RESEARCH ARTICLE

REMOVAL OF TOXIC ANIONS FROM WASTEWATER BY FISH SCALES BIO-WASTE MATERIAL

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ARTICLE INFO	ABSTRACT
	In this work, fish scales waste biomaterial was used as an alternative adsorbent for the removal of anions from wastewater. The pulverized waste materials revealed a rough surface which is often associated with effective sorbent. Fourier transform infrared spectroscopy revealed the presence of hydroxyl, carboxylate esters, phosphate and amine functional groups. X-ray diffractometer also show the presence of hydroxyapatite in the fish scale waste. The optimum parameters for anions removal were found to be 7.03, 73.18 mgL-1, 69.19 min and 23.11mgL-1for pH, pulverized fish scale dosage, contact time and initial anions concentration respectively at n = 3. Kinetic studies showed that pseudo-second-order reaction model best described the adsorption process. The percentage removal of anions from the wastewater by the waste material was averaged at $88 \pm 2\%$ at n = 3.

Citation: *Morlu Stevens and Bareki S. Batlokwa, 2018.* "Removal of toxic anions from wastewater by fish scales bio-waste material", *International Journal of Current Research*, 10, (06), 70350-70357.

INTRODUCTION

Over the past decade, researchers have focus on the occurrences; both naturally-occurring and anthropogenic origin, properties and removal of many chemical and biological components found within wastewater effluents (Uyak *et al*., 2008). In most cases, possible hazardous effect on the ecosystem and humans have been identified, subsequently leading to the introduction of constrict regulations relating to their existence within wastewater effluents (El-Hassan and Al-Sulami, 1994). For example, in Botswana, a number of national water laws have been enacted; water act of 1968, borehole act of 1956 and the Botswana national water master plan established in 1991 (was reviewed in 2006), to regulate the qualities of waters in Botswana (Report, 2013) (Orange-Senqu, 2017). Several contaminants mentioned within these regulations/acts have straight and tight laws on their existing standards following reports on their health effects. Examples of this is sulphate and bromate, for which the maximum allowable concentration (MAC) in water at consumption is 250 mgL^{-1} and 10 μgL^{-1} respectively due to evidence of potential carcinogenicity (Ismodes, 2016). Bromate is usually considered as an

undesirable product of wastewater treatment processes, formed especially during ozonation (Uyak *et al*., 2008) (Richardson *et al*., 2003). It is formed as a disinfection by-product (DBP) by oxidation of naturally-occurring bromide within runoff water and groundwater that eventually enter wastewater system , where concentrations up to 60 μgL^{-1} (>10 μg/L) have been observed in treated wastewater effluents (Cancho *et al*., 1999). Sulphate on the other hand also occur naturally in numerous minerals, including barite (BaSO4), epsomite (MgSO$_4$·7H$_2$O) and gypsum (CaSO$_4$·2H$_2$O) (WHO, 2006). These dissolved minerals contribute to the mineral content of many waters. However, the levels of sulphate are elevated in wastewater due acid rain, dry deposition, surface runoff (agriculture, mine drainage, urban runoff and industrial runoff) and oxidation of organic soil by fire or drought, rendering it toxic and hazardous (9). Therefore, it is essential that these excess toxic anions be removed from wastewater prior to its intended use.

Several techniques have been employed over the years to effectively remove sulphate and bromate from wastewater (Watson *et al*., 2012). For example, batch-scale experiments have shown that BrO$_3^-$ and SO$_4^{2-}$ can be remove via ultraviolet irradiation (Ismodes, 2016), high energy electron beam irradiation (Vauthier and Bouchemal, 2009) and heterogeneous redox catalysis (13), reverse osmosis, distillation, or ion exchange (Boyer, 2005), nevertheless, the practical performance of these techniques to remove BrO$_3^-$ from ozonated waste waters appears extravagant and not eco-friendly, hence, the need for an economical and eco-friendly removal method (Chuang *et al*., 2006).

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The current study is based around Gaborone, Botswana where, during routine preliminary sampling for analytical method development, sulphate and bromate concentration in excess of the Water Supply regulations was detected. Due to the potentially carcinogenic nature of BrO^{3-} and SO_4^{2-} pollution, effluents from wastewater plants that are used (for irrigation and animal consumption) in and around Gaborone are being affected (Asare and Darkoh, 2001) (Maina *et al.*, 2016). As the result of the negative and sustained effect of these pollutants, development of an economical and robust removal method was identified as a priority area for research, hence, the use of vinegar-treated fish scales waste biomaterials.

