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Kinetic and Thermodynamic Studies on Adsorption of Pb^{2+} and Cr^{3+} from Petroleum Refinery Wastewater using Linde Type a Zeolite Nanoparticle.

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Abstract: *In this research work, lynde type Zeolite (LTA-Zeolite) nanoparticles (ZANPs) were synthesized using kaolin obtained from Darazo Bauchi State, the X-ray fluorescence (XRF) result shows SiO_2, Al_2O_3 percentage of 60.247 and 38.316 respectively and SiO_2/Al_3O_2 ratio of 1.57 which is suitable for the synthesis of Zeolite-A. The produced nano adsorbent was characterized using X-ray fluorescence (XRF), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), Ultraviolate-visible spectroscopy (UV-visible spectroscopy) and N_2-Brunauer–Emmett–Teller(BET)surface analysis. The SEM micrographs revealed well-dispersed Zeolite-A nanoparticles (ZANPs) and the N_2-BET showed a high surface area of 106.250m^2/g, pore diameter of 2.1132 (nm) and a pore volume of 0.052 (cc/g) for ZANPs. The array of removal of Heavy metal pollutants Pb, 96.0% Cr, 90%, ZANPs removing a higher percentage of Lead pollutants. Isothermal models indicated that the Freundlich model (R^2)of 0.999 was most suitable for describing the adsorption process, which conformed to pseudo-second-order kinetics(R^2) of 0.999Cr.*

Keywords: *Remediation, heavy metal, nanoparticles, zeolites; petroleum industrial wastewater*

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1.0 Introduction

Based on the World Health Organization findings, the volume of contaminated water in the global society is several times more than the volume of potable water (Eddy *et* al., 2023a-b; Jimoh and Umar, 2015). Several point and non-point pollution sources have been investigated and such results have always led to the conclusion that industrial activities are the major sources of contaminants in most of our water sources (Adefemi and Awokunmi, 2007). The consequence could range from mild symptoms to chronic and finally death (Deziel & Villanueva, 2024). Among the notable industries, whose contamination problems have been significantly published is the petroleum industry. (Ugya *et al*., 2017). Several hydrocarbon, heavy metal, other organics and physicochemical parameters of

water contaminated with wastes from the petroleum sectors have never been favourable to man and the environment (Dey and Islam, 2015). In the water sector, such observations have been widely targetted by the development of different water treatment measures including adsorption, photodegradation, electrophoresis, electrodialysis, ozonation, oxidation, etc (Tijjani *et al*., 2014; Garg *et al*., 2022). Adsorption is generally accepted as a sound measure because of its flexibility regarding cheap raw materials options, cost-effectiveness, biodegradability and environmentally friendliness.(Ibrahim and Abdullahi, 2017) However, the right choice of adsorbent can be a major challenge towards the success of achieving optimum or complete removal of contaminants (Baral *et al*., 2021). Widely acceptable properties of good adsorbent borders on surface properties such as large surface area, high porosity, large surface area to volume ratio high thermal stability and resistance to chemical attack as well as mechanical stability (Ibrahim and Abdullahi, 2017). Over some decades, investigative reports suggest that most materials can meet some of the listed conditions but nanoparticles are unique when considering the listed conditions (Makarov *et al*., 2014; Odoemelam *et al*., 2023). Recently, nanomaterials have been considered good materials for wastewater treatments (Shannon *et al.*,2008). However, it is reported that, when the size of the metal decreases to the nanometer range, the increased surface energy leads to their poor stability (Lee *et al.*,2015; Baqer *et al.*, 2017). Since heavy metals are one of the most endangering contaminants in aquatic systems, their presence in petroleum wastewater is significantly unacceptable. Therefore, there is a need to offer an effective remediation approach.. Therefore, this study is aimed at synthesizing zeolite A type from koaline obtained from some locations in Nigeria.

2.0 Materials and Methods

The wastewater was collected from the Kaduna Refinery and Petrochemical Company (KRPC) in Kaduna, Kaduna state. The kaolin used in this research work was collected from Fate Darazo Local Government Area in Bauchi state, Nigeria. Both distilled and deionized water were used throughout the laboratory studies as well as sample treatment and analysis.

2.1 Pre-treatment of the raw Kaolin

The refining or treatment process started by crushing 700 g of the raw Fate-Darazo kaolin using a porcelain mortar and pestle. It was soaked in 15 litres of water for 24 hours to form a slurry, and dissolve impurities and other unwanted materials present(slurry) at the top surface water was decanted and the slurry was sieved with a sieve of mesh size 350μm and then air dried. The dried cake was pulverized and sieved to allow only particles with sizes ≤ 100μm to pass through and characterized using XRF, XRD, FTIR and SEM.

2.2 Metakaolinization process

The meta-kaolinization process was carried out by subjecting the sample to elevated temperatures ranging from 600 to 900 ^{o}C for 2 hours using a muffle furnace (Mgbemere *et al.*, 2018). It was characterized using XRF.

