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Removal of Toxic Nitrate and Nitrite from Wastewater by Valuarized Fish Scales Waste Remains

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Abstract- In this work, the adsorption efficiency of fishscales was investigated as an environmentally-friendly and cheap alternative sorbent for removing excess nitrate and nitrite from wastewater. The pulverized size of the fishscales was found to be ≤60 μm, with rough surfaces. Multivariate methodology was employed for optimization of parameters that affect sorption; initial ion concentration which were found to be 28.44 mg/L (NO_2^-) and 28.29 mg/L (NO_3^-), the sorbents; 78.48 mg/L (NO_2^-) and 71.17 mg/L (NO_3^-), contact time, which were found to be 65.72 min (NO_2^-) and 74.84 min (NO_3^-), and solution pH 7.97 (NO_2^-) and 7.00(NO_3^-). The optimized adsorption method exhibited high percentage removal efficiencies toward nitrite and nitrate removal from real wastewater samples at 91.42% and 74.60% with a relative standard deviation (RSD) of 1.44% and 2.09% for n = 3 respectively. Physico-chemical characterization of the fishscales showed multiple functional groups including, carboxylic, hydroxyland carbonyls. The adsorption of ions onto valuarized fishscales was endothermic and spontaneous and the adsorption data followed second-order kinetics.

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Abstract- In this work, the adsorption efficiency of fishscales was investigated as an environmentally-friendly and cheap alternative sorbent for removing excess nitrate and nitrite from wastewater. The pulverized size of the fishscales was found to be ≤60 μm, with rough surfaces. Multivariate methodology was employed for optimization of parameters that affect sorption; initial ion concentration which were found to be 28.44 mg/L (NO_2^-) and 28.29 mg/L (NO_3^-), the sorbents; 78.48 mg/L (NO_2^-) and 71.17 mg/L (NO_3^-), contact time, which were found to be 65.72 min (NO_2^-) and 74.84 min (NO_3^-), and solution pH 7.97 (NO_2^-) and 7.00(NO_3^-). The optimized adsorption method exhibited high percentage removal efficiencies toward nitrite and nitrate removal from real wastewater samples at 91.42% and 74.60% with a relative standard deviation (RSD) of 1.44% and 2.09% for n = 3 respectively. Physico-chemical characterization of the fishscales showed multiple functional groups including, carboxylic, hydroxyland carbonyls. The adsorption of ions onto valuarized fishscales was endothermic and spontaneous and the adsorption data followed second-order kinetics.

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I. Introduction

Nitrate (NO_3^-) and nitrate (NO_2^-) are two different oxidation states of nitrogen (N) that are of environmental health concerns to many researchers [1]because of their solubility nature in water, which has a toxic health effect to humans and aquatic life. The advancement of technology, rapid pace of industrialization, population expansion, agricultural activities and unplanned urbanization contribute to the increased quantities of the two ions thus contaminating surface and ground waters [2]. Nitrate contaminations occur due to the widespread applications of fertilizers containing nitrate for agricultural activities and inadequate treated or untreated human and animal wastes. Nitrate and nitrite have been detected in surface waters, drinking water, ground water and wastewater effluent. Nitrogen exists naturally in soils, typically bounded to organic matter and mineral soil material usually at low concentrations[3]. They also form part of the human diet and can be found in vegetables, fruits, cured meats, fish, dairy products, beers, cereals, and cereal products[4]. However, high level of nitrate concentration in the aquatic environment causes a serious health risk, responsible for methemoglobinemia, decreases in blood pressure, increased heart rate, reduced ability of the blood to carry oxygen to tissues, headaches, abdominal cramps, vomiting, and even death [5].

Reverse osmosis[6], ion exchange[7], powdered activated carbon adsorption[8], the biofilm-electrode reactor (BER),combined membrane bioreactor [9] and adsorption process [1] have been over the past years been employed as conventional removal methods of nitrate and nitrite anions removal from wastewater. However, these methods present some drawbacks, such as high cost and the disposal of the resulting sludge [10].Because of the drawbacks, researchers have turned their attentions to the use of low-cost alternative adsorbents for the removal of nitrate and nitrite anions from wastewater.