Materials and Instrumentations: The adsorbents used for the experiments were fish scales collected from fishes Palapye, Botswana. Analytical grade HCl (37%) purchased from ACE (Johannesburg, South Africa) was employed for pH optimization. SPAR white spirit Vinegar, which was employed to treat the waste materials, was purchased from SPAR (Palapye, Botswana). Elemental standard solutions used (1000ppm – BrO_3^- and SO_4^{2-}) and NaOH (97%) pellets were purchased from Rochelle Chemicals (Johannesburg, South Africa). A 0.45 µm pore sized Whatman filter papers (Hardened Ashless Circles 45 mm) that was used for all filtering processes were purchased from Sigma-Adrich (Johannesburg, South Africa). A Mars6 One Touch Microwave Assisted Extractor/Digester (CEM Microwave Technology Ltd, North Carolina, USA) obtained from CEM (Johannesburg, South Africa) was employed to digestion and extraction of inorganic pollutants from the VTFSWB. For determination of size, morphology and nanoparticle composition, JSM 1700 SEM coupled with EDX, obtained from (California, USA) was employed. Perkin Elmer System, Spectrum two Fourier transform infrared (FTIR) spectroscopy was employed to determine the functional groups of the VTFSWB. A powder D8 Advanced Powder X-Ray Diffractometer (XRD) obtained from Bruker (Karlsruhe, Germany) was employed for characterization of the fish scales. BrO_3^- and SO_4^{2-} were determined by 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 Fish Scales Waste Biomaterials: The fish scales were collected from fishes Palapye, Botswana. The biomaterials were washed thoroughly with deionized water to remove dirt and impurities. It was then sun dried for 48 hrs and the dried materials were pulverized employing a Fritsch pulverisette 5 pulverizer obtained from Fritsch (Berlin, Germany), operated at 400 rpm for 90 min in both reverse and milling mode. The pulverized materials were then sieved to 63 micron mesh size. After pulverizing and sieving, they were washed with deionized water several times to further remove impurities. The material was than treated with SPAR white spirit vinegar to remove inorganic and organic pollutants. Finally, they were dried in an oven at 65 ± 5 ˚C for 6 hrs (Bhatnagar and Sillanp, 2010).

Fourier Transform Infrared Spectroscopy (FT-IR): Fourier transform infrared (FTIR) spectrometer was employed to identify the functional groups responsible for adsorption of anions present on the surface of the biomaterials before and after used. The FTIR spectra were recorded in the wavelength range 500-4000 cm^{-1} on a Nicolet iS10 Thermo Scientific FTIR. The data were collected at 2.0 cm^{-1} resolution, with a resulting spectrum being of 256 scans.

X-ray Powder Diffraction (XRD): A powder D8 Advanced Powder X-Ray Diffractometer (XRD) was employed to investigate the physical properties; especially the crystallinity of the biomaterials before and after adsorption. The XRD was operated with Cu Kα emission (λ = 1.54105Å, 40 kV, 40 mA per sec) and with high efficiency linear detector of Lynx Eye type. The scanning mode used was coupled with 2Θ/Θ on the scanning range 10° - 120° values. The crystallite size of the sample was calculated by Deby-Scherrer method.

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 biomaterials and to determine its elemental composition. An E6700 Polaron range high vacuum pressure sputter coater (Quorum Technologies, UK) was employed to coat the biomaterials with carbon. The coated biomaterials were subjected to SEM-EDX analysis under high vacuum and beam acceleration voltage of 10.0 kV (the recommended operating voltage for organic material samples).

Batch Adsorption Studies for BrO_3^- and SO_4^{2-} Anions Adsorption by VTFSWB: All experiments were carried out in batches and done in triplicates. A 100 mgL^{-1} standard mixture of the selected anions was prepared from 1000 mgL^{-1} stock solution of each of the anions. The VTFSWB employed were of particle size of ≤ 63 µm. A multivariate optimization methodology employing Minitab Release 14 statistical software (Minitab Inc. USA) was used for experimental designs.