2.3 Synthesis of LTA-zeolite from kaolin

Synthesis of zeolite was carried out using the metakaolin sample calcined at 700 ^{0}C and 900^{0}C while NaOH Pellets as the source of Na_2O. Using 6 g of NaOH dissolved in 100 cm^3 of deionized water and stirred briefly for 10 minutes. 5 g of metakaolin was then added gently to obtain the aluminosilicate gel. The gel was stirred continuously at room temperature allowed to age for 24 hours and transferred into a 100 ml stainless autoclave.

A hydrothermal treatment was performed in an oven (Model No:0607034; 2006-2007) maintained at 120^{o}C for 6 hours. At the end of the hydrothermal reaction, the mixture was

filtered and washed with deionized water until a $_pH$ of about 7 was obtained and dried in an oven at 100^oC for 4 hours and calcined in a furnace (Model SXL Muffle furnace). The ZeoliteA obtained was characterized using FTIR, XRD, EDS and SEM.

2.4 Batch Adsorption Experiment

A batch adsorption study was employed. Equilibrium isotherms were obtained by studying the adsorption process of Lynde type A Zeolite(LTA-zeolite) at different contact times, temperatures and adsorbent dosages. The effect of contact time was studied to establish the adsorption equilibrium. The effects of temperature were studied to evaluate the adsorption kinetics parameters and the effects of adsorbent dosage were also to investigate adsorption isotherms.

Adsorption equilibrium and percentage removal were calculated using equations 1 and 2 respectively (Eddy *et al.*, 2024a-b)

$$q_e = \frac{C_1 - C_2}{1} \times \frac{V}{m} \quad (1)$$

$$q_e = \frac{C_1 - C_t}{1} \times \frac{V}{m} \quad (1)$$

$$\%\, Removal\ (R) = \frac{C_1 - C_2}{C_1} \times \frac{100}{1} \quad (3)$$

q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), $_t$ is the amount of adsorbate adsorbed at time t. C_1; the initial adsorbate concentration in (mg/L), C_2; the concentration of adsorbate at equilibrium (mg/L), m is the mass of adsorbent (g) and V; the volume of the solution (mL) (Ibrahim and Abdullahi, 2017).

2.5 Regeneration studies

The desorption of Pb, and Cr, loaded into ZANPs and regeneration of the ZANPs adsorbent were performed four times using 0.002 M HNO_3 to study the reusability of the prepared nanoadsorbent. Then, the ZANPs adsorbent was separated using filter paper washed four times with deionised water and dried at 60^{0}C overnight for reuse. This process was repeated three times (Abdullah *et al*., 2017).

3.0 Results and Discussion

3.1 Characterization of Kaolin

Samples of kaolin were analysed for SiO_2/Al_2O_3 ratio using X-ray fluorescence (XRF) and the results obtained are shown in Table 1 below. The samples were taken from Darazo, Kankara and Bida. The presented results indicate that the Al_2O_3 and SiO_2 constituted up to 95% of the analysed kaolin samples.

Table 1: XRF Analysis of Darazo (Fate), Kankara and Bida raw kaolin (weight%)).

Oxides	Darazo	Kankara	Bida
SiO_2	60.247	55.090	56.210
Al_2O_3	38.316	38.935	36.549
V_2O_5	0.001	0.351	0.137
$Cr_2.O_3$	0.007	0.011	0.045
MnO	0.049	1.084	0.048
Fe_2O_3	0.379	1.224	1.763
Co_3O_4	0.005	0.003	0.007
NiO	0.005	0.309	0.011
CuO	0.035	0.033	0.032
Nb_2O_3	0.014	0.012	0.013
MoO_3	0.003	0.003	0.001
WO_3	0.003	0.006	0000
P_2O_5	0.000	0.000	0.101
SO_3	0.073	0.000	0.062

CaO	0.078	1.390	0.138
MgO	0.000	0.000	0.000
K_2O	0.000	0.559	0.516
BaO	0.076	0.136	0.165
Ta_2O_5	0.050	0.024	0.014
TiO_2	0.056	0.190	3.271
ZnO	0.005	0.007	0.004
Ag_2O	0.042	0.010	0.019
Cl	0.043	0.604	0.578
ZrO_2	0.114	0.017	0.316
Total	100%	99.998%	100%
SiO_2/Al_2O_3	1.57	1.43	1.53

For Darazo (Fate), Kankara and Bida kaolin, the SiO_2 and Al_2O_3 amounts are 60.247 and 38.316% respectively, Kankara 55.090 and 38.935% respectively while that of Bida sample the values are 56.210 and 36.549% respectively.

The elemental composition of the untreated, treated and metakaolin produced from Fate-Darazo kaolin is presented in Table 2.

