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Research Article

Removal of Phosphate and Ammonium Ion from Domestic Wastewater Using Clay Feldspar in Wupa Sewage Treatment Plant Abuja

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Abstract: The aim of this study is centered on the sustainability of feldspar as an adsorbent as opposed to other clay minerals such as plastic clay, red clay and barite. Brauner-Emmert-Teller (BET) analysis of the clay minerals considered in this study revealed that raw feldspar had the highest surface area and pore volume of 332.8 m^2/g and 0.218 cc/g respectively. Similarly, the clay minerals were used in adsorption study with feldspar producing the best removal efficiency of 90.00% and 73.96% for ammonium and phosphate ions respectively. The BET results and the adsorption test showed that feldspar was a better adsorbent than the other adsorbents. Thermal activation of feldspar was carried out at temperatures of 500–700 °C using muffle furnace. The BET results of the thermal activation revealed that feldspar activated at 600 °C has the highest surface area and pore volume of 533.9 m^2/g and 0.272 cc/g respectively. The Fourier's transformed infrared (FT-IR) results indicated that several functional groups were involved in the adsorption process of the phosphate and ammonium ions some of which were O-H, N-H and C-O groups. The results showed that irregular-layered structures of the raw feldspar became smooth and regular after thermal activation. The effects of pH, adsorbent dosage, temperature, contact time and initial PO_4^{3-} and NH_4^+ concentrations on the adsorption of phosphate ions and ammonium ions were investigated using atomic adsorption spectroscopy (ASS). The adsorption studies of phosphate ion and ammonium ion onto feldspar increased with contact time, adsorbent dosage and temperatures until optimum values were reached.

***Keywords*:** feldspar, domestic wastewater, phosphate, ammonium

1. Introduction

In recent times several causes of environmental degradation among water sources are related to excess disposal of nitrogen and phosphorus nutrients at aqueous environments after which the dominant phenomenon of eutrophication that was reported via visible cyanobacterial of algal blooms, floating plant materials, surface scums, and benthic macrophyte accumulations [1]. Safe disposal of wastewater remains a serious problem in Nigeria where it has the potential of causing contamination and create environmental pollution. This result in corresponding increase in polluted water generating in urban areas, and stringent effluent discharge regulations and public preferences concerning environmental quality were the motivation for countries with adequate wastewater management practices [2]. However, several treatment processes have been utilized as constructed wetlands technology that utilizes plant and microbial communities from the rhizosphere, biological processes coagulation /flocculation and precipitation as well as chemical processes such as

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chemical precipitation[3–5]. The sewage if it is not treated before being discharged into waterways, serious pollution is the result. In recent years, because of continuous population growth, rapid industrialization and accompanying technologies involving waste disposals increases the rate of discharge of the pollutants into the environment is far higher than the rate of their purification[6]. Wastewater comprises of liquid wastes discharged by domestic residences, and commercial, industrial, and/or agricultural activities. It can encompass a wide range of potential contaminants and concentrations. Domestic wastewater contains human waste, food scraps, oil, soaps, chemicals, and countless living organisms[7]. The number of wastewater treatment plants in most developed countries is also on the increase because of industrialization, so more sludge is being produced[8].

To eliminate impurities and different exchangeable cations from clay minerals and to prepare a well-defined material for use as a catalyst and adsorbent, various activations methods have been used, most often with acids. Indeed, the treatment with mineral acids significantly changed their textural characteristics and effects on the mineralogical, composition of the raw material and related properties. This process causes an increase in surface area, and surface acidity and introduces permanent mesoporosity which removes metal ions from the crystal interlayer, and partially delaminated the clay[9]. The production of mixed materials allows the use of a material of a small fraction of photocatalysts to increase the pollutant removal efficiency of the clay[10].

Clay minerals can remove approximately 70% of the waste and the remaining 30% can be removed using activated carbon. However, activated carbon is costly and cannot be used at large scale. This situation compelled scientists toward the development of low-cost adsorbents that is readily available and eco-friendly. The source of clay has received little or no investigative study on its pollutants. Hence, this study was undertaken to assess the removal of phosphate and ammonium ion from domestic wastewater using clay feldspar in Wupa sewage treatment plant Abuja, Nigeria.

Ref.[11] in their work titled 'Phosphate and ammonium removal from wastewaters using natural-based innovative bentonites impacting on resource recovery and circular economy' listed the different approaches for phosphate removal as shown in Figure 1 below.