Optimization of Factors Affecting BrO_3^- and SO_4^{2-} Anions Adsorption by VTFSWB: The optimization process was carried out with the use of Minitab Release 14 statistical software (Minitab Inc., USA). The screening design was carried using the experimental conditions as described in Table 1 for the biomaterial. The low and high levels of each factor were established considering previous experiments from literature. It was then filtered into a 100 mL volumetric flask and deionized water added to the mark. It was investigated for anions employing IC. The experiments were done with two replicates to evaluate the adequacy of the method and lack-of-fit. The CCD was used as the experimental matrix for the response surface method. The significant factors from the screening phase (two-level ½ fraction factorial design) were employed for the optimization phase (CCD). Two replicates were also carried out for this set of experiments. It was then filtered into a 100 mL volumetric flask and deionized water added to the mark. The effluent was investigated for anions residuals by employing IC.

Application of the Optimized Adsorption Method to Real Wastewater Sample: Prior to application of the optimized adsorption method to the wastewater sample, the wastewater was firstly investigated for the presence of sulphate and bromate anions by employing ion chromatography. After which, the extraction efficiency for the biomaterial was evaluated by applying it to the wastewater sample under the optimized conditions. The mixture was subjected to a rotary shaker at 200 rpm for the optimized time, after which it was

then filteredusing a whatman No. 1 filter paper and put into 50 mL volumetric flasks and filled to the mark by deionized water. The analysis was done in triplicates, andBrO_3^-, and SO_4^{2-} standards (from 5 - 50 mgL^{-1}) were prepared for the calibration curve. The effluent was subjected to IC analysis and the results analysed using Microsoft Excel 2016. The percentage removal of anions was calculated using the formula below

$$\frac{Ci - Cf}{Ci} \times 100 \qquad (1)$$

Where C_i is the initial concentration of metal ions in wastewater sample and C_f is the final concentration of nitrate and nitrite anions in wastewater after applying the biomaterial.

Equilibrium Studies: Adsorption equilibrium studies were conducted to study the kind of the adsorption isotherms and the adsorption capacity of the biomaterial for the removal of sulphate and bromate. For the isotherm studies, the initial anions concentrations were varied from 1.5 to 50mgL^{-1}using 1 gL^{-1} (dry weight) biomaterial powder. The mixture was batched in a rotary shaker at 400rpm and samples were collected at specified time intervals, and then filtered. The effluent was investigated employing IC.

Kinetic studies: Kinetic studies were carried out at different intervals of 5 min to 180 min. The effluents were analysed for residual anions concentration. Three kinetic models, pseudo first order, second order and intra particle diffusion models were employed to investigate the kinetics of adsorption.

Thermodynamic studies: Thermodynamic studies 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 sulphate and bromate ions concentrations at the end of the experiments. Reaction occurs spontaneously at a given temperature if ΔG is a negative quantity (Przybyłek and Gaca, 2012). The free energy of the sorption reaction considering the sorption equilibrium constant is given by the following equation:

$$\Delta G = -RTlnb \qquad (2)$$

(Bhaumik et al., 2012) Where ΔG is the changes in Gibbs free energy, R (8.314 Jmol^{-1}K) is the universal gas constant, T (K) the absolute temperature and b (Lmol^{-1}) the thermodynamic equilibrium constant. Considering the relationship between free energy and the equilibrium constant, change in equilibrium constant can be obtained in the differential form as follows (Esen *et al.*, 2009):

$$\frac{dlnb}{dT} = \frac{\Delta H}{RT^2} \qquad (3)$$

(Hanafi & Abdel Azeema, 2016) After integration,

$$lnb = -\frac{\Delta H}{RT} + Y \qquad (4)$$

(Hanafi & Abdel Azeema, 2016) Where Y is a constant, the above equation can be rearranged to obtain

$$-RT\,lnb = \Delta H - TRY \qquad (5)$$

Let $\Delta S = RY$ (6)

Substituting equations (2) and (6) into (5), the Gibbs free energy change, ΔG, can be represented as follows.

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

(Joshi, Kulkarni, & Mashelkar, 2000). A plot of Gibbs free energy (ΔG) versus temperature T was found to be linear. The values of enthalpy change ΔH and entropy change ΔS were determined from the slope and intercept of the plots (Bhaumik *et al.*, 2016).