In this work, a method employing *valuarized fish scales waste remains* for simultaneously removing toxic nitrate and nitrate anions from wastewater was developed. The study was aimed at developing a cheaper, faster, non-toxic and environmental friendly treatment of wastewater effluent for the removal toxic anions.

II. Materials and Instrumentations

The adsorbent used for the experiments was fish scales waste remains collected from Lake Ngami in Sehitwa, Botswana. Reagents used were: white spirit Vinegar, employed to treat the waste materials, purchased from SPAR (Palapye, Botswana), elemental standard solution of NO_2^-, and NO_3^- with a concentration of 1000 mg/L and NaOH (97%) pellets were purchased from Rochelle Chemicals (Johannesburg, South Africa).A JSM 1700 SEM coupled with EDX, obtained from USA was employed for morphological and elemental analysis. Perkin Elmer System, Spectrum two fourier transform infrared (FTIR)spectroscopy was used to determine the functional groups of materials. ALabRAM HR Evolution Raman S0 – TNO4 Spectrometer (JobinYVon Technology, France) obtained from JobinYVon Technology (Villeneuve d'Ascg, France)

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was employed for characterization of the adsorbents. Meanwhile, nitrate and nitrite anions were determined by a Shimadzu S 150 ion chromatography system (SHIMADZU, Japan) obtained from SHIMADZU (Johannesburg, South Africa).

III. Pre-Treatment of the Fish Scales Waste Remains

The waste remains were washed thoroughly with deionized water to remove mud and unwanted contaminants. After washing the remains, they were sun dried for 48hrs, than pulverized employing a Fritsch pulverisette 5 pulverizer, operated at 400 rpm for 90 min. The pulverized materials were then sieved using 65 – 200 micron mesh size, rewashed with deionized water several times to remove color and dust, and then treated with SPAR white spirit vinegar to remove inorganic pollutants. Finally, they were dried in an oven at 65 ± 5 °C for 6hrs. Characterization of the VFSWR showed the effectiveness of the vinegar during the treatment process (see figures: 1 and 2).

IV. Characterization of Valuarized Fish Scales Waste Remains

To evaluate and reveal details on the physical and chemical properties of the valuarized fish scales waste remains, fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) were employed for the characterization.

Fourier Transform Infrared Spectrometer (FTIR) was employed to investigate the functional groups responsible for analyte interaction with the VFSWR. Figure 1 below shows the functional groups of fish scales before removal (black) and after removal (red) of nitrate and nitrite anions. 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}

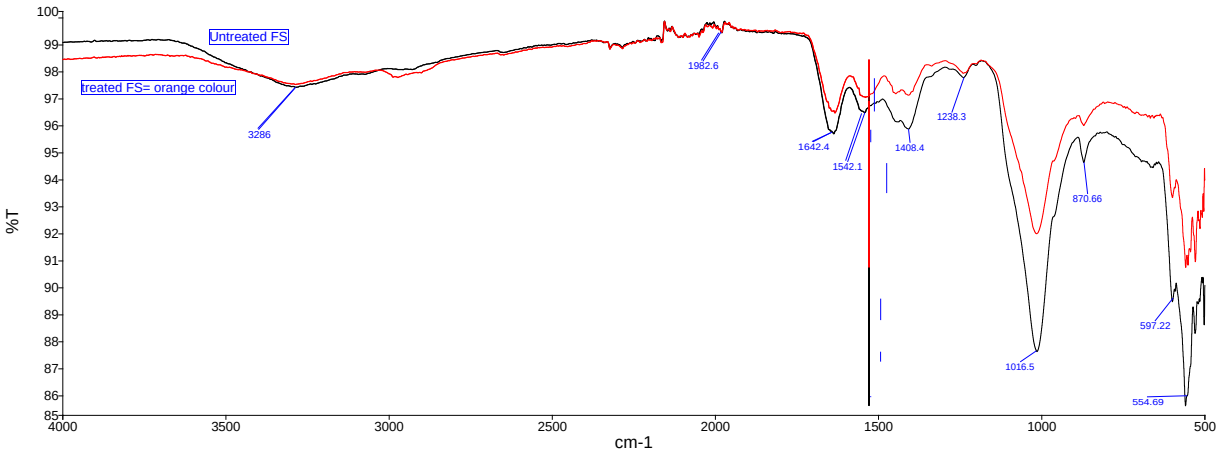

Figure 1: FTIR of fish scales before removal (black) and after removal (red) of target analytes