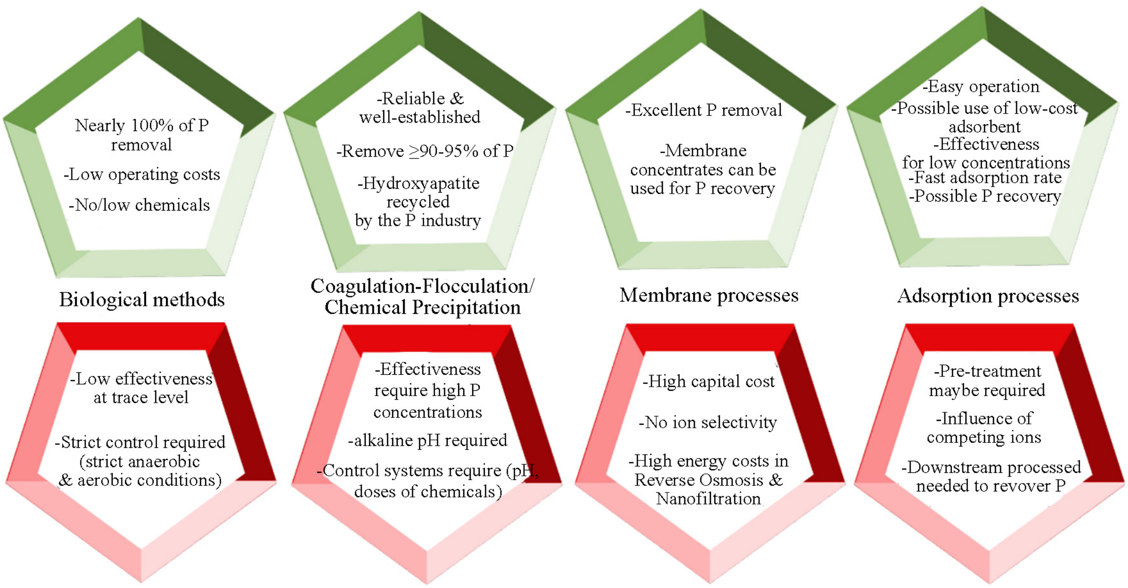

Figure 1. Synopsis of different approaches for Phosphate removal and recycling from wastewater, modified[11]

However, the success of these methods shown in Figure 1 was determined by the preconditions of highly concentrated phosphate or under the synchronicity of ammoniacal nitrogen with phosphate. In their findings, Zamparas et al. (2019)[12] indicate the estimation of phoslock as a P&N-P&N-inactivation agent in the overlying water and sediment cores under oxic and anoxic conditions from a polluted pond. The work developed innovative approaches to remove phosphate to support the degraded lake and reservoir. Ref.[12] in their work titled "Novel composite materials as P-adsorption agents and their potential application as fertilizers" review the role of phosphorus in fertilizer stating that it is a harmful heavy metal and when absorbed can be used as fertilizer to enrich the soil. This is a novel material for water purification.

2. Materials and methods

2.1 *Description of study area*

The study area for feldspar is situated in Kutigi, in Lavun Local Government Area of Niger State. It lies between longitude 5° 35′ E and 5° 39′ E and latitude 9° 10′ N and 9° 13′ N and covers an area of about 39.88 km^2. Kutigi clay occurs as residual clay due to the weathering of feldspar from feldspathic sandstone. Figure 2 shows the flow chat for the procedure adopted while taking this research.

