

# Removal of Excess Toxic Chloride and Fluoride Anions from Wastewater Employing Eggshells Waste Remains

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**Abstract**— Eggshells waste was investigated for its sorption ability as an environmentally-friendly and cheap sorbent for removing excess anions from wastewater. The milled size of the waste was found to be  $\leq 63 \mu\text{m}$ , with round and smooth morphology. Moreover, the Fourier transform infrared spectrometer spectrum showed functional groups such as carbonate and hydroxyl. The X-ray diffractogram of the eggshells showed the presence of calcite, which mostly compose of calcium and carbonate ions. Multivariate methodology was employed for optimization of factors that affect sorption studies; initial ions concentration which was found to be 24.45 and 23.24 mg/L, the sorbents dose which was found to be 85.20 and 81.56 mg/L, contact time, which were found to be 69.37 and 70.28 min and solution pH 7.19 and 7.97 for chloride and fluoride anion respectively. The eggshells also exhibited high percentage removal efficiencies for chloride (80.70%  $\pm$  2.01%) and fluoride ion (93.18%  $\pm$  1.67%) from real wastewater samples. The adsorption isotherm was satisfactorily fitted with Langmuir isotherm model. The thermodynamics kinetics studies showed that the adsorption of fluoride and chloride ions onto the eggshells was endothermic and spontaneous and the adsorption data followed second-order kinetics supporting that chemisorption process was involved.

**Keywords**—Chloride, fluoride, eggshells waste-remains, adsorption and wastewater.

## I. INTRODUCTION

Processed wastewater is widely employed to compensate for the shortage of benign and uncontaminated freshwater (Stevens & Batlokwa, 2017). Wastewater treatment methodologies have been developed by several researchers for treating and reutilizing wastewater for use in irrigation, animal and human consumption, groundwater boost, non-potable reuse and domestic activities. Nevertheless, the presence of excess and toxic anions such as chloride and

fluoride ions in the wastewater pose a serious health hazard to aquatic animals and the environment (Chuang, Chang, Chang, & You, 2006). Agricultural activities such as the use of potash fertilizers for soil enrichments, road salts, industrial activities and natural calamities have continuously increased the amount of chlorine and fluoride ions in the aquatic ecosystems (Butt & Riaz, 2017). Naturally, chloride and fluoride ions exist in fresh or ground waters in considerable concentrations and are essential to life. For example, chloride ions are micronutrients essential for plant development and it constitute approximately 0.05% of the earth's crust (Hunt, Herron, & Green, 2012). It is required in low concentrations by most plants, and it plays an essential role in stomatal regulation. However, high levels of chloride ion may alter reproduction rates, increase species mortality and may also change the characteristic of the entire local ecosystem. Furthermore, as the concentration of chloride ion increases due to the above-mentioned activities or reasons, and filters into underground waters and wastewaters, it may strain plant respiration and change the quality of the wastewater effluent as well as drinking water (Asche & Lead, 2013). Fluoride on the other hand, is essential to human health specifically for the bones and dental health, however, this is plausible only at low levels ( $\leq 1.0 \text{ mg/L}$ ) (Bhaumik et al., 2012). Consumption of high levels of fluoride ions is detrimental to human health and aquatic life. For example, ingesting high levels of fluoride ions browning and mottling of the teeth, bones fluorosis (Fawell & Nieuwenhuijsen, 2003), depression (Crisp et al., 1998), urinary tract malfunction and red blood cell deformities (Thole, 2013).

Henceforth, it is essential that the concentration of chloride and fluoride ions in recycled wastewater be considerably reduced to acceptable levels (200 mg/L and 1.0 mg/L for chloride and fluoride respectively) as set out by international monitoring agencies such as the World Health

Organization (WHO) (Javed & Usmani, 2013), Food and Agriculture Organization (FAO) (Elnabris, Muzyed, & El-Ashgar, 2013) and Botswana Bureau of Standards (BOBs)(BOTSWANA BUREAU OF STANDARDS, 2011). Adsorption has wide been employed as an efficient and economically viable technology for the removal of removing excess and toxic chloride and fluoride ions from water. Lately, low cost sorbents, especially naturally occurring materials such as activated carbon from plant materials (Chuang et al., 2006), calcium alginate beads (Bhaumik et al., 2012), fly ash (The & Convention, 2008), rice husk (Xu, Chen, & Jiang, 2015), tea ash powder, clay materials, limestone as well as commercially available calcium containing materials such as calcium hydroxide, and calcium sulphate have been employed to remove chloride and fluoride from water (Bhaumik et al., 2012) (El-Hassan & Al-Sulami, 1994). However, these methods present some drawbacks, including the high cost (Hanafi & Abdel Azeema, 2016), and the disposal of the resulting sludge (Gilbert, Woodhouse, Stieb, & Brook, 2003)

Eggshell is mainly composed of calcium carbonate (94.03%) and it also contains calcite and valerite. Additionally, eggshells are composed cellulosic structure and contains amino acids; making it an excellent adsorbent (Yi, Guo, Zhang, Yu, & Li, 2004). In Botswana, eggshells are largely produced as waste domestically, commercially as well as industrially. These waste (eggshells waste remains), are usually disposed in landfills and have no economic values.

In this paper, pulverized eggshells were employed as an environmentally friendly and readily available adsorbent for the removal of excess toxic chloride and fluoride ions from wastewater sample. FTIR, SEM and XRD were employed for characterization of the eggshells waste remains. The significance of various sorption parameters including pH, adsorbent dose, contact time, initial concentration of the anions was investigated. Adsorption isotherm models were employed to describe the adsorption equilibrium data. Pseudo-first and second-order and intraparticle diffusion were employed to investigate the kinetics of the adsorption process. The thermodynamic parameters, such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were also calculated from the adsorption measurements.