RESULTS

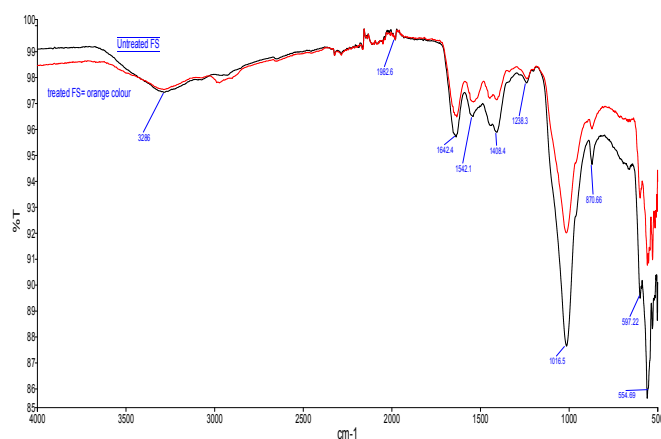**FT – IR**

Figure 1. FTIR of the biomaterial before removal (black) and after removal (red) of sulphate and bromate ions
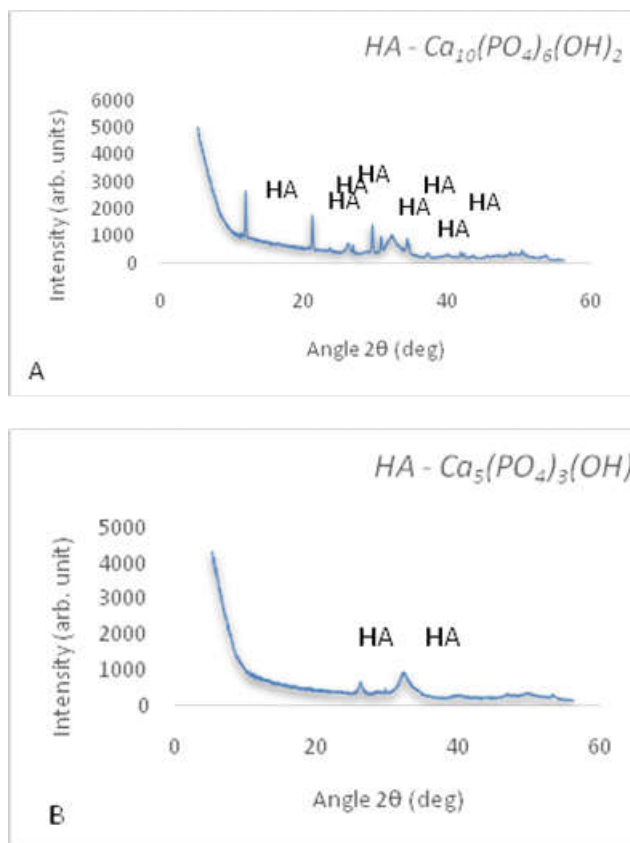
XRD

Figure 2. XRD diffract to grams of the A) loaded biomaterials and B), treated biomaterial powders

Sem-Edx

Table 1. EDX atomic % of biomaterial elemental constituents

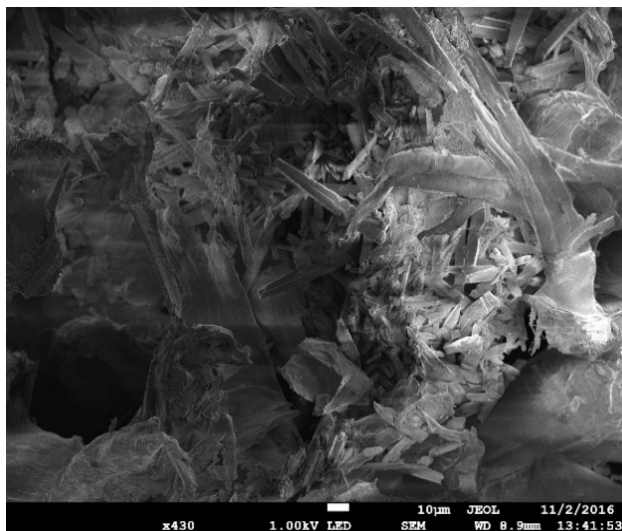| O	C	P	N	Ca
13.16	27.93	33.70	35.11	38.38
19.17	37.58	31.04	35.02	31.38
24.95	45.76	27.00	32.55	27.25
9.07	20.42	35.42	34.79	44.17

Figure 1: SEM image of the treated biomaterial

Table 1. Factors and their levels for the two-level fractional factorial design for the optimization of the VTFSWB