Table 2: Elemental composition of Untreated, Treated and metakaolin

Oxides	**Untreated Kaolin (%)**	**Treated(%)**	**Metakaolin(%)**
SiO_2	54.501	51.398	51.035
Al_2O_3	41.463	40.003	40.365
V_2O_5	0.034	0.186	0.206
Cr_2O_3	0.006	0.000	0.025
MnO	0.064	0.041	0.016
Fe_2O_3	1.603	0.934	1.179
Co_3O_4	0.010	0.003	0.010
NiO	0.011	0.005	0.003
CuO	0.043	0.040	0.067
Nb_2O_3	0.011	0.147	0.143
MoO_3	0.003	0.000	0.000
WO_3	0.000	0.000	0.015
P_2O_5	0.000	0.000	0.015
SO_3	0.000	0.205	0.000
CaO	0.525	0.743	2.166
MgO	0.000	0.000	0.000
K_2O	0.714	0.035	0.167
BaO	0.088	0.268	0.319
Ta_2O_5	0.028	0.039	0.025
TiO_2	0.211	4.059	4.001
ZnO	0.008	0.003	0.034
Ag_2O	0.011	0.008	0.018
Cl	0.024	0.758	1.517

ZrO_2	0.041	0.758	0.795
SnO_2	0.000	0.000	0.000
Total	99.858%	100%	100%
SiO_2/Al_2O_3	1.31	1.28	1.26

The results revealed the presence of SiO_2 and Al_2O_3 as the main constituents. It further shows the reduction in SiO_2 content of the untreated, treated and metakaolin, a decrease in treated and an increase in Al_2O_3 of metakaolin respectively. The percentage of SiO_2 decreased from 54.50 to 51.04% and Al_2O_3 increased from 37.44 to 40.37% for treated and metakaolin, respectively.

3.2 Characterization of the adsorbent.

addition to XRD in the treated, untreated and metakaolin, the adsorbent was also characterised by XRD, SEM, EDX and FTIR, BET, UV-visible. The XRD pattern of the metakaolin, treated and untreated kaolin are shown in Fig.1,.2 and 3 respectively. . The result shows that the main peaks at $2\omega = 12.24^0$ and 24.76 ^{0} which were the main peaks in identifying kaolinite in refined kaolin were no longer observed in the metakaolin diffraction pattern.