## II. MATERIALS AND METHOD

### Materials and Instrumentation

The eggshells waste remains employed for this experiment was collected from the Moghul Refectory located on the main campus of the Botswana International University of Science and Technology (BIUST), Palapye, Botswana.

Ultra-pure water of 18.0 M $\Omega$ /cm resistivity, Type I, was prepared by a Elix 5 Millipore water purification system from Merck, (Darmstadt, Germany) and was used to prepare all solutions. Reagents used were: SPAR white spirit Vinegar, which was employed to treat the waste materials, was purchased from SPAR (Palapye, Botswana), elemental standard solution of Cl<sup>-</sup>, and F<sup>-</sup> with a concentration of 1000 mg/L and NaOH (97%) pellets were purchased from Rochelle Chemicals (Johannesburg, South Africa). For determination of size, morphology and nanoparticle composition, JSM 1700 SEM coupled with EDX, obtained from USA was used. The instrument resolution was about 50eV at amplification time of 5 microseconds, it uses an Electron Dispersive X-ray (EDX) back scattering detector operated in spectra mode (elemental composition), point and shot mode and mapping mode (distribution of compounds). Analysis was done employing a Philips GSR v, 3.2 software. The SEM worked at beam voltage of 1.0 kV LED, low vacuum (typically 2 to 6 Torr), and utilizes a chamber gas (H<sub>2</sub>O) for imaging, charge suppression and sample humidity. An E6700 Polaron range high vacuum evaporator sputter coater, obtained from the United Kingdom (UK), was used to coat the fish scales remains and untreated waste materials prior to SEM-EDX analysis. Perkin Elmer System, Spectrum two Fourier transform infrared (FTIR) spectroscopy was used to determine the functional groups of materials. The FTIR spectra were recorded in the wavenumber range 400-4000 cm<sup>-1</sup> on a Perkin Elmer system 2000 FTIR. The adsorbents were kept at ambient temperature. 1mg of the adsorbents per 200 mg of KBR was weighed. The powder was pressed into pellets by using a 15 ton hydraulic press. The data were collected at 2.0 cm<sup>-1</sup> resolution, and each spectrum was a result of 256 scans. A powder D8 Advanced Powder X-Ray Diffractometer (XRD) obtained from Bruker (Karlsruhe, Germany) was employed for characterization of the eggshells waste remains. Meanwhile, the presence of chloride and fluoride anions effluents during the entire experiment were investigated by employing a Shimadzu S 150 ion chromatography system (SHIMADZU, Japan) obtained from SHIMADZU (Johannesburg, South Africa). The instrumental parameters were those recommended by the manufacturer.

### Pre-treatment of the Eggshells Waste Remains

The eggshells waste remains employed for this experiment was collected from the Moghul Refectory located on the main campus of the Botswana International University of Science and Technology (BIUST), Palapye, Botswana. The remains were washed thoroughly with deionized water to

remove dirt and eggs remains. Then it was sun dried for 48hrs, after which, it was pulverized employing a Fritsch pulverisette 5 pulverizer, operated at 400 rpm for 90 min in both milling and reverse mode. The pulverized materials were then sieved to 63 – 200 micron mesh size, after which they were rewashed with deionized water several times to remove color and dirt. The product was then treated with SPAR white spirit vinegar to remove inorganic pollutants. Finally, they were dried in an oven at  $65 \pm 2$  °C for 6hrs 11.

#### X-ray Powder Diffraction (XRD)

A powder D8 Advanced Powder X-Ray Diffractometer (XRD) analysis was employed to investigate the physical properties as it relates to the crystallinity of the waste material. The XRD was operated with Cu K $\alpha$  emission ( $\lambda = 1.54105\text{\AA}$ , 40 kV, 40 mA per sec) and with high efficiency linear detector of Lynx Eye type. The scanning mode used was coupled with  $2\theta/\theta$  on the scanning range  $10^\circ - 120^\circ$  values. The crystallite size of the sample was calculated by Deby-Scherrer method.

#### Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared (FTIR) spectrometer was employed to identify the functional groups craved on the surface of the eggshells waste remains. The FTIR spectra were recorded in the wavelength range 500-4000  $\text{cm}^{-1}$  on a Nicolet iS10 Thermo Scientific FTIR. The data were collected at  $2.0 \text{ cm}^{-1}$  resolution, and each spectrum was a result of 250 scans.

#### Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX)

Scanning Electron Microscope coupled with Energy-dispersive X-ray spectrometer (SEM - EDX) (JSM -

7100F), was employed to determine the surface morphology of the eggshells waste and to determine its elemental composition. An E6700 Polaron range high vacuum pressure sputter coater (Quorum Technologies, UK) was employed to coat the eggshells wastes with carbon. These were then taken for SEM-EDX analysis, which operated under high vacuum and beam acceleration voltage of 10.0 kV (the recommended operating voltage for organic material samples). The results from this analysis were then used to determine the surface morphology and elemental composition of the eggshells waste.

#### Batch Adsorption Studies for Cl<sup>-</sup> and F<sup>-</sup> Removal Employing Eggshells Waste

All experiments were carried out in batches and done in triplicates. A 100 mg/L standard mixture of chloride and fluoride was prepared from 1000 mg/L stock solution of each of the anions.

#### Optimization of Adsorptive Parameters of the Eggshells Waste

Optimization studies were carried out by employing multivariate optimization methodology. In this study, the eggshells were optimized by looking at four factors: contact time, pH, sorbent dosage, and initial concentration. These were first screened through the use of a two-level fractional factorial design. This evaluates the significance of each factor towards the experimental output.