Variable	Factor	Low level	High level
A	VTFSWB dosage (mg)	10	1000
B	pH	2	10
C	Contact time (minutes)	5	180
D	Concentration (mgL^{-1})	0	50

Adsorption Isotherm

DISCUSSION

FT – IR: FTIR was employed to identify the functional groups present in the biomaterial. Figure 1above shows the functional groups of the biomaterial before removal (black) and after removal (red) of sulphate and bromate. The functional groups that are prominent in the fish scales are 1016cm^{-1} due to carboxyl bands and primary amines, 554 to 597 cm^{-1} due to alkanes, 870 cm^{-1} due to sulphonates, -OH and N-H groups at 3286 cm^{-1}, C-O group at 1542.1 to 1642.4 cm^{-1} and C-H, -CH$_3$, -CH$_2$ groups at 1408.4 cm^{-1}. The anions interact with different functional groups and cause the decrease of intensities and shift of the cited peaks. These interactions could be due to complex formation of analytes with the surface functional groups. Altering pH helps in changing the surface charge of the sorbents thereby improving on the removal efficiency of the sorbent. The functional groups such as amines, carboxylic, hydroxyl, carbonyls form anionic sites as pH is raised from acidic to basic conditions. The positively charged sites are responsible for binding with the selected anions and may also be removed through anionic exchange.

XRD: The X-ray powder diffractometer phase analysis of the biomaterials were performed using JCPDS (Joint Committee on Powder Diffraction Standards) card number 01-073-0293 which showed a compound of *hydroxyapatite* with a chemical formula Ca$_5$(PO$_4$)$_3$(OH), and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ for the treated biomaterials powder, and the biomaterial powder after adsorption respectively as shown in Figure 2.The powder X-ray diffraction patterns of the biomaterials showed increasing intensity of the reflections in the order of loaded biomaterial > treated biomaterial, with *d-spacings* of 0·735, 0·564, 0·534, 0·466, 0·401, 0·342, 0·243, and 0·182 for the loaded biomaterials; and 0·242 and 0·189 for the treated biomaterial corresponding to the hydroxyapatite structure (Kumari and 2014) (Teramoto *et al.*, 2012).

SEM – EDX: The biomaterial appears to have a rough surface and is characterized by having two regions, one being darker and the other being white.

Table 2. Isotherm parameters for the adsorption of sulphate and bromate unto the biomaterial

Ions		Langmuir Model			Freundlich Model			Dubinin – Radushkevich Model		
	Temp. (K)	R^2	q$_{max\ (mgg^{-1})}$	b (Lmg^{-1})	R^2	K	1/n	R^2	E (Jmol^{-1})	q$_{max\ (mgg^{-1})}$
SO$_4^-$	298.15	0.9815	41.84	0.07	0.8129	0.63	1.13	0.9657	421.99	16.40
	308.15	0.9885	38.46	0.05	0.9026	0.83	1.06	0.9527	544.77	16.81
	318.15	0.9974	35.24	0.01	0.9888	1.73	1.13	0.9315	793.21	17.22
	333.15	0.9819	41.94	0.01	0.9306	1.30	1.01	0.9255	980.90	17.45
BrO$_3^-$	298.15	0.9624	29.07	0.11	0.7433	0.56	1.04	0.9275	393.30	16.81
	308.15	0.9892	19.34	0.06	0.9555	1.46	1.30	0.9029	673.26	17.22
	318.15	0.9983	25.36	0.02	0.993	1.66	1.14	0.999	783.87	14.80
	333.15	0.9905	11.27	0.08	0.9288	0.91	1.17	0.9137	1102.77	17.06

Adsorption Kinetics

Table 3. Kinetics parameters for the adsorption of the sulphate and bromate onto the biomaterial

Ions	q$_{exp}$ (mg/g)	Second Order			First Order			Intra Particle Diffusion	
		R^2	K$_2$ (gmg^{-1}min^{-1})	q$_{cal}$ (mgg^{-1})	R^2	K$_1$ (min^{-1})	q$_{cal}$ (mgg^{-1})	R^2	K$_d$ (mgL^{-1}min$^{-1/2}$)
SO$_4^-$	13.87	0.9983	0.017	12.67	0.9204	0.022	0.17	0.5572	0.187
BrO$_3^-$	12.76	0.9957	0.016	12.91	0.9397	0.021	0.15	0.9355	0.420