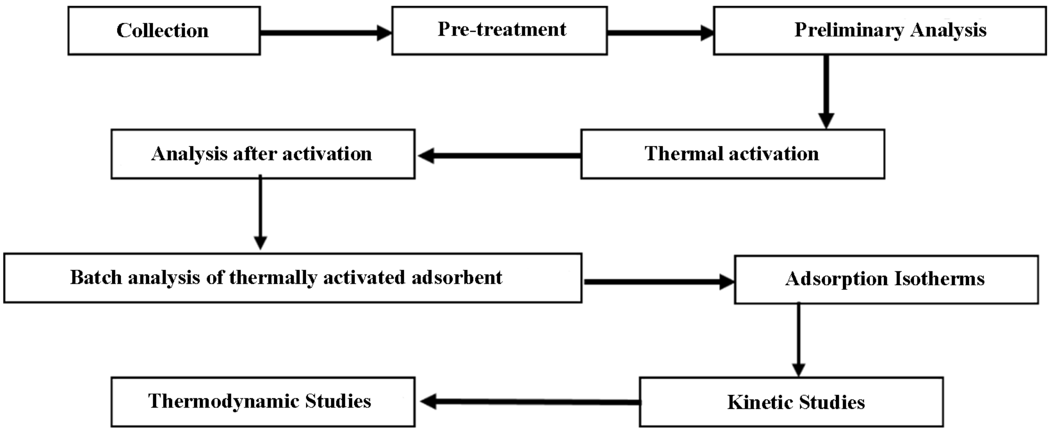

Figure 2. Summary of the experimental procedure

2.2 *Sample collection*

Barite samples were collected from different locations in the area of Wuse in Nasarawa state, Nigeria. The characterization of these samples was carried out using the screening electronic microscopy (SEM)S. Plastic clay was sourced locally from Agaie, Niger state. The Red clay samples were collected and their physico-chemical properties were analysed. Raw sewage was collected using a sterile sample bottle and placed in the direction of the flow of water at wupa sewage treatment plant Abuja. The powdered sample of the feldspar was oven dried, grounded with mortar to fine particle sizes and screened to 60 µm size.

2.3 *Physiochemical parameters*

The pH and temperature were measured using the standard pH electrode meter (Hanna HI 98129 pH EC/TDS Waterproof Combo Tester/Meter), biochemical oxygen demands using respirometry method, chemical oxygen demand using closed reflux colorimetric method (using a COD reactor), total suspended solid analysis using gravimetric method, determination of phosphate (PO_4^{3-}) and ammonium (NH_4^+) were carried out using colorimetric method determined using photometer (Palintest Photometer 7100).

2.4 *Characterization of the raw and activated clay*

The effect of raw and activated clay minerals was analysed with various characterization methods such as Thermo-Gravimetric Analysis (TGA) using PerkinElmer TGA 4000 instrument, Fourier Transformed Infrared Spectroscopy (FTI-R) using Bruker Alpha II infra-red spectrometer, Brunauer-Emmett-Teller (BET) (by nitrogen adsorption-desorption method using nitrogen with an autosorb apparatus, Micrometrics ASAP 2020, surface area and porosity analyzer), Scanning Electron Microscope (SEM) with a ASPEX 3020 scanning electron microscope, model SIRIUS50/3.8 with an attached energy dispersive X-ray spectroscopy (SEM/EDX) machine, X-ray Fluorescence (XRF) spectrometry using PAN analytical XRF spectrometer (MiniPal 4).

3. Results and discussion

3.1 *Preliminary analysis on the clays minerals*

The results of the physiochemical analysis of the clay minerals are as shown in Table 1. The percentage reduction and removal efficiency of the different clay minerals were also calculated and the results shown in Table 2.

Chemical oxygen demand (COD) measures the oxygen required by organic matter for its oxidation, Biological oxygen demand (BOD) estimates the amount of oxygen needed by bacteria to break down simpler substances to the decomposable organic matter present in any water, wastewater or treated effluent and Total suspended solids (TSS) plays an important role in wastewater treatment. TSS test results are done routinely to evaluate the operation of conventional treatment processes and are useful for effluent filtration in reuse application.

Table 1. The physicochemical analysis of raw domestic wastewater using clay minerals

Parameter	Raw Wastewater	Plastic Clay	Red Clay	Barite	Feldspar	WHO's Limit for Effluent	F.M.Envlimit For Effluent
pH	6.689	7.443	7.49	7.601	7.527	6.5–8.5	06-Sep.
Temp (°C)	26.1	24.4	24	23.7	23.3	<40	<40
Conductivity (μS/cm)	580	548	570	672	643	1250	
NH_4^+(mg/L)	50	15	25	25	5	10	10
PO_4^{3-}(mg/L)	14.4	3	2.2	0.6	3.75	5	5
Fe^{2+}(mg/L)	2	1.15	0.8	0.25	1.05	1	
COD	750	120	300	200	280	80	80
BOD	350	40	120	80	120	30	50
TSS	1000	40.5	40	12	41	30	30

Table 2. The analysis of raw domestic wastewater in percentage removal using clay minerals

Parameter	Raw Sample	Plastic Clay	Red Clay	Barite	Feldspar
NH_4^+	50	70.00%	50.00%	50.00%	90.00%
PO_4^{3-}	14.40	79.17%	84.72%	95.83%	73.96%
Fe^{2+}	2.00	42.50%	60.00%	87.50%	47.50%
COD	750.00	84.00%	60.00%	73.33%	62.67%
BOD	350.00	88.57%	65.71%	77.14%	65.71%
TSS	1000.00	95.95%	60.00%	95.95%	95.90%

As clearly observed from the Tables 1 and 2, comparing the removal efficiencies of the different clay minerals tested in the removal of the pollutants, it was observed that the feldspar clay gave a better result (higher removal efficiency) in ammonium than the other clay minerals especially in the removal of the pollutants under study (ammonium ion). Hence, the feldspar was selected for use as adsorbent in the removal of ammonium and phosphate ions from domestic wastewater.