Fig. 2 shows SEM micrographs of the loaded VFSWR, and VFSWR. The VFSWR as shown in Fig. 2A appears to have a rough surface and are 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. From energy, dispersive X-ray (EDX) analysis, inorganic ions were confirmed in the fish scales before valuarization and after adsorption of ions. Figure 2B clearly shows that the presence of new shiny bulky particles over the surface of ions loaded VFSWR which are absent in the VFSWR. These results confirm the binding of ions in fish scale through adsorption.

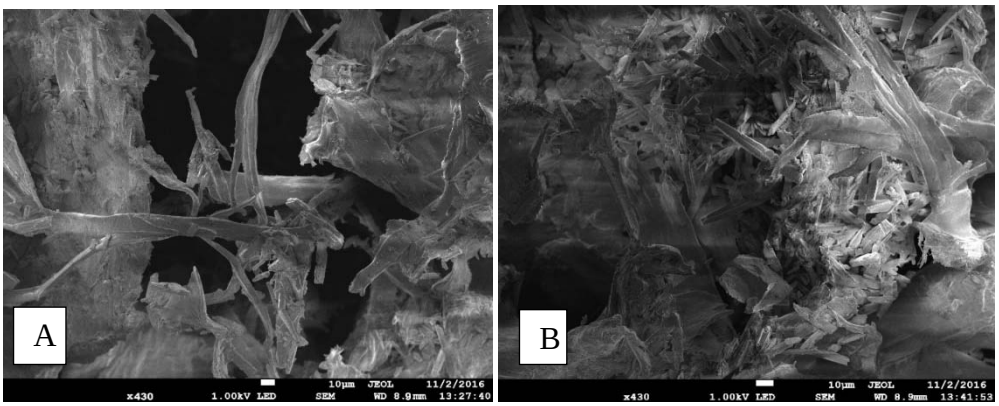

Figure 2: SEM images of the A) VFSWR and B) loaded VFSWR

V. Optimization of Adsorptive Parameters of the Valuarized Fish Scales Waste Remains

Optimization studies were carried out using multivariate optimization methodology. In this study, VFSWRwas optimized by looking at four factors; contact time, pH, VFSWR dosage, as well as concentration. These were first evaluated by employing a two-level fractional factorial design. This design enabled identification of the significance of each factor towards the experimental output. Following this, a face centered central composite design was then performed to determine the optimum conditions for each factor that would result in a maximum response of the experiments. The optimization process was carried out with the use of Minitab Release 14 statistical software (Minitab Inc., USA).

Analysis of the ½ fraction factorial design data was in the forms of normal probability plots of standardized effects as shown by Figures 3. 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 is represented by its distance from the solid line and 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 fall if the effects were zero, while the percentage in the y-axis signifies the weight age of each factor's contribution towards the obtained yield. The normal probability plots of standardized effects of NO_2^- showed that there was a significant contribution towards the obtained yield as a result of interaction between factors (Factor A and Factor B), while, that of NO_3^- showed that there was a significant contribution towards the obtained yield as a result of interaction between factors (Factor A and Factor C).