The screening design was carried using the experimental conditions as described in Table 1. It was then filtered into a 100 mL volumetric flask and deionized water added to the mark. It was investigated for chloride and fluoride anions employing IC. The experiments were done in replicates to evaluate the adequacy of the method.

Table.1: Factors and their levels for the two-level fractional factorial design for the optimization of the eggshells waste remains

Variable	Factor	Low level	High level
A	dosage (mg)	10	1000
B	pH	2	10
C	Contact time (minutes)	15	180
D	Concentration (mg/L)	0	50

Following this, a face centered central composite design (CCD) was performed to investigate the optimum conditions for each factor that would result in a maximized response of the experiments. The optimization process was carried out with the use of Minitab Release 14 statistical software (Minitab Inc., USA).

#### Application of the Optimized Eggshells Waste Adsorption Method to Real Samples

The sorption nature of the eggshells waste remains was studied by applying the optimized parameters to wastewater samples collected from Gaborone waste water treatment plant. The eggshells waste remains were used for the adsorptive removal of chloride and fluoride anions from samples. 100 mL of wastewater samples were used and the

optimized conditions applied to the water samples. The mixture was subjected to a rotary shaker at 200 rpm under the optimal conditions, after which it was then filtered employing a whatmann No. 1 filter paper and put into 100 mL volumetric flasks. Deionized water was added to the flasks and filled up to the mark. The analysis was done in triplicates. Chloride and fluoride standards (from 5 – 10 mg/L) were prepared for the calibration curve. The effluents were investigated for the presence of chloride and fluoride ions by employing ion chromatography (IC) and the results analysed using Microsoft Excel 2016.

The percentage removal of chloride and fluoride anions was calculated using the formula below

$$\frac{C_i - C_f}{C_i} \times 100$$

(1)

Where  $C_i$  is the initial concentration of metal ions in wastewater sample.

$C_f$  is the final concentration of metal ion in wastewater after applying the eggshell waste remains.

#### Equilibrium studies

Adsorption equilibrium studies were conducted to determine the nature of the adsorption isotherms and the adsorption capacity of the eggshells waste remains for the removal of chloride and fluoride. For the isotherm studies, the initial ions concentrations were varied from 10 to 100 mg/L using 1 g/L (dry weight) eggshells waste powder. The adsorption flasks were agitated in a rotary shaker at 400rpm and samples were collected at specified time intervals,

followed by separation of the eggshells waste powder by filtration. The resulting solutions were analyzed employing IC for the residual anions concentrations.

#### Kinetic studies

Kinetic studies were carried out in a volumetric flask and samples were collected at different intervals of 15 min to 90 min. The samples were analysed for residual ions concentration.

The kinetics of adsorption was studied by using three kinetic models, pseudo first order, second order and intra particle diffusion models.

#### Thermodynamic studies

The experiments were conducted at different temperatures in the range of 0 – 50 °C in a rotary shaker for 90 min. The samples were filtered and analysed employing IC for the residual anions concentrations at the end of the experiments.

### III. RESULTS AND DISCUSSIONS

#### X-ray Powder Diffraction (XRD)

The XRD phase analysis of the eggshells waste powder was performed employing JCPDS (Joint Committee on Powder Diffraction Standards) card number 01-073-0293. It was evident that a compound, calcite with the chemical formula  $\text{CaCO}_3$  was the major component of the eggshell waste powder with a with *d- spacings* 0.845, 0.784, 0.712, 0.684, 0.600, 0.563, 0.489, 0.389, 0.301, 0.289, and 0.200 corresponding to the calcite structure as shown in Figure 1.

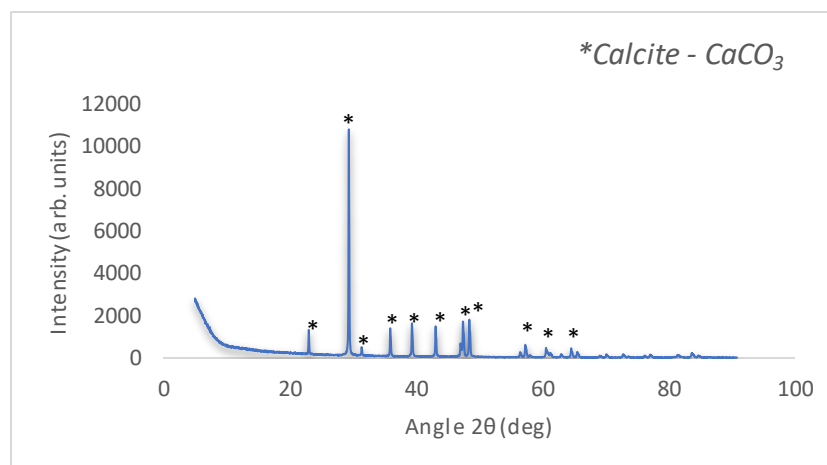


Fig.1: XRD diffractogram of the eggshells waste powders

Calcium and carbonate ions are the major constituents of calcite. Both ions have unsatisfied partial charges within the compound (Bhaumik et al., 2012). This charge imbalance is decreased by the hydrolysis of water, resulting in the

formation of calcium hydroxide ions and bicarbonate ions which has the ability to react with any other ions in solution based on the pH of the solution. At pH between 6 – 7.85, there is an increase in the number of  $\text{CO}_3^{3-}$  and  $\text{Ca}^{2+}$  sites on

the eggshells powder surface resulting in high adsorption efficiency for chloride and fluoride ions by the eggshell waste powder (Tsai et al., 2006).

**Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX)**

Figure 2 shows SEM micrographs of the eggshells waste powder. The fish scale appears to have a round and smooth

morphology with a particle size of  $\leq 63 \mu\text{m}$ , which are excellent characteristics associated with excellent adsorbents. The micrograph is characterized by having two regions, one being darker and the other being white. The white region is rich in inorganic material containing high proportion of calcium and phosphorus, whereas the dark region is rich in protein because it has high proportion of carbon and oxygen as soon by Figure 3.

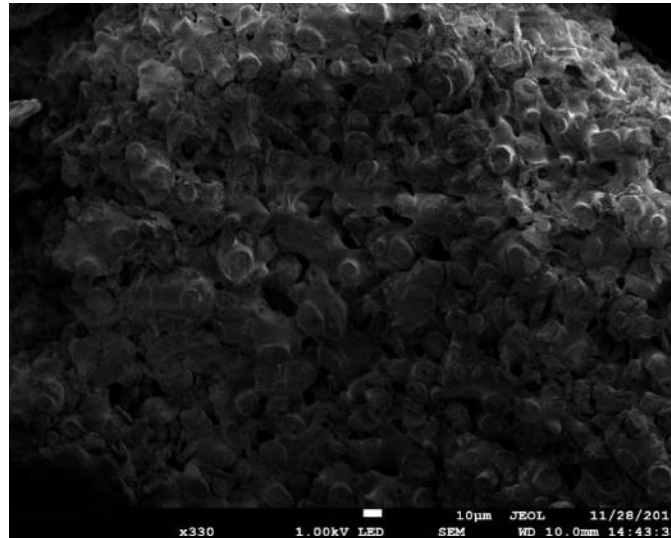


Fig.2: SEM image for the eggshell waste remains powder

Full scale counts: 1378

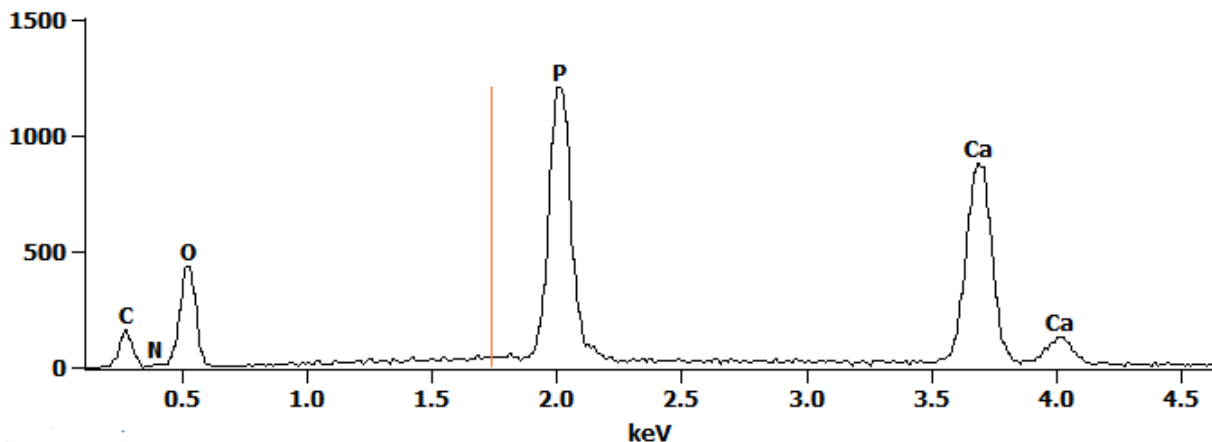


Fig.3: EDX of the eggshell waste remains powder

**Fourier Transform Infrared Spectroscopy (FT-IR)**

Eggshell is mainly composed of calcium carbonate (94.03%) and it also contains calcite and calcareous soil. Eggshell has a cellulosic structure and contains amino

acids; thus, it is expected to be a good adsorbent. Figure 4 below shows an FTIR of eggshells before removal (blue) and after removal (pink) of the chloride and fluoride ions from wastewater.

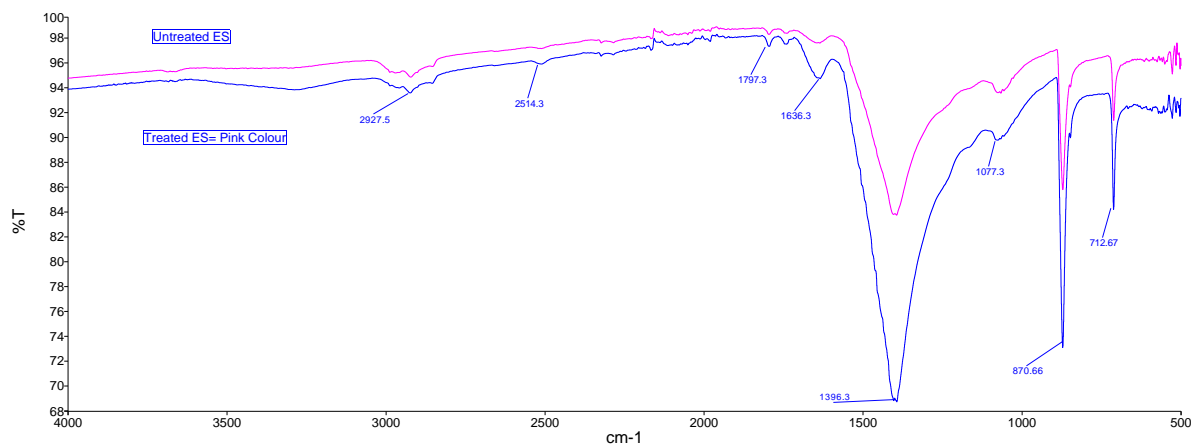


Fig.4.4: FTIR of Eggshells before removal (blue) and after removal (pink) of target analytes

The two most significant peak intensities were observed at 1396 and 870  $\text{cm}^{-1}$ , which were strongly associated with the presence of calcium carbonate in the eggshell matrix (Haynes & Dean, 2010). The peak at 870  $\text{cm}^{-1}$  confirmed the presence of valerite (Tsai et al., 2006). A moderately observable peak at 712 indicated the in-plane and out-planes deformation modes of calcium carbonate (Thomas et al., 2015). It has been reported that the most prominent peak in FTIR spectra of eggshell particles matched with that of carbonate minerals. The peak at 2927.5  $\text{cm}^{-1}$  is due to presence of C-H stretching mode (Tsai et al., 2006).