3.2 *Characterization of raw and thermal activated clay minerals*

3.2.1 *BET analysis of the clay minerals*

As shown in Table 3, the feldspar adsorbent is seen to be higher in surface area, pore volume and pore size than plastic clay by 66.7%, 75.5% and 13.9% respectively. The feldspar adsorbent was similarly seen to be higher in surface area and pore volume than barite by 1.14% and 7.8% respectively. This implies that feldspar adsorbent will provide more active sites for adsorption compared to plastic clay and barite, hence its selection for use in the adsorption study [13]. The equipment used was BET surface area analyzer. The raw clay was treated by hand picking to remove dirt and other foreign bodies and after which it was sieved with a 60 μm mesh sieve.

Table 3. BET of the clay minerals

Sample	Surface Area m²/g	Pore Volume cc/g	Pore Size nm
Plastic clay	110.9	0.0519	2.096
Feldspar	332.8	0.2123	2.433
Barite	329.0	0.1775	2.452

3.2.2 *XRF analysis of feldspar*

The Table 4 shows that the mineral composition of feldspar clay as revealed from the characterization of the sample with X-ray flurescence, the clay mineral consists mainly of silica and alumina, with metallic oxides present in trace or small amount. This results agrees with [14] although the silica content of the clay mineral was higher which could be due to the origin of formation of the feldspar clay.

Table 4. XRF analysis of feldspar clay sample

Element	Concentration	Peak (CPS/MA)
Fe_2O_3	0.99%	3027
SiO_2	80.48%	4586
Al_2O_3	14.16%	211
MgO	2.78%	3
P_2O_5	0.20%	49
SO_3	0.07%	35
TiO_2	0.03%	123
MnO	0.05%	510
CaO	0.53%	861
K_2O	5.20%	5106
CuO	0.00%	7
ZnO	0.00%	27
Cr_2O_3	0.00%	7
V_2O_5	0.00%	7
As_2O_3	0%	0
PbO	0.02%	10

3.2.3 *TGA of raw feldspar*

Figure 3 shows the Thermogravimetric Analysis (TGA) of raw feldspar. The weight variance is categorised into 3 regions (phases). In Phase I (25 °C–280 °C) correspond to the loss of moisture content in the raw feldspar. Phase II which corresponds to temperature range of 280 °C–470 °C gave a sharp drop in the weight of the feldspar. This could be attributed to the loss of volatile content present. Phase III which starts from the temperature of 470 °C depicts the genesis of thermal decomposition whereby the calcium carbonate in powder is converted to calcium oxide due to the liberation of carbon (IV) oxide. Process of dehydration is completed when an atomic structure is destroyed, heating up to the temperature higher that it's needed for observed material, effects of sintering and formation of non-active mullite are always expected [15].