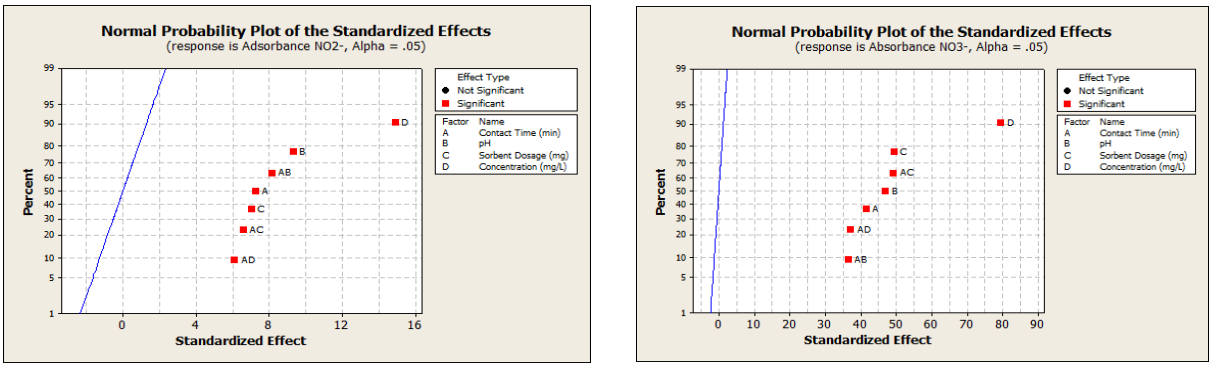

Figure 3: The normal probability plots of standardized effects of nitrite and nitrate for the VFSWR

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

Variable	Factor	Low level	High level
A	VFSWR dosage (mg)	25	1000
B	pH	2	10
C	Contact time (minutes)	15	180
D	Concentration (mg/L)	0	50

Response surfaces and the response optimizer were employed to determine the optimum conditions of each factor in relation to the VFSWR. Test for the significance of the quadratic model was done using the F-test for ANOVA at 95% confidence level. The optimal parameters following performance of the experiments are shown in Tables 2.

Table 2: Optimal parameters for adsorptive efficiency of the VFSWR

Anions	pH	VFSWR dose (mg/L)	Contact time (min)	Initial concentration (mg/L)
Nitrate	7.00	71.17	74.84	28.29
Nitrite	7.97	78.48	65.72	28.44

VI. Application of the Optimized Adsorption Method to Real Samples

After determining the optimum parameters as shown in Table 2, the parameters were applied in a 50 mL of the wastewater sample and the resulting solution was analysed using IC. The percentage removal of ions was calculated using the formula below:

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

Where; C_i is the initial concentration of metal ions in wastewater sample, C_f is the final concentration of nitrate and nitrite anions in wastewater after applying the VFSWR. The percentage removal of nitrate and nitrite were 91.42% and 74.60% with % RSD of 1.44% and 2.09% respectively after the experiment was done in triplicate as showed in Figure 4.

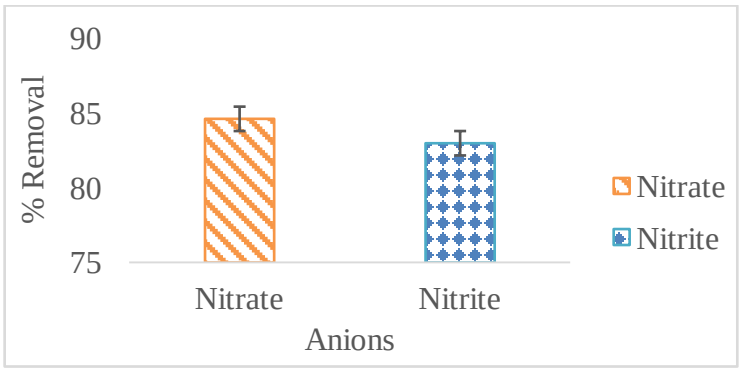

Figure 4: Percentage removal of nitrate and nitrite anions by VFSWR from wastewater

VII. Adsorption Kinetics

In order to define the adsorption kinetics of the anions, the kinetic parameters for the adsorption processes were studied for the VFSWR. The contact times employed for the experiment were ranging between 1 to 90 min and first order, second order and intra particle diffusion models were applied to the experimental data employing mathematical models. The first order kinetic equation is

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303} t \quad (2)$$

Where *qe* and *q* are the adsorption capacity at equilibrium and at time t respectively and k_1 is the rate constant of the pseudo first order adsorption process.

Plot of $\log(q_e\text{-}q)$ vs. t gives a straight line for first order adsorption kinetics and the rate constant k_1 is computed from the plot.