Adsorption Thermodynamics

Table 4: Thermodynamic parameters for the adsorption of the sulphate and bromate onto the biomaterial

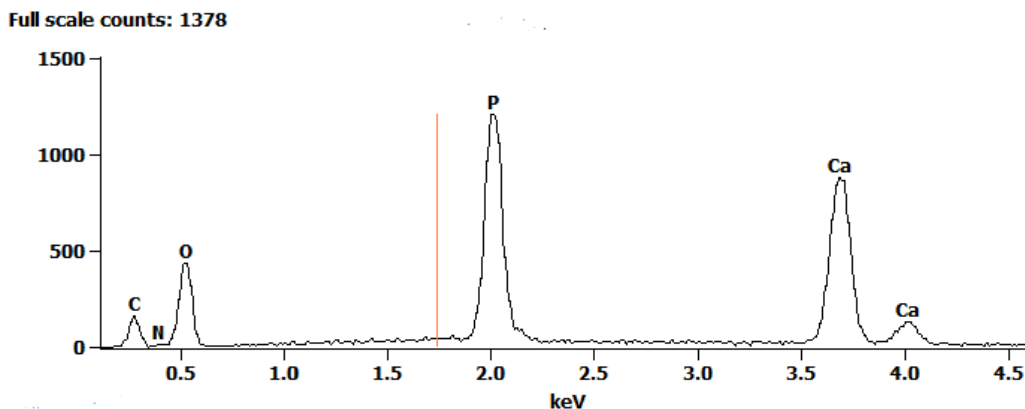| Ions	Temp. (K)	b (Lmol^{-1})	ΔG (kJmol^{-1})	ΔH (kJmol^{-1})	ΔS (kJmol^{-1}K)	R^2
SO$_4^-$	298.15	7703.29	-22.18	57.31	0.4751	0.9991
	308.15	17370.70	-25.01			
	318.15	35977.50	-27.75			
	333.15	87406.70	-31.52			
BrO$_3^-$	298.15	10207.70	-22.88	43.32	0.3583	0.9871
	308.15	21388.50	-25.54			
	318.15	41126.40	-28.10			
	333.15	64015.50	-30.65			

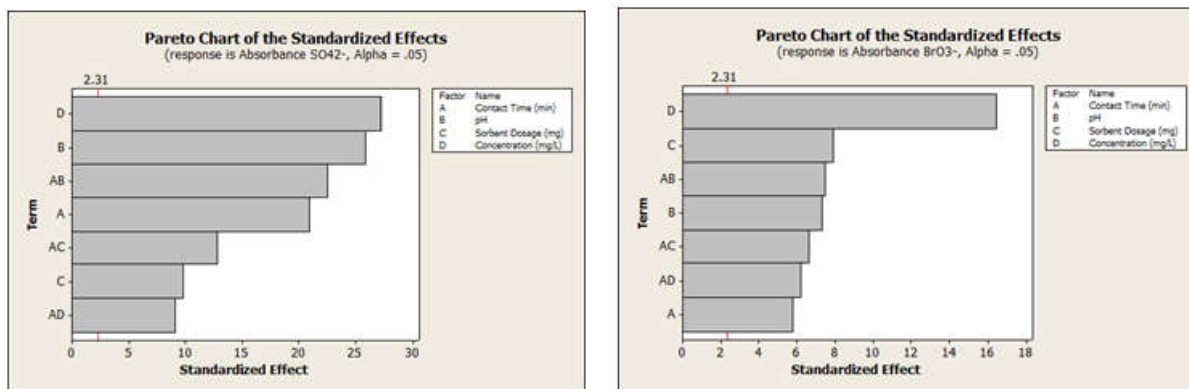**Figure 2: EDX micrograph for the biomaterial**