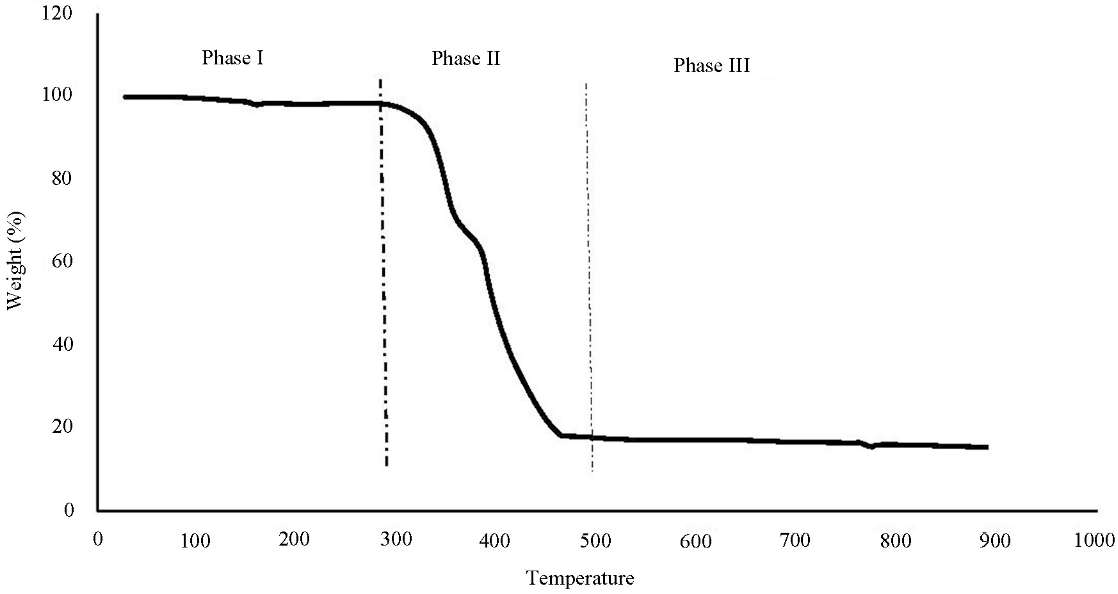

Figure 3. Thermo-gravimetric analysis (TGA) plot of feldspar adsorbent

3.2.4 *Thermal activation of feldspar*

Heat treatment was carried out on 80 g samples in the laboratory furnace at different temperatures (500, 600, and 700 °C) for 60 min. The samples were quenched at room temperatures on heating at ambient conditions to avoid crystallization. The samples were used to adsorb pollutant ions and the optimum temperature was determined [16].

It was observed that from Tables 5 and 6 the adsorption efficiency gradually increased when calcination temperature increased from 500 to 600 °C, however, the adsorption efficiency reduced a bit when the calcination temperature was increased to 700 °C. The main reason for this is that increasing calcination temperature helps to increase the specific surface area and develop cracks from the surface of the mineral to its center [17]. The slight negative effect of the calcination temperature observed at 700 °C indicated that the optimum calcination temperature is between 600 °C and 700 °C. Studies have shown that thermal treatment generates more adsorption sites for pollutants.

Table 5. Effect of calcination temperature on removal efficiency

Temperature		**500 °C**			**600 °C**			**700 °C**		
Time (mins)	RAW	10	30	60	10	30	60	10	30	60
Phosphate	12	8	7.3	5.1	4.7	4.4	4.2	6.9	7	5.9
Ammonium	20	16	14.4	9.8	9.8	8.1	7	10.9	11	11.9

Table 6. Effect of calcination temperature on removal efficiency (in percentage)

Temperature	**500 °C**			**600 °C**			**700 °C**		
Time (mins)	10	30	60	10	30	60	10	30	60
Phosphate removal (%)	33.3	39.2	57.5	60.8	63.3	65	42.5	41.7	50.8
Ammonium ion removal (%)	20	28	51	51	59.5	65	45.5	45	40.5

3.2.5 *Fourier transform infrared spectra (FTIR) analysis of feldspar*

The FTIR pattern for the raw feldspar is as presented in Table 7 while for the treated and used feldspar adsorbent are as presented in Tables 8 and 9 respectively.

Table 7. Bands and suspected bonds in raw feldspar

IR	Band	Bond Suspected
4000–3800	3473.91	O-H strech,free hydroxyl
3300–2900	2360.95	N-H group streching
2400–2150	2000.25	C-O
2000–1950	1803.5	C-C
1790–1660	1639.55	C=O
585–570	534.30	M-O

Table 8. Bands and suspected bonds in treated feldspar

IR	Band	Bond Suspected
3300–2900	3126, 2876	N-H group streching
2400–2150	2392	C-O Stretch
1790–1660	1786	C=O Stretch
1615–950	872	N-H wag
500–430	420	S-S Stretch

Table 9. Bands and suspected bonds in used feldspar

IR	Band	Bond Suspected
3300–2900	3218, 2876, 2782	N-H group stretching
2400–2150	2000.25	C-O
2000–1950	1803.5	C-C
1790–1660	1786, 1564	C=O
1615–950	872	C-H
500–430	420	S-S Stretch

As shown in Tables 8 and 9, the bands of some groups of the treated feldspar had changed in their amplitudes and positions after the treated feldspar was used for adsorption. The N-H and C=O groups had shifted from 3126 cm^{-1} and 1786 cm^{-1} to 3218 cm^{-1} and 1564 cm^{-1} respectively. These shift in bands indicated that the functional groups played an important role in the adsorption process [13]. Figure 4 shows the graphical combination of Tables 8 and 9.