The sorption data was also studied by second order kinetics

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (3)$$

The applicability of this equation can be studied by a plot of t/q vs. t. Intra particle diffusion was observed using the relationship between specific sorption (q) and the square root of time ($t^{1/2}$). The relation is expressed as follows:

$$q = k_d t^{1/2} \quad (4)$$

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 anions 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 as shown in Table 3[11].

Table 3: Adsorption Kinetics parameters of the VFSWR

Anions	q_{exp} (mg/g)	Second Order			First Order			Intra Particle Diffusion	
		R^2	K_2 (gmg^{-1}min^{-1})	q_{cal} (mg/g)	R^2	K_1 (min^{-1})	q_{cal} (mg/g)	R^2	K_d (mgL^{-1}min$^{-1/2}$)
NO_2^-	12.47	0.9976	0.036	12.92	0.9278	0.022	0.15	0.6343	0.288
NO_3^-	12.10	0.9976	0.046	12.95	0.9297	0.022	0.15	0.5898	0.108

VIII. Thermodynamics Parameters

The changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption process were obtained using the following equations

$$lnb = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

Where R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and b (L/mol) the thermodynamic equilibrium constant. As reflected by the R^2 values shown in Figure 5the plot of Gibbs free energy (ΔG) versus temperature for VFSWR was found to be linear.

The negative values for the Gibbs free energy for all the anions, show that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature [12]. The overall adsorption process seems to be endothermic (ΔH =46.19 and 51.25 kJmol-1 for NO_2^- and NO_3^- respectively). The ΔS 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 (NO_2^- and NO_3^-) and adsorbent (VFSWR).

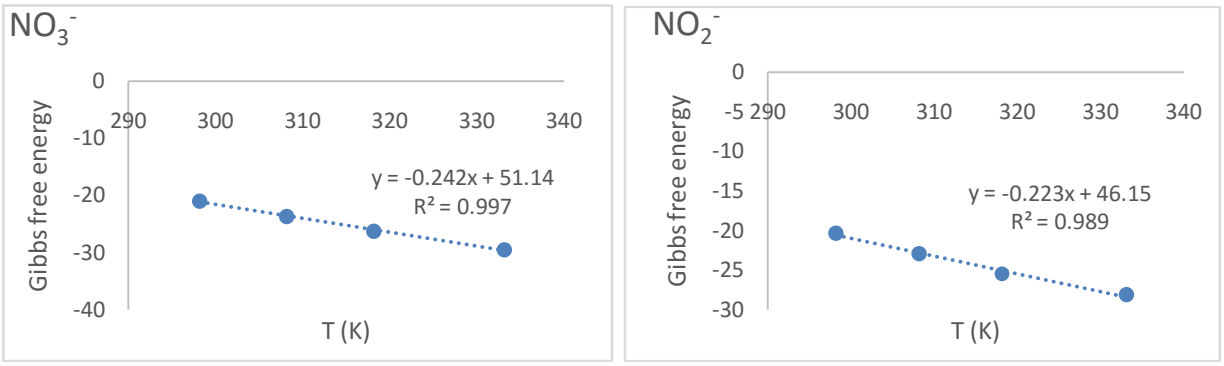

Figure 5: Adsorption thermodynamics of NO3- and NO2- by the VFSWR

IX. Conclusion

This study indicated that valuarized fish scales waste remains, which is widely available at no cost, can be used as an efficient adsorbent for removal of NO_2^-, and NO_3^- from wastewater. IR spectrum analysis suggested the different functional groups which are present in the given samples are OH, CH stretching, C=C stretching, C-O stretching. The thermodynamic study shows that the adsorption of the anions was of endothermic nature. The negative values of ΔG reveal the feasibility and spontaneity of the process. Initial concentration of adsorbates, pH, contact time, VFSWR dosage and adsorbent characteristics are the factors responsible for anions adsorption capability. This study demonstrated that valuarized fish scales waste remains are environmentally friendly, economical and readily available waste materials with high efficacy for the removal of excess toxic anions from wastewater as shown by the two model anions, NO_2^-, and NO_3^-.

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