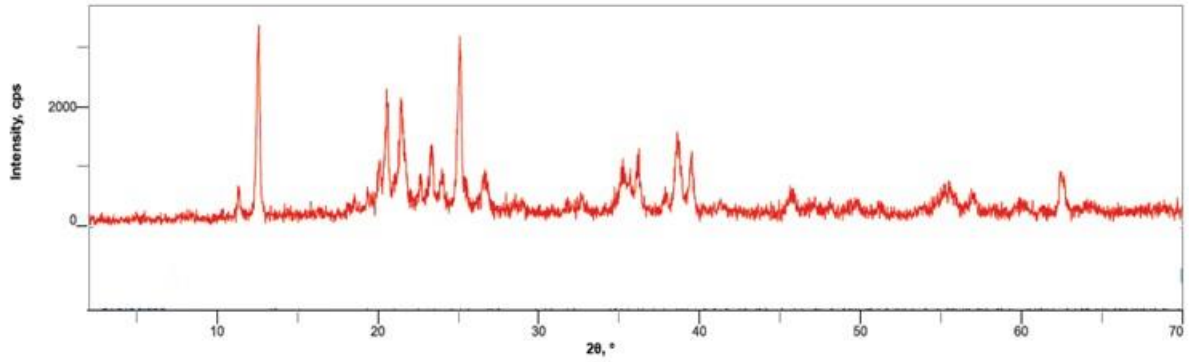

Fig. 1: XRD pattern of Metakaolin

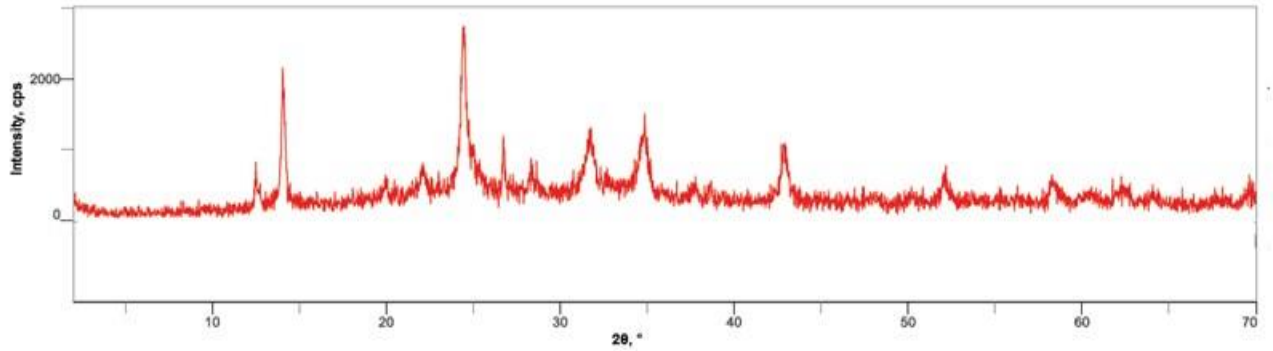

Fig.2: XRD pattern of treated kaolin

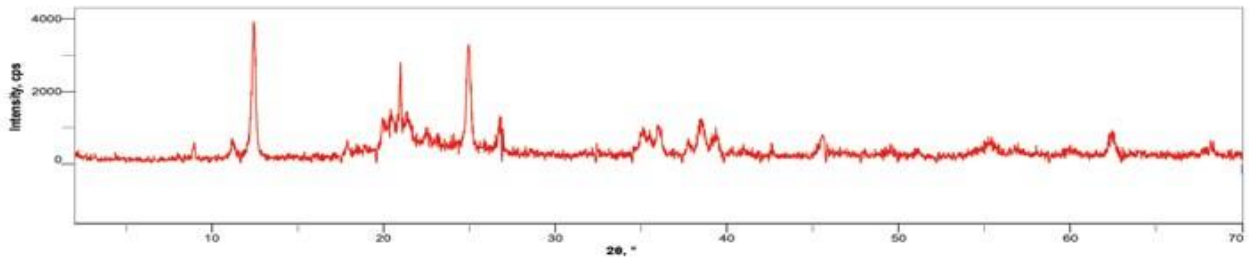

Fig. 3: XRD pattern of untreated kaolin

The observation of samples by SEM (image) Fig. 4 reveals little porosity on the surface before adsorption, this could promote the adherence of the metal in molecules. Fig. 5 reveals tiny pore spaces on the surface after adsorption, this is caused by filling in gaps in the zeolite A by the adsorbate deposited molecules. Also, Data obtained from EDS of the zeolite are shown in Table 3. The results indicate a high concentration of carbon (85.34%) and oxygen (11.11%)

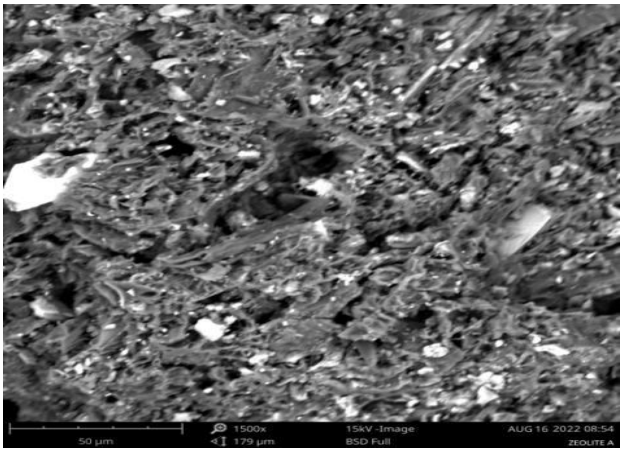

Fig. 4: SEM micrograph of Zeolite A nano-particle before adsorption

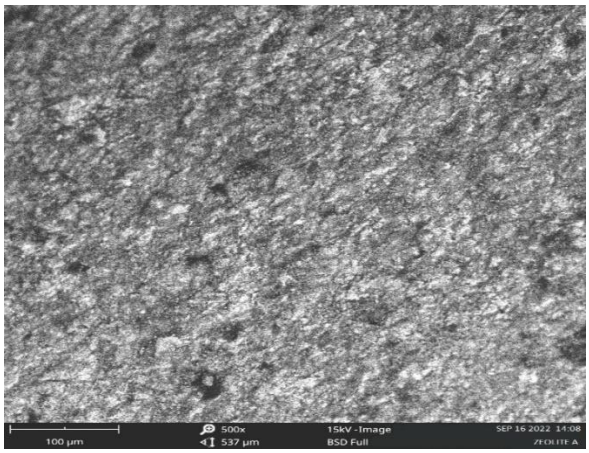

Fig. 5: SEM micrograph of ZeoliteA after adsorption

Table 3:Energy Disperse Spectroscopy (EDS) of zeolite A.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	85.34	78.80
8	O	Oxygen	11.11	13.66
14	Si	Silicon	0.58	1.25
7	N	Nitrogen	1.00	1.08
26	Fe	Iron	0.23	0.98
19	K	Potassium	0.32	0.97
13	Al	Aluminium	0.32	0.67
20	Ca	Calcium	0.20	0.61

12	Mg	Magnesium	0.26	0.49
15	P	Phosphorus	0.20	0.47
16	S	Sulfur	0.16	0.40
17	Cl	Chlorine	0.12	0.32
11	Na	Sodium	0.17	0.29

EDX was is employed to determine the elemental characterization of zeolite nano-particles samples, before adsorption. From the result (Table 3), carbon showed the highest elemental percentage of 85.34 followed by oxygen with 11.11% . The observed results are consistent with the works published by (Sherifat *et al*., 2019).

Fig. 6, the FT-IR of the zeolite A sample is shown. Observed peaks and the frequencies, they occurred as well as the assignment are presented in Table 4. Notably, the FTIR spectrum displayed a characteristics peak that is known to zeolite nanoparticles at 3339.7cm^{-1} which is the O-H bond representing the hydroxyl group of water molecules present in zeolitic pores spaces.It also depicts aldehydes and phenols functional groups.