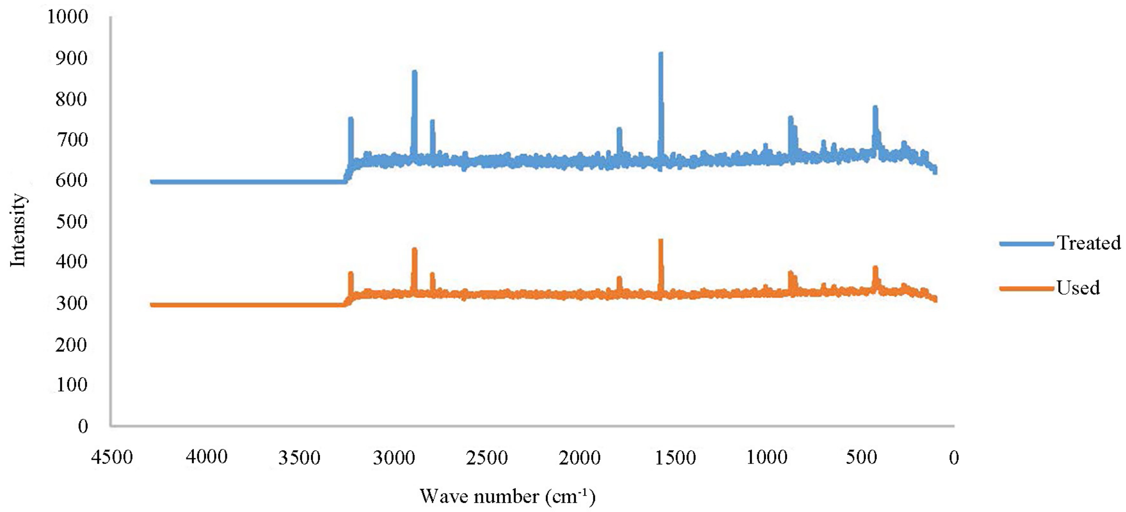

Figure 4. Combined Raman spectra of used and treated feldspar adsorbent

3.2.6 *Scanning electron microscopy (SEM) analysis of feldspar*

The structure of raw feldspar particles as shown in Figures 5 and 6 at magnifications of 330× and 500× consisted of crystalline and irregular layered structures, whereas the thermally activated feldspar (treated) as shown in Figures 7 and 8 at magnifications of 340× and 500× displayed relatively smooth structure with cracks on the surface. The significant difference in the surface morphology confirms the presence of more pores and cracks on the surface which could supply a large surface area for the reaction [18].

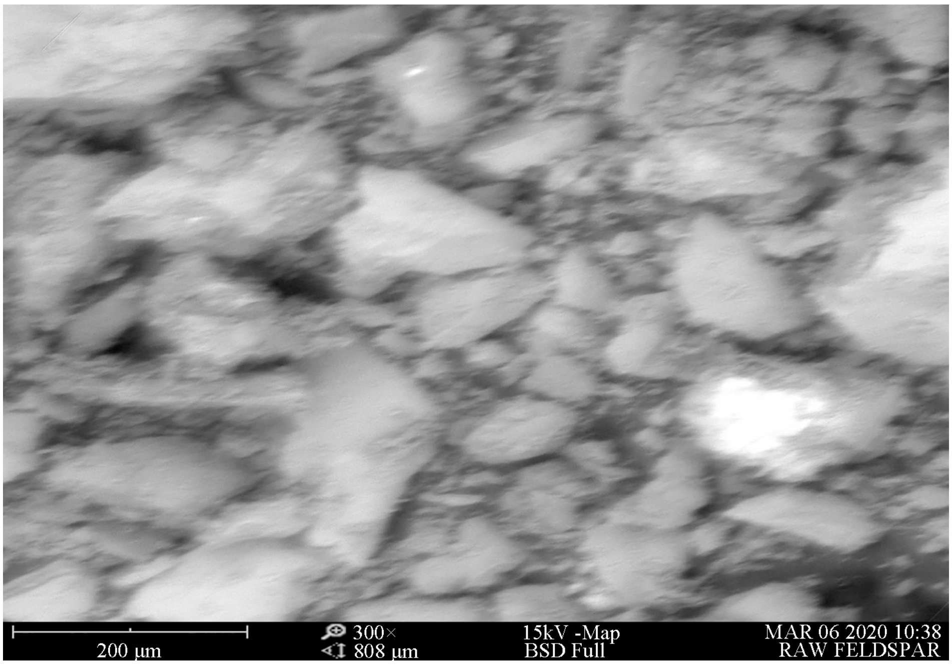

Figure 5. SEM of raw feldspar adsorbent at a magnification of (330X)