#### Optimization of Adsorptive Parameters of the Eggshells Waste Remains

Experimental matrices were designed using Minitab for the optimization purposes. The yields were followed by the use of IC separation measurements of chloride and fluoride. Before performing the actual optimization, a  $\frac{1}{2}$  fraction factorial design was employed in order to assess the level of significance of each factor under investigation. The factorial design comes as a screening phase, which allows screening a relatively large number of factors in a relatively small number of experiments that cover the whole experimental domain, with the result identifying the most influential factors towards obtained yields. Analysis of data was in the forms of normal probability plots of standardized effects, and residuals plots; as shown by Figures 5 and 6, respectively.

From the normal probability plot of standardized effects, the magnitude of the main effects of each factor as well as the effects brought about by the interaction of factors, towards the obtained yield are investigated. The magnitude of each type of effect is represented by its distance from the solid line, as well as the side on which the effect lies with respect to the solid line. Negative effects lie to the left while positive effects lie to the right of the solid line. The solid line indicates where the points would drop if the effects were zero, while the percentage in the y-axis signifies the weightage of each factor's contribution towards the obtained yield. The investigated effects exhibited a positive magnitude as they all appeared to the right of the graph, as can be observed in Figures 5. The main effects, due to Factors A (Contact time), B (pH), C (eggshells waste remains dosage) and D (initial concentration) were significant for chloride and fluoride. Factor D for both anions lay furthest to the right of the solid line, signifying that factor D had a greater positive magnitude towards contribution of the yields obtained. However, the contribution of each factors (A, B, C, and D) showed higher weightage towards the output as compared to that of effects brought about by the interaction of factors. The powder normal probability plots of standardized effects of Cl<sup>-</sup> showed that there was a significant contribution towards the obtained yield as a result of interaction between factors (Factor A and Factor B) and the same for Factor A and Factor D for F<sup>-</sup>.

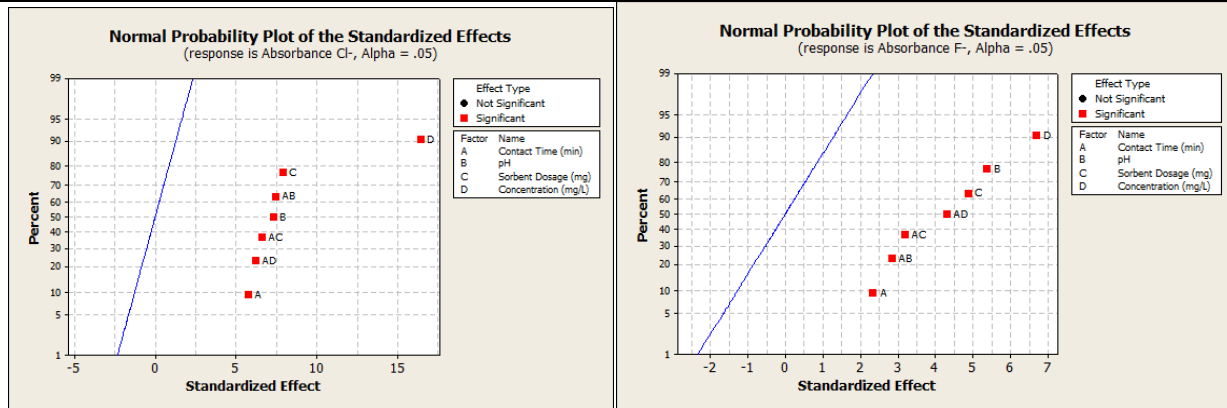


Fig.5: The normal probability plots of standardized effects of Cl<sup>-</sup> and F<sup>-</sup> for the eggshells

Figure 6 shows the residual plots for the yield obtained when using the eggshells waste powders. The plots probe into the distribution pattern of data points through the use of residuals. Residuals are the outcome of the difference between the observed and the fitted values (Ryan, 2006). Normal probability and histogram plots investigate whether the data obtained exhibits a standard Gaussian distribution. For normal probability plots, if the data points fall approximately along the straight line, then the residuals are said to be normally distributed, meaning the data follows the Gaussian distribution (Ziegel, 2004), which was the case for this work. A plot of residuals against fitted responses

(values) is used to detect unequal error variances and outliers, while the plot of residuals against order of the data checks for correlation of the residuals. The residuals against fitted values plot revealed a constant variance of the residuals about the center line. The plot of residuals against order of the data showed a randomized shifting pattern about the center line, signifying that the data was uncorrelated with each other. The plots for the eggshells show that the residuals were randomly distributed, hence, signifying absence of systematic errors and hence adequacy of the model.