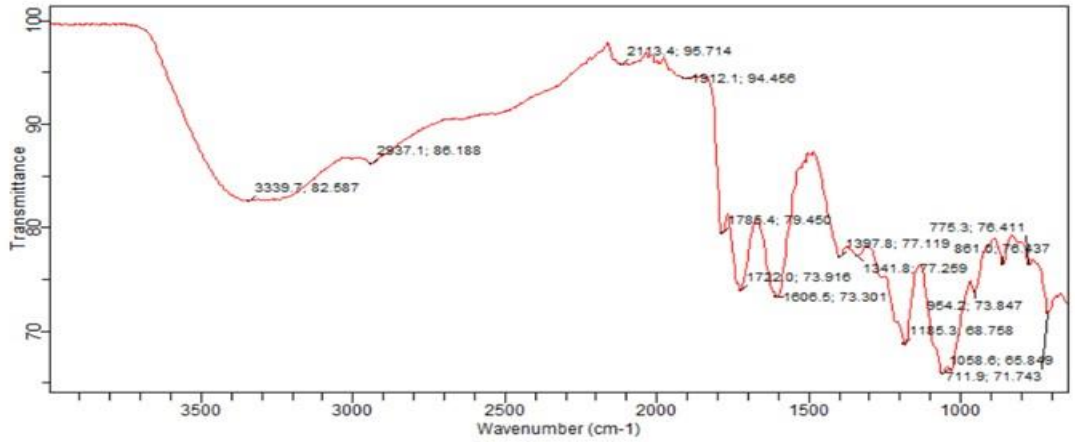

Fig.6: FT-IR pattern of ZeoliteA.

Table 4 :Results of FT–IR of Synthesized Zeolite-A

S/NO.	Peaks (cm^{-1})	Bond	Functional groups
1.	3340	O – H	Hydroxyl group
2.	2937	N – H stretch	Amines
3.	2143	O – H stretch-free hydroxyl OH.	Aldehydes, phenols
4.	1912	– C ≡ C – stretch	Hydroxyl group, lipids
5.	1785	– C – O – stretch	Alkyne
6.	1722	– N – O asymmetric stretch	Nitro cards
7.	1398	– C – H bond	Alkane

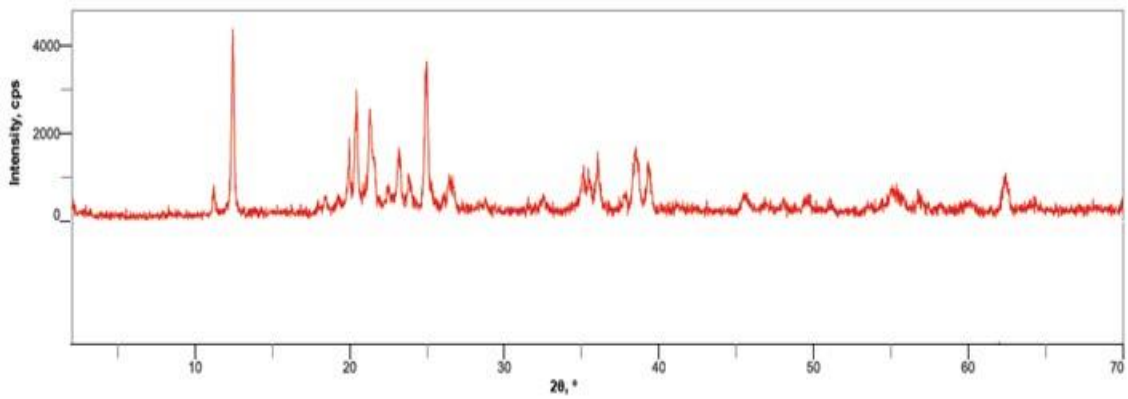

Fig.7: XRD pattern of ZeoliteA

The result of the phase composition investigated by x-ray diffractometer is presented in Fig.7 for zeoliteA nanoparticle sample, the XRD pattern obtained from the quantitative analysis report showed a visible sharp peak around 2 theta as this proves the phase nature of the solid to be a crystalline solid.

Table 5: BET analysis of synthesized zeoliteA adsorbent

Adsorbent	surface area(m^2/g)	Pore Diameter (nm)	Pore Volume (cc/g)
ZANPs	106.250	2.132	0.052

ZeoliteA exhibited isotherm adsorption behaviour due to the presence of zeolitic micropores, (Abdallah *et al.*,2017), as well as mesopores formed by the aggregation of crystals which are in agreement with the SEM image (Fig. 4. and 5).

The UV spectra obtained for the biosynthesis of zeolites as shown in. Fig. 8. A colour change from light yellow to white was observed after the reaction time, which is an indication of the formation of zeolite A

The characterization of the adsorbent with the UV –Spectrophotometer was carried out in the range of 190-240nm. The strong surface Plasmon resonance (SPR) band position at 210nm was observed for the ZANPs, (fig. 8). The position of SPR is sensitive to particle shape, size and interaction with the medium

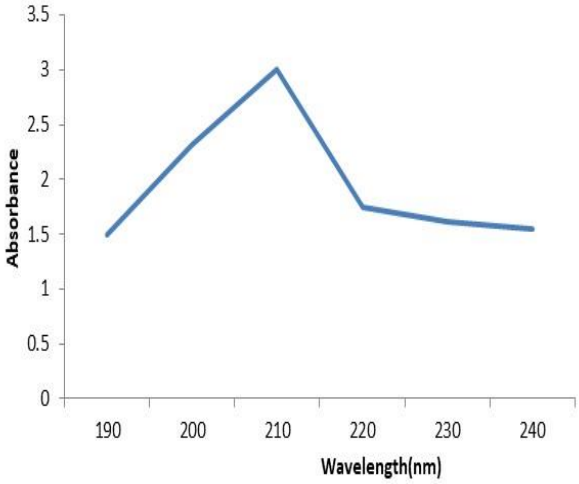

Fig. 8: UV-Vissible Spectroscopy of zeolite A nanoparticles.

and the particle (Ibrahim and Abdullahi 2017).The broad spectra indicate that there is a mixture of particles (Sosa *et al.*,2003).