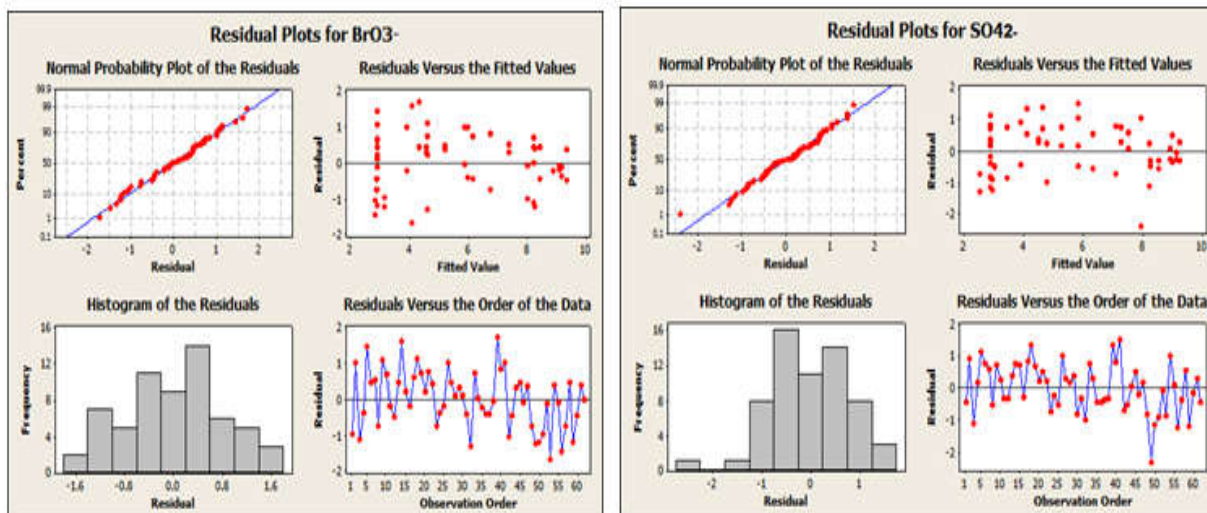**Figure 5. Pareto charts of standardized effects on biomaterials.**

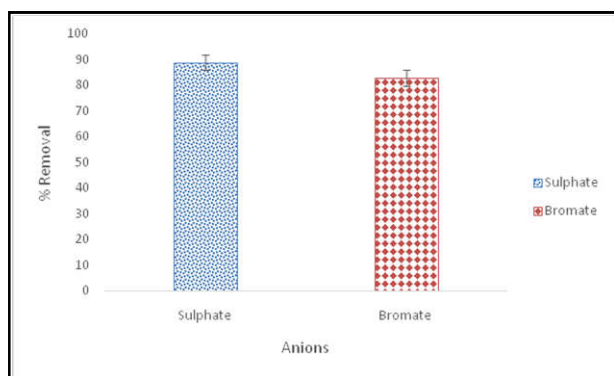**Figure 6. Residuals plots of standardized effects on the biomaterial**

Figure 7. Percentage removal of anions from wastewater sample employing the biomaterial

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. Figure 3 represents the micrograph of the treated biomaterial. From energy, dispersive X-ray (EDX) analysis, show no indication of bromate or sulphate in the biomaterial as shown in figure 4.

Optimization of Factors Affecting Adsorption: Experimental matrices were designed using Minitab for the optimization purposes. The yields were followed by the use of IC separational measurements of sulphate and bromate ions residuals. A ½ fraction factorial design was employed in order to assess the level of significance of each factor under investigation prior to optimization. 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. Pareto chart of standardized effects (Figure 5) is used for the identification of factors and interaction effects most significant for this study. A reference line is drawn on the graph, above which any effect that crosses it is significant. The line zero is determined by Minitab based on standardized effects (if an error term exists) or through the use of Lenth's pseudo-standard error (if there is no error term) (Prakash *et al*., 2008).

In simple terms, this chart can be thought of as application of a p-value test at a 95 % level of confidence. The Pareto chart reflects statistical relevant effect of each factor on the response, sorted from largest to smallest; with the reference line corresponding to a p-value of 0.05 (Ponnusami *et al*., 2008). In figure 5, the main effects (due to Factors A (contact time), B (pH), C (sorbent dosage) and D (concentration) were all significant as each term crossed the reference line as well as interactions of factors. Factor D was observed to be the most significant factor towards adsorption efficiency of the biomaterial. Figure 6 on the other hand, shows the residual plots for the absorbance obtained when employing the biomaterial. The plots investigate the distribution pattern of data points through the use of residuals. Residuals are the result of the difference between the observed and the fitted values (Pokhrel and Viraraghavan, 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 (Mathews, 2004). This was the observed behavior as shown in Figure 6. A plot of residuals against fitted responses 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 graph of residuals versus order of the data showed a randomized fluctuating pattern about the center line, signifying that the data was uncorrelated with each other. Both plots for biomaterial show that the residuals were unsystematically scattered, thus reflecting the lack of logical errors and hence adequacy of the model. Following evaluation 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 biomaterial adsorption of sulphate and bromate anions were 23.23 and 22.02mgL^{-1} for the initial ions concentration respectively, the sorbents dose was found to be 79.73mgL^{-1} (sulphate) and 83.38mgL^{-1} (bromate), contact time, were found to be 71.17 min (sulphate) and 71.19 min (bromate) and solution pH 7.97 (sulphate) and 7.78 (bromate). Furthermore, the regression coefficient, R^2, was also used to assess the fit of the model to the experimental data which were 0.9994 (SO_4^{2-}) and 0.9983(BrO_3^-). The relative standard deviations (RSD) for the experimental data were found to be 2.22% (SO_4^{2-}), and 1.09% (BrO_3^-).