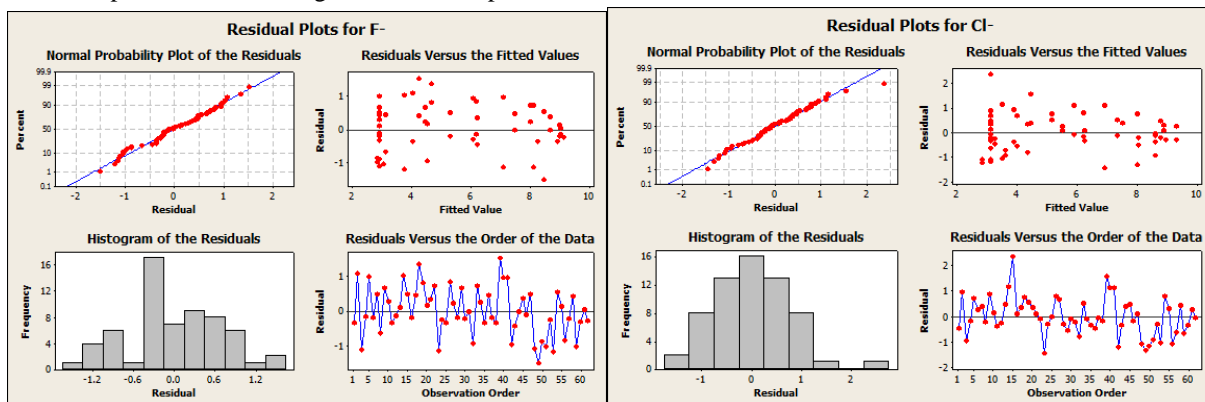


Fig.6: Residuals plots of standardized effects on the eggshells waste remains

Following the screening of significant factors using fractional factorial design, a response surface design was then created to determine the optimum conditions of each factor. This was achieved through the use of a CCD. The optimal conditions obtained for the eggshells waste adsorption of chloride and fluoride anions were 24.45 and 23.24 mg/L for the initial ions concentration respectively, the sorbents dose was found to be 85.20 mg/L (chloride) and 81.56 mg/L (fluoride), contact time, were found to be 69.37 min (chloride) and 70.28 min (fluoride) and solution

pH 7.19 (chloride) and 7.97 (fluoride). Furthermore, the regression coefficient,  $R^2$ , was also used to assess the fit of the model to the experimental data which were 0.9901 (Cl<sup>-</sup>) and 0.9891 (F<sup>-</sup>). The relative standard deviations (RSD) for the experimental data were obtained to be 1.4% (Cl<sup>-</sup>), and 2.21% (F<sup>-</sup>).

**Application of the Optimized Eggshells Waste Adsorption Method to Real Samples**

After determining the optimum parameters, the parameters were applied in a 100 mL of the wastewater sample and the resulting solution was analysed using IC. Figure 7 below represent the percentage removal of chloride ( $80.70\% \pm$

$2.01\%$ ) and fluoride ion ( $93.18\% \pm 1.67\%$ ) from real wastewater samples. The eggshells waste showed excellent removal efficiency towards the selected anions.

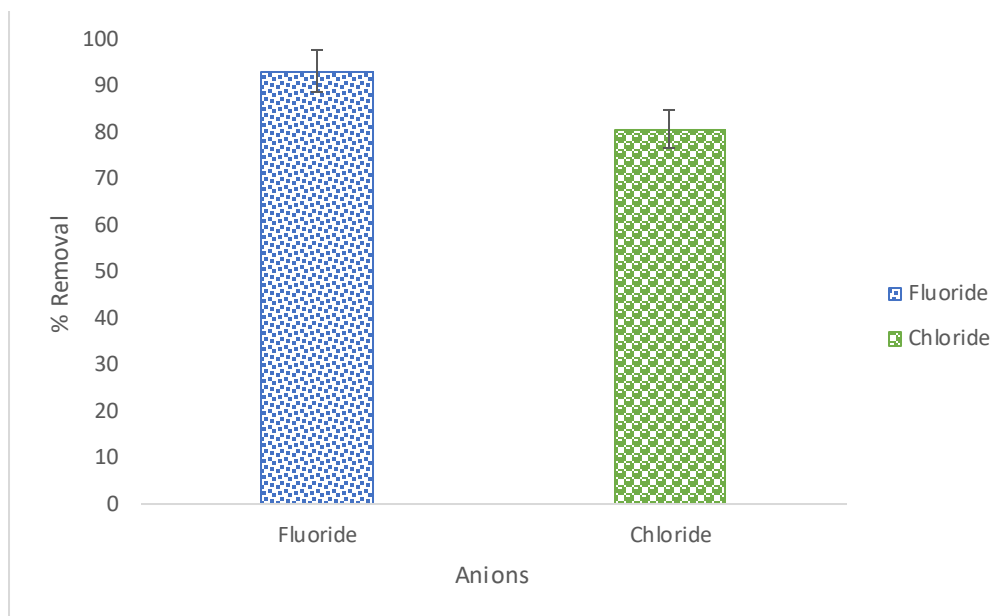


Fig.7: Percentage removal of chloride and fluoride anions from wastewater sample

### Adsorption Isotherms

Adsorption isotherms show the distribution of solute between the liquid and solid phases and can be described by several mathematical relationships such as the standard Langmuir and Freundlich and Dubinin-Radushkevich models as described above. The linearized Langmuir and Freundlich adsorption isotherms as well as Dubinin-Radushkevich model obtained for the eggshells waste are shown in the Table 2, with the values of linear regression coefficients. In view of the values of the linear regression coefficients, Langmuir model fits very well to the sorption data in the studied concentration range studied. The higher the  $b$ , the higher is the affinity of the adsorbent for ions.  $q_{\max}$  can also be interpreted as the total number of binding sites that are available for adsorption and  $q_e$  as the number of binding sites that are in fact occupied by the ions at the concentration  $C_e$  (Umpleby et al., 2001). According to Table 2, the affinity order of the eggshells is  $Cl^- > F^-$ . The constant  $K$  and  $1/n$  were determined by linear regression from the

plot of  $\log q_e$  against  $\log C_e$ .  $K$  is a measure of the degree or strength of adsorption. Small value of  $K$  indicates the more adsorption (Whitcombe, Martin, & Vulfson, 1998) while  $1/n$  is used as an indication of whether adsorption remains constant (at  $1/n = 1$ ) or decreases with increasing ions concentrations.