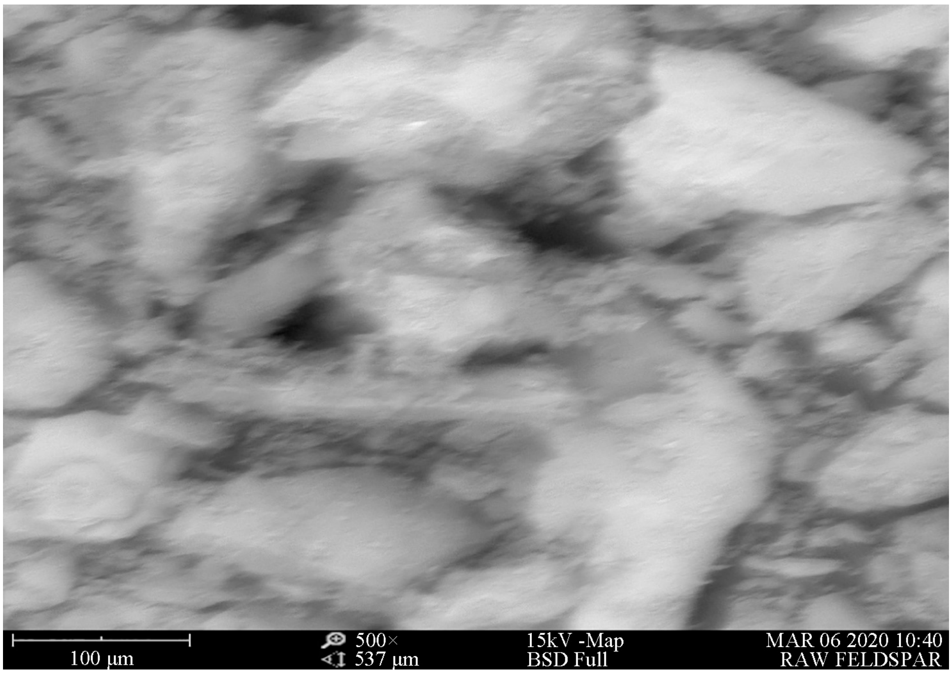

Figure 6. SEM of raw feldspar adsorbent at a magnification of (500X)

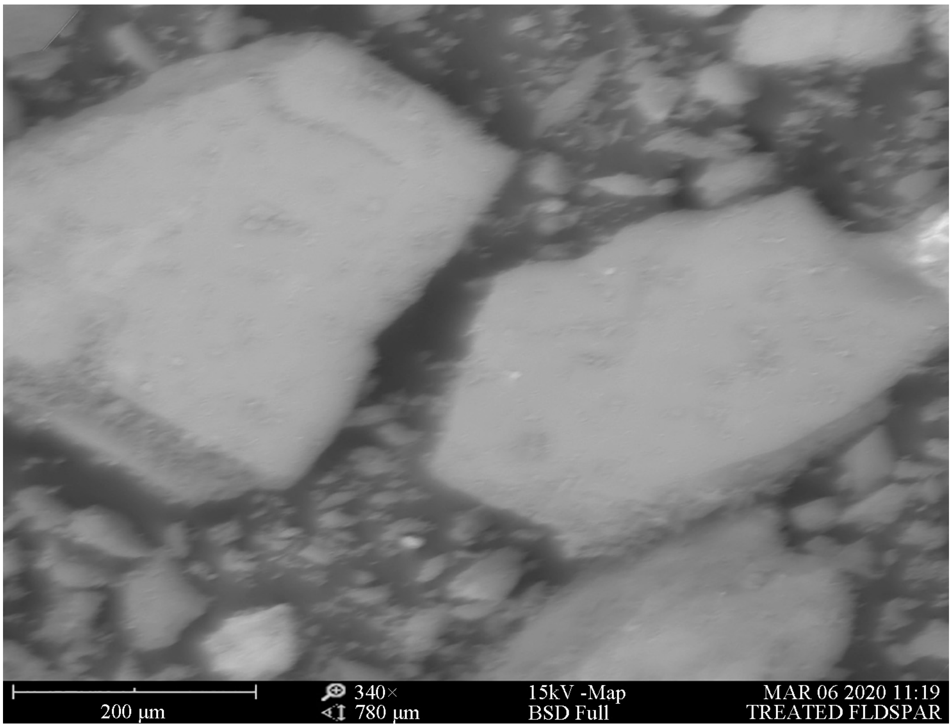

Figure 7. SEM of treated feldspar adsorbent at a magnification of (340X)