Application of the Optimized Conditions to Real Wastewater Sample: The wastewater sample was firstly investigated for sulphate and bromate ions. It was found that the level of both anions (0.581 ± 0.04 and 24.563 ± 0.025 for BrO_3^- and SO_4^{2-} respectively) were within the recommended limits as set by BOBs water standards. Therefore, the sample was spiked with 2 mgL^{-1} of the selected anions. The optimum parameters were applied to a 50 mL of the wastewater sample and the resulting effluent was analysed employing IC. Figure 7 represent the percentage removal of sulphate ion (89.01% ± 3.01%) and bromate ion (88.23% ± 1.34%) from real wastewater samples. The biomaterial showed excellent removal efficiency towards the selected anions. The recoveries of spiked ions were 106% and 102% for sulphate and bromate respectively.

Adsorption Isotherm: Based on the linear regression coefficients, Langmuir model fits very well to the sorption data in the studied concentration range studied. According to the Table 3, the affinity order of the biomaterials is $SO_4^{2-}> BrO_3^-$. The higher the b, the higher is the affinity of the adsorbent for anions. 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). The adsorption energies wereless than 2 kJmol^{-1} suggesting that the sorption process was dominated by physical forces.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 *et al*., 1998) while $1/n$ is used as an indication of whether adsorption remains constant (at $1/n = 1$) or decreases with increasing ions concentrations.

Adsorption Kinetics: The comparison of experimental sorption capacities (q_{exp}) and the predicted values (q_{cal}, k_1, k_2,

k_d, R_2) from pseudo first order, pseudo second order and intra particle diffusion constants are given in Table 4 for the biomaterial. The pseudo first order was not satisfactory to explain the experimental data, whereas the calculated, q_{cal} values derived from the pseudo second order model for sorption of the selected ions were very close to the experimental (q_{exp}) values. The second order equation appeared to be the better fitting model than first order and intra particle diffusion equations because it has higher R^2 value.

Adsorption Thermodynamics: The negative values for the Gibbs free energy for sulphate and bromate ions show that the adsorption process was spontaneous and that the degree of spontaneity of the reaction increased with increasing temperature. The entire adsorption process was observed to be endothermic (ΔH =57.31 and 43.32 kJmol^{-1} sulphate and bromate respectively). Table 5 shows that the ΔS values were positive hence, entropy increases as a result of adsorption. This may be due to the redistribution of energy between the adsorbate and adsorbent. Before adsorption occurs, the selected ions 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 molecules increase with increasing adsorption by producing a positive value of ΔS and randomness will increase at the solid solution interface during the process of adsorption.

Conclusion: This study showed that fish scales waste which are usually obtainable at low cost, can be used as an efficient biomaterial for the removal of sulphate and bromate from wastewater. IR spectrum analysis showed different functional groups present in the VTFSWB including hydroxyl, carboxylate esters, phosphate and amine functional groups. The XRD diffractogram suggested the presence of hydroxyapatite in the valuarized fish scales, which acted as an ion exchanger by giving its phosphate group and hydroxide ion site for the selected anions ions. Initial anions concentration, pH, contact time, VTFSWB dosage and its characteristics were the factors responsible for sulphate and bromate ions adsorption. This study demonstrated that fish scales waste biomaterials are environmentally friendly, economical and readily available waste biomaterials with high efficacy for the removal of excess toxic sulphate and bromate ions from wastewater. Most significantly, this study has created an alternative method for fishscales waste values. Additionally, the study achieved the phenomenon of valuarizing waste material which is essential for wastewater treatment.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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