The Langmuir constants of  $q_{\max}$  and  $b$  were determined from  $1/q_e$  versus  $1/C_e$  plot. The applicability of Langmuir isotherms implies that monolayer adsorption exists under the experimental conditions. The Langmuir isotherm constants do not explain the chemical or physical properties of the adsorption process. However, the mean adsorption energy ( $E$ ) calculated from the D-R isotherm provides important information about these properties (Pamukoglu, 2008)(Branger, Meouche, & Margailan, 2013). The adsorption energies are less than  $2 \text{ kJmol}^{-1}$  suggesting that the sorption process was dominated by physical forces at all studied temperatures.



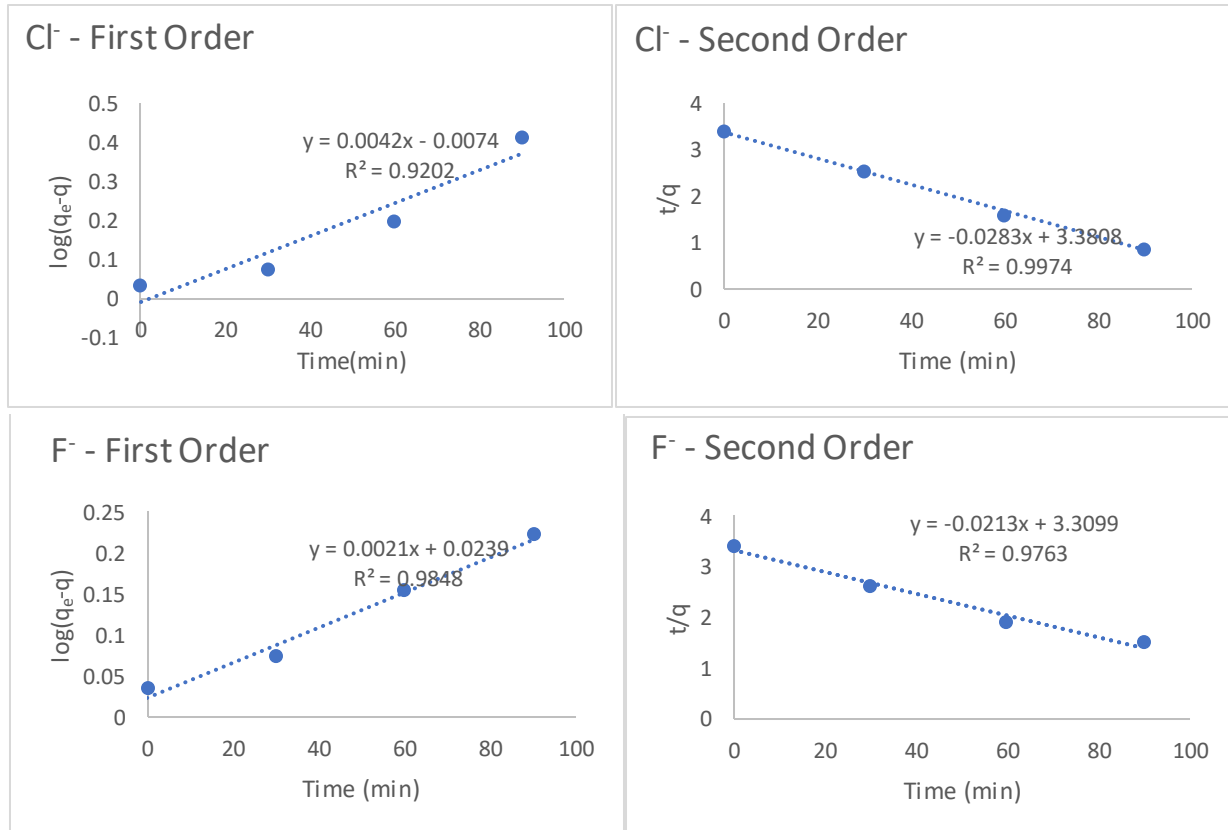
Table.2: Isotherm parameters for the adsorption of chloride and fluoride anions unto the eggshells waste remains

Ions	Langmuir Model				Freundlich Model			Dubinin Radushkevich Model		
	Temp. (K)	R <sup>2</sup>	q <sub>max</sub> (mg/g)	b (L/mg)	R <sup>2</sup>	K	1/n	R <sup>2</sup>	E (J/mol)	q <sub>max</sub> (mg/g)
F <sup>-</sup>	298.15	0.959	30.12	0.14	0.6557	0.46	1.02	0.9918	338.85	16.09
	308.15	0.9761	44.07	0.05	0.8516	0.72	1.11	0.9448	485.80	15.59
	318.15	0.8857	14.35	0.18	0.788	0.74	0.88	0.9445	584.91	17.68
	333.15	0.9907	1.30	0.45	0.91	0.89	1.15	0.9352	1125.10	17.50
Cl <sup>-</sup>	298.15	0.9628	32.26	0.14	0.6395	0.44	1.03	0.9464	325.45	15.68
	308.15	0.9715	31.15	0.08	0.8464	0.72	1.07	0.9873	492.38	15.15
	318.15	0.9417	17.39	0.12	0.8718	0.86	0.92	0.9024	638.17	18.18
	333.15	0.9908	36.08	0.00	0.9548	1.31	1.01	0.9267	977.47	17.10