3.3 Adsorption Study

The result in Fig. 9: below shows the extent of Pb, Cr removal by ZANPs, it was found to increase with increasing the contact time each a maximum value after 10 min. With Pb having the highest % Removal of 60%.

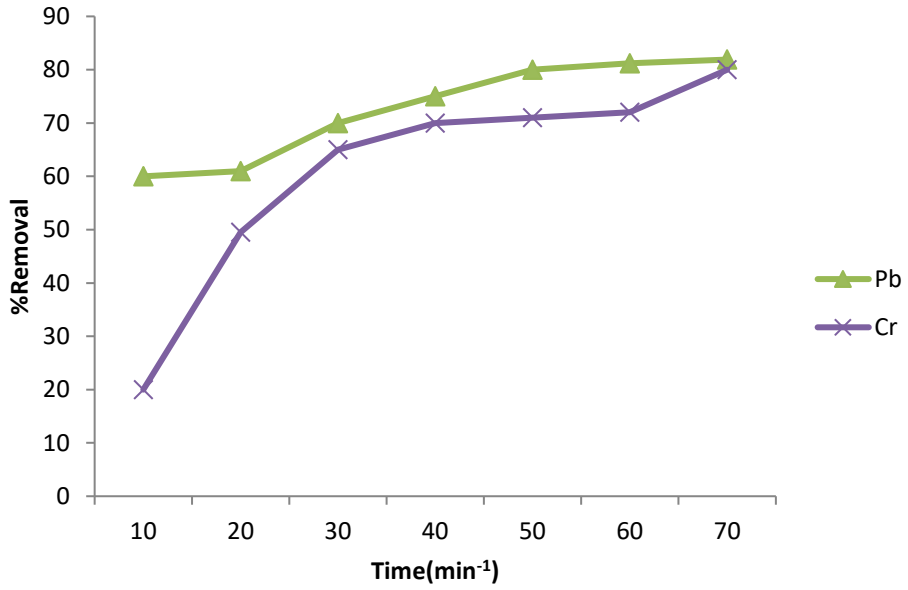

Fig. 9: Variation of percentage removal of Pb^{2+} and Cr^{3+} by ZANPs with time (at a temperature =40°C, speed =300rpm,pH = 4 and adsorbent dosage of 1.0g/50ml)

The amounts of Pb, Cr adsorbed by different amounts of ZANPs adsorbent are shown in Fig. 9. The increase in adsorbent dosage from 0.2 to 1.0 g increased the adsorptions percentage of Pb^{2+}, Cr^{3+} with Cr having the highest % Removal of 90%.

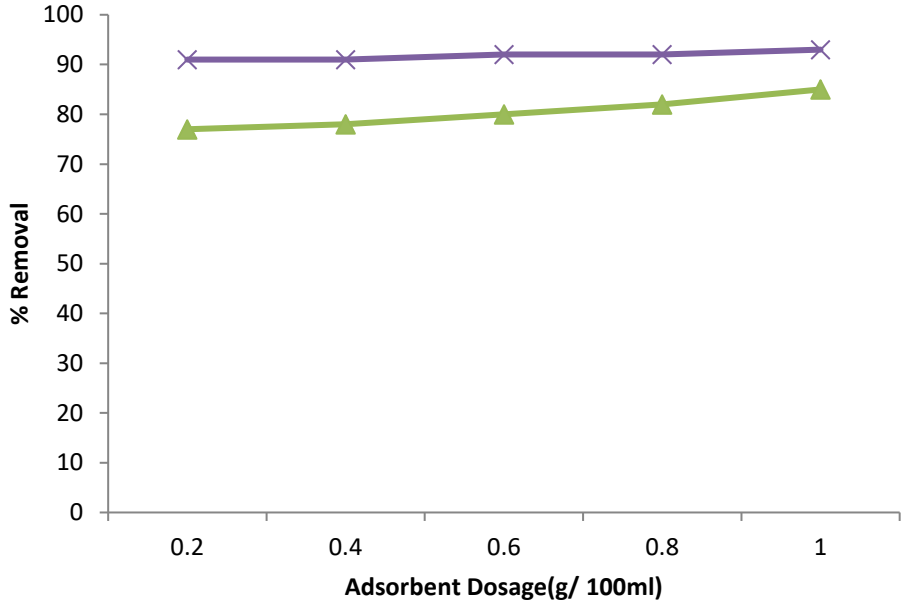

Fig.10: **Result on effect of Adsorbent Dosage on removal of Chemical parameters onto ZANPs, (temperature=40°C, speed=300rpm, pH =4 and time 30min.)**

