energy values were found to be -67716.68, -68917.38, -70118.08, and -71318.78 (kJ/mole) at the temperatures of 303,313,323 & 333K (30℃ *to* 60℃) respectively. The negative values of Gibbs free energy suggests the spontaneous and feasibility of the process, [20].

Table4. *Thermodynamic parameters for adsorption of fluoride*

Parameters	ΔH (KJ/mole)	ΔS (J/mole/K)	ΔG (kJ/mole)				R^2	Equation
Temperature (K)			303	313	323	333		
ACSC	-28808.01	123.62	-65355.87	-67501.07	-68737.27	-69973.47	0.971	Y=-3465x + 14.87
AMMT	-19388.25	91.62	-47149.11	-48065.25	-48981.51	-49597.71	0.99	Y=-2332x + 11.02
ARHA	-31335.47	120.07	-67716.68	-68917.38	-70118.08	-71318.78	0.84	Y=-3769x + 14.75

ACSC: *Activated coconut shell carbon, AMMT: Activated Montmorillonite and ARHA: Activated Rice husk ash*

4. Conclusion

The temperature effects and the thermodynamic properties for adsorption of fluoride on various adsorbents; activated coconut shell carbon, activated montmorillonite and activated rice husk ash were studied. The study revealed that the removal percentage of fluoride increases with the increase in temperature for each adsorbent. The negative value of enthalpy for each adsorbent indicates the exothermic nature of the process while the positive value suggests an increased randomness at the solid/liquid interface during the adsorption of fluoride into the adsorbents.

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