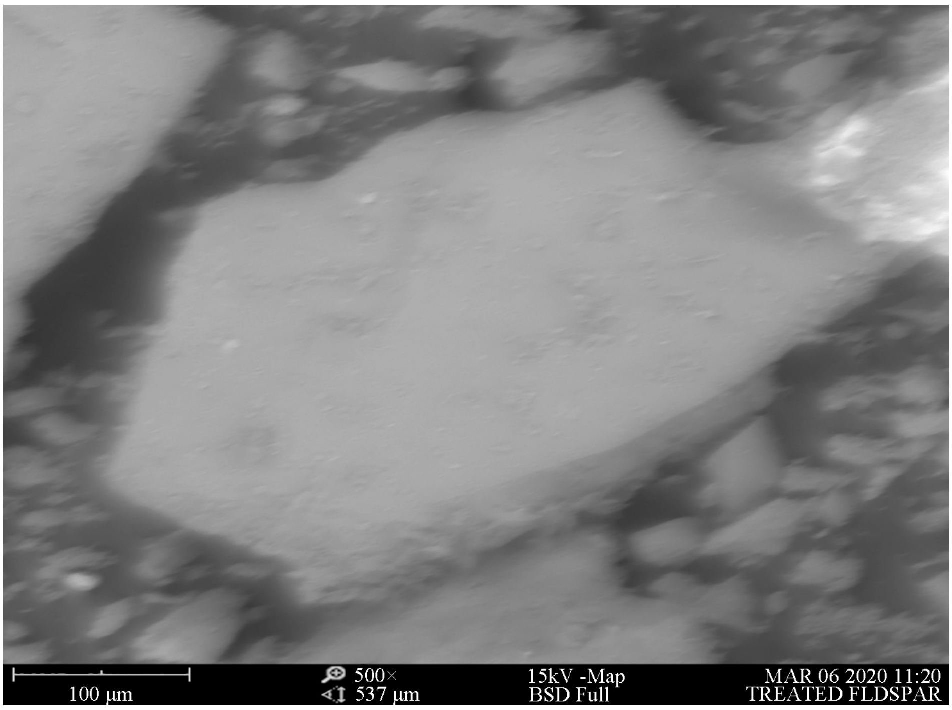

Figure 8. SEM of treated feldspar adsorbent at a magnification of (500X)

3.2.7 *Domestic wastewater analysis*

The domestic wastewater was analyzed to determine the physiochemical properties pH, Turbidity, Total Dissolved Solids, Conductivity, Chlorine, Total hardness, Phosphate ion and Ammonium ion. The results are as shown in Table 10.

Table 10. Physicochemical properties of the well water after treatment

Physicochemical Parameters	Wastewater before Treatment	Wastewater after Treatment	WHO Limit for Effluent
PH	8.22	4.21	6.5–8.5
Conductivity (µS/cm)		783	<1250
Turbidity (NTU)	185	120	
TDS (mg/L)	1338.16	255.85	
Total hardness	230	135	2000
Chlorine (mg/L)	330.75	232.75	
Calcium (mg/L)	132.2	39.94	
Magnesium (mg/L)	52.15	16.25	
Phosphate (mg/L)	12	4.2	5
Ammonium (mg/L)	35	6	10

4. Conclusions

In this research, the removal of phosphate ions and ammonium ions from domestic wastewater compared to the other clay minerals was investigated and samples were collected from different locations in the area of Wuse in Nasarawa state and Agaie, Niger state, Nigeria. The Fourier Transform Infrared (FTIR) analysis indicated the presence of O-H, N-H and C-O groups which were responsible for the adsorption of the phosphate and ammonium ions from the wastewater. The BET results of the thermally activated feldspar revealed surface area and pore volume of 533.9 m^2/g and 0.272 cc/g respectively, providing the active sites for the adsorption of the ions. The adsorption process extremely depends on the contact time, pH, adsorbent dosage, initial pollutant concentration and temperature. The adsorption of the phosphate and ammonium ions increased with increasing contact time, temperature and adsorbent dosage, the removal of the ions were higher in the acidic medium (lower pH) than in basic medium. Maximum adsorption efficiencies were achieved for the removal of phosphate ions and ammonium ions from the domestic wastewater using the activated feldspar adsorbent. It is expected in the future that other harmful pollutants should be removed, acid treatment recommended and a sand bed attached to the sewage.

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