**Adsorption Kinetics**

The comparison of experimental sorption capacities (q<sub>exp</sub>) and the predicted values (q<sub>cal</sub>, k<sub>1</sub>, k<sub>2</sub>, k<sub>d</sub>, R<sup>2</sup>) from pseudo first order, pseudo second order and intra particle diffusion constants are given in Table 3 eggshells waste. The pseudo first order (plot of log(q<sub>e</sub>-q) vs. t) was not satisfactory to explain the experimental data, whereas the calculated, q<sub>cal</sub>

values derived from the pseudo second order model for sorption of the selected ions were very close to the experimental (q<sub>exp</sub>) values. The second order equation (plot of t/q vs. t) appeared to be the better fitting model than first order and intra particle diffusion equations because it has higher R<sup>2</sup> value as shown in Figure 8 (Abd. Hadi, A. Rohaizar, & Sien, 2011)(Ikram et al., 2016).



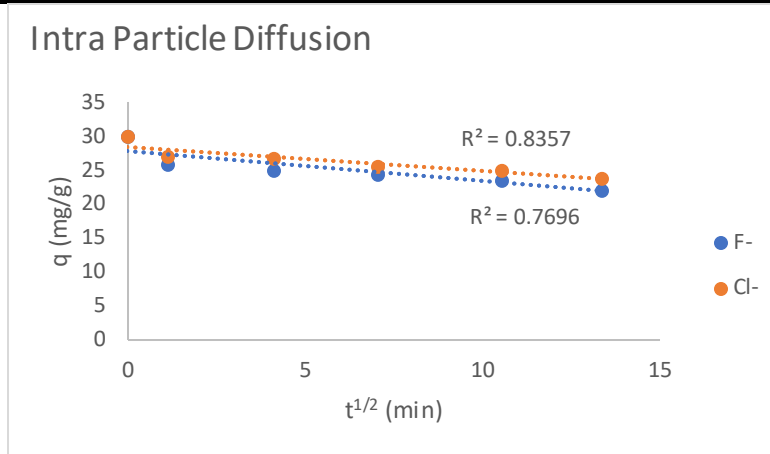


Fig.8: Pseudo first and second order adsorption kinetic and intra particle diffusion of the eggshells waste remains

Table.3: Kinetics parameters for the adsorption of the selected ions onto the eggshells waste remains

Ions	q <sub>exp</sub> (mg/g)	Second Order			First Order			Intra Particle Diffusion	
		R <sup>2</sup>	K <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	q <sub>cal</sub> (mg/g)	R <sup>2</sup>	K <sub>1</sub> (min <sup>-1</sup> )	q <sub>cal</sub> (mg/g)	R <sup>2</sup>	K <sub>d</sub> (mg L <sup>-1</sup> min <sup>-1/2</sup> )
F <sup>-</sup>	12.46	0.9763	0.012	13.66	0.9848	0.017	0.12	0.7539	0.289
Cl <sup>-</sup>	12.02	0.9974	0.002	12.53	0.9202	0.023	0.18	0.7208	0.262

**Thermodynamics Parameters**

The results of these thermodynamic calculations are shown in Table 4. The negative values for the Gibbs free energy for all the selected ions, show that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. The overall adsorption process seems to be endothermic ( $\Delta H = 39.37$ , and  $53.26 \text{ kJmol}^{-1}$  for Cl<sup>-</sup> and F<sup>-</sup> respectively). Table 4 also shows that the  $\Delta S$  values were positive (which implies that entropy increases as a result of adsorption). This occurs as a result of redistribution of energy between the adsorbate (chloride and fluoride anions) and adsorbent (eggshells

waste powder). Before adsorption occurs, the anions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free anions to anions interacting with the adsorbent will be higher than in the adsorbent state. As a result, the distribution of rotational and translational energy among a small number of ions increase with increasing adsorption by producing a positive value of  $\Delta S$  and randomness will increase at the solid solution interface during the process of adsorption. Adsorption will occur spontaneously at normal and high temperatures if  $\Delta H > 0$  and  $\Delta S > 0$ .

Table.4: Thermodynamic parameters for the adsorption of chloride and fluoride anions onto the eggshells waste remains

Ions	Temp. (K)	b (L/mol)	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/molK)	R <sup>2</sup>
F <sup>-</sup>	298.15	1398.97	-17.96	39.37	0.2744	0.9917
	308.15	2904.89	-20.43			
	318.15	4193.82	-22.06			
	333.15	7421.09	-24.68			
Cl <sup>-</sup>	298.15	2789.38	-19.67	53.26	0.4366	0.9871
	308.15	7119.08	-22.73			
	318.15	14589.71	-25.36			
	333.15	26656.39	-28.23			

#### IV. CONCLUSION

In this paper, an attempt to employed eggshells waste remains as an ecofriendly adsorbent for removing fluoride and chloride anions from wastewater was achieved. Adsorption studies were developed and evaluated. These studies demonstrated that pH, sorbent dose, contact time and concentration are significant factors in adsorption. The use of eggshell waste remain was found to be a green method therefore conserving the environment. Eggshells waste remains were proposed as cheap, easily available and efficient method for removal of chloride and fluoride anions from the environment. The adsorption isotherm was more satisfactorily fitted with Langmuir isotherm model. The thermodynamics various kinetics models including the Pseudo-first-order, Pseudo-second-order and intra particle diffusion constants of the adsorption process,  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  were evaluated. The results showed that the adsorption of nitrate and nitrite ions onto activated carbon was endothermic and spontaneous. The adsorption data followed second-order kinetics supporting that chemisorption process was involved.

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