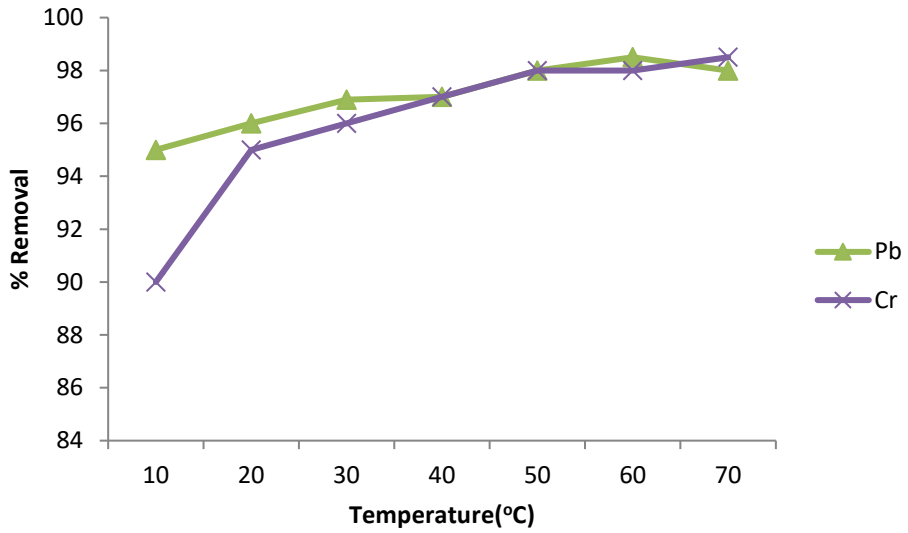

Fig. 11: **Result on the effect of temperature on removal of Chemical parameters onto ZANPs, (Adsorbent Dosage= 1.0 g/ml, speed=300rpm, pH =4 and time 30min.)**

The results obtained are presented in Fig. 8. The Fig. 8 result revealed that the adsorption rate of the chemical parameters onto ZANPs increased with an increase in temperature in all cases. This is attributed to the immobility of the chemical parameters molecules as the temperature increased, which subsequently; resulted in the formation of a strong binding force between the contaminants and the zeolites A (Acemioglu, 2010; Al-Anber, 2011; Yusuf-Alaya, 2014; Bankole *et al*., 2017). The result depicts that Pb has the highest percentage removal at 94%. This is in agreement with the result reported by (Sherifat *et al.*,2019)

3.*4* *Kinetics and adsorption isotherms*

Kinetics models such as pseudo-first-order and pseudo-second-order kinetics were applied in this research for testing the experimental data which conformed to pseudo-second order as shown in Table 6. Two isotherm models were tested and the parameters are shown in Table 5. From the results (Table 5), R^2 value of the Freudlich isotherm model was higher than the Langmuir model, this explains that the experimental equilibrium data fitted better by the Freundlich equation.

Table 5:Adsorption parameters for the removal of Pb^{2+} and Cr^{3+} by adsorption onto ZANPs at pH = 4

Adsorption Isotherms	**Pb**	**Cr**
Langmuir		
$q_{e(exp)}$ (mg/L)	0.901	0.751
q_m(mg/g)	0.847	0.653
K_L(L/g)	7.687	5.032
R_L	0.014	0.022
R^2	0.983	0.960

Freudlich		
1/n	0.121	0.070
K_f(L/g)	0.284	0.456
R^2	0.999	0.959
Harkin-Jura		
B	0.072	0.086
A	0.695	0.678
R^2	0.967	0.977

Tale 6: Kinetics kinetic parameters for the removal of Pb^{2+} and Cr^{3+} by adsorption onto ZANPs at pH = 4

Pseudo-first order				**Pseudo-second order**			
Contaminants	**k_1(min^{-1})**	**q_e (mg/g)**	**R^2**	**k_2(min^{-1})**	**$q_{e(cal)}$ (mg/L)**	**$q_{e(exp)}$ (mg/L)**	**R^2**
Pb	3.701	0.071	0.959	0.554	0.016	0.009	0.991
Cr	0.439	0.008	0.982	0.398	0.211	0.111	0.999

Table 7:Intraparticle diffusion model for ZANPs and MDZA-NCs onto the conterminant

Contaminant	**K_m (mg/g min ^{½})**	**C (mg/g)**	**R^2**
ZANPs			
Pb	10.60	38.08	0.998
Cr	9.218	24.02	0.009

Key: k_1: Pseudo first-order rate constant, K_2: Pseudo -second-order rate constant, q_e: Equilibrium adsorption capacity, q_t: Adsorption capacity at time t, t: Adsorption time, k_{diff}: Intraparticle diffusion rate constant, C: Intercept which is related to the thickness of the boundary layer

The thermodynamic parameters such as Gibb's free energy, ΔG^o; the enthalpy ΔH^o and the entropy ΔS^o (Table 9 and 10) were also evaluated using the Transition state plots and the Gibb Helmholtz equation (Eddy *et al*., 2024a-b). These parameters are vital for the determination of the feasibility of the adsorption process. The equilibrium constant of adsorption was evaluated using equation 4 (Liu, 2009; Bankole *et al.*, 2017). However, the the enthalpy and entropy changes were evaluated using equation 5 while the free energy change was calculated using equation 6.

$$k = \frac{q_e}{C_e} \quad (4)$$

$$ln(k/T) = \frac{R}{Nh} + \frac{\Delta S^0}{R} - \frac{\Delta S^0}{RT} \quad (5)$$

$$\Delta G^*_{ads} = -RTlnk_e = -RTln(k) \quad (6)$$

k is the equilibrium constant; q_e and C_e are the equilibrium concentrations of the chemical parameters (mg/L) in solution and on the adsorbents, respectively. The plots of ln K vs. 1/T are shown in Fig. 12 and ΔH^o and ΔS^o were evaluated from the slopes and intercepts are shown in Table 9. It can be deduced from the results obtained that the adsorption process is endothermic since the obtained values of enthalpy ae positive. The adsorption process also occurred with increasing degree of association since the negative values of entropy change indicate increase in orderliness. We also observed that the free energy change are negative which confirmed that the adsorption is

spontaneous. However, based on the magnitude of the free energy change, adsorption can be regarded as a physical or chemical mechanism. Values of free energy change negatively less than -40 kJ/mol are representative of physical adsorption and those negatively higher than -40 kJ/mol are indications of chemisorption data. Based on the results obtained in this study, it is significant to state that the adsorption mechanism is chemisorption. The pattern of relationship obtained from the experimental data showing the variation of % removal with temperature also indicated that the adsorption increases with an increase in temperature, which is a confirmation for chemical adsorption

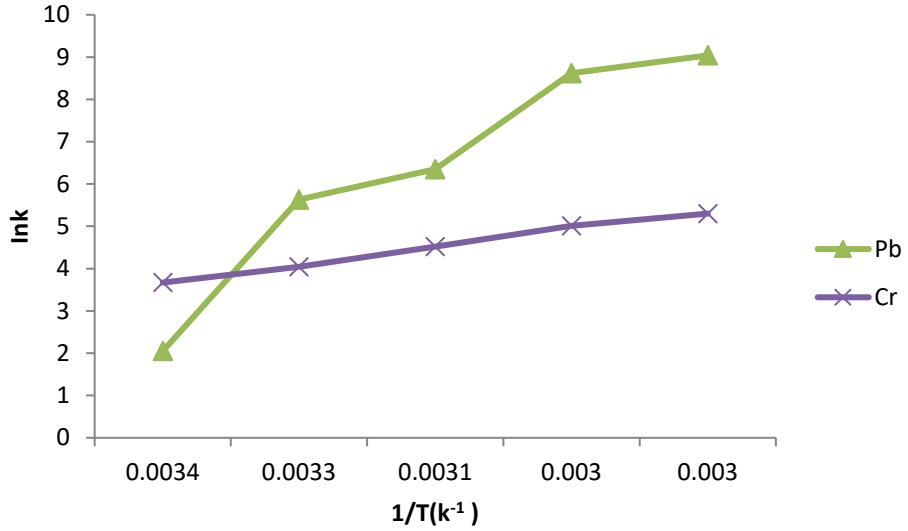

Fig. 12:A plot of lnk versus 1/T for ZANPs.

Table 8: k- values of sorption for chemical parameters onto ZANPs at various degrees of temperatures

Contaminant ZANPs	20º C	30º C	40º C	50º C	60º C
Pb	1.89	5.20	6.01	7.16	8.40
Cr	35.36	50.65	65.10	100.01	120.14

Table 9: Adsorption thermodynamics of chemical parameters onto synthesize ZANPs

Contaminants	ΔHº (kJ/mol)	ΔSº (kJ/mol)
Pb^{2+}	12.47	-10.31
Cr^{3+}	2.49	-27.44

Table 10: ΔGº Free energies of the contaminant after adsorption by ZANPs at various temperatures

T (°C)	Pb^{2+}	Cr^{3+}
20	-218.77	-551.29
30	-296.80	-825.65
40	424.83	-1100.02
50	-527.92	-1374.37
60	-631.02	-1648.73

4.0 Conclusion

This study successfully synthesized zeolite A nanoparticles (ZANPs) from kaolin sourced from Fate-Darazo, Nigeria, and investigated their potential for removing lead (Pb) and chromium (Cr) from petroleum wastewater. The characterization results confirmed the formation of zeolite A with a high surface area and the presence of functional groups suitable for adsorption. Batch adsorption experiments revealed that ZANPs effectively removed Pb and Cr, with Pb showing a higher removal efficiency (up to 94%) compared to Cr (up to 90%). The adsorption capacity increased with increasing contact time, adsorbent dosage, and temperature. Kinetic studies indicated that the adsorption process followed a pseudo-second-order model. The Freundlich isotherm model better described the equilibrium data, suggesting a multi-layered adsorption process. Thermodynamic parameters revealed a spontaneous and feasible adsorption process with an exothermic nature. Overall, this study demonstrates the promising potential of ZANPs synthesized from local kaolin for remediating heavy metal contamination in petroleum wastewater. We also recommend that further study in exploring the reusability and regeneration cycles of ZANPs for cost-effective application. Investigation of the effect of co-existing ions and real wastewater matrices on the adsorption performance as well as scaling up the synthesis process for pilot-scale and real-world applications are also recommended for future research.

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Compliance with Ethical Standards Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data Public.

Competing interests

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