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DEVELOPMENT OF ZEOLITE-A DOPED IRON, SILVER AND ZINC NANOCOMPOSITE FOR OIL REFINERY WASTEWATER TREATMENT

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ABSTRACT
In this research work, nano-zinc, nano-silver and nano-iron were synthesized using Calotropis procera leaves extract as a reducing agent multiple doped onto synthesized zeolite A (sZA), produced from kaolin via wet impregnation route. The produced adsorbents were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR),Ultraviolate-vissible spectroscopy(UV-visible spectroscopy.) and N_2-Brunauer–Emmett–Teller(BET)surface analysis.The SEM micrographs revealed well dispersed zinc, silver and iron nanoparticles (ZnNPs, AgNPs, FeNPs) multiple doped onto zeoliteA nanoparticles (ZANPs) to form doped zeoliteA nanocomposite (DZA-NCs) and the N_2-BET showed a surface area of 5.015m^2/g,3.105m^2/g, 4.390m^2/g for ZnNPs, FeNPs, AgNPs respectively and it also revealed high surface areas of 106.250m^2/g and 650.162m^2/g for ZANPs and DZA-NCs respectively. The array of removal of the physicochemical pollutants was 99.6% Turbidity, 97.7% chemical oxygen demand(COD), 97.0% Pb, 96.0% Cr, 90% biological oxygen demand(BOD) and 86.8% Oil& grease for multiple doped Zeolite A adsorbent removing the higher percentage of COD pollutants. Isothermal models indicated that Freundlich model (R^2)of 0.999 was most suitable for describing the adsorption process, which conformed to pseudo-second order kinetics.
Keywords: Physico-chemical Parameters, Nanoparticles, zeoliteA; Oil refinery wastewater.

INTRODUCTION

One of the most important and necessary elements to life on earth is water. The adverse effect of untreated wastewater on the environment has necessitated the governments of most countries to impose stringent legislations for treatment of industrial wastewater before disposal to avoid both acute chronic toxicities (Dey and Islam, 2015). The growth in refining of oil refinery products, has increased chemical oxygen demand(COD), the release of pollutants such as sulphide, phosphate, Cr, among others into the ecosystem in Nigeria.

Recently, nanomaterials are considered as good materials for water treatments (Shannon *et al.,*2008). However, it is reported that, when the size of metal decreases to nanometer range, the increased surface energy leads to their poor stability (Lee *et al.,*2015; Baqer *et al.,* 2017). To improve the applicability of the metal nanoparticles for wastewater treatment, nanocomposite (NCs) materials have emerged to overcome the limitations of growth nanoparticles by employing porous zeolite A supports materials of large area as a matrices (Pan, 2009). This method was used to load AgNPs,ZnNPs and FeNPs into zeoliteA type frame work developed from Darazo(Fate) kaolin to prepare Fe/Zn/Ag/zeoliteNCs using a capping and stabilizing agent *Calotropis procera* leaves extract for treatment of petroleum refinery wastewater.

MATERIALS AND METHODS

The wastewater was collected from Kaduna refinery and petrochemical company (KRPC) Kaduna state.

Preparation of leaves extract *(Calotropis procera)*

Leaves extracts was prepared by taking approximately 40g leaves. These was thoroughly washed with distilled water, dried, powdered and finely crushed with the help of mortar and pestle. 6 g of powdered leaves was taken into 100 cm^3 of distilled water in a 500 ml beaker and boiled at 80^{0}C for 45min which was filtered using Whatman no:1 filter paper. (pathanayak and Nayak,2013) and(Wang *et al.,*2014a).

Figure 1: Leaves of *Calotropis procera*

Preparation of Nanocomposites

A known mass (5g) of zeolite A nanoparticles (ZANPs) was dispersed in 50ml of deionized water and slowly stirred for 15 min to obtain a homogeneous mixture. 0.05M $ZnSO_4.5H_2O$, 0.02M $AgNO_3$ and, 0.01M FeSO4.7H2O was prepared respectively, 20ml each was added to the zeolite A solution. The mixture was then stirred vigorously for a period of 45 min at room temperature before introducing 6ml of *calotropis procera* leaves extract into it and stirred for another 30 min. The obtained mixture was centrifuged at 3000 rpm for 40 min, washed and dried in an oven for 2 hr. It was then allowed to cool in air (Sherifat *et al.,*2019). The doped zeoliteA nanocomposites adsorbent formed was stored in dark bottle and characterized.

Batch Adsorption experiment of the nanocomposites

Adsorption studies

Batch adsorption study was employed. Equilibrium isotherms were obtained by studying the adsorption process of (DZA-NCs) at different contact time, temperature and adsorbent dosage. The effect of contact time was studied to establish the adsorption equilibrium. Effects of temperature was studied to evaluate the adsorption kinetics parameters and effects of adsorbent dosage was also investigated to investigate adsorption isotherms.

Adsorption equilibrium and percentage removal were calculated using the relationship as thus;

$q_e = C_1 - C_2 \diagup_m x V$ ………… (1)

% removal = $C_1 - C_2 \diagup C_1 x\ 100$ …………………(2)

q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), 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).

Regeneration studies

The desorption of BOD, COD, Pb, Cr, turbidity, oil and grease loaded into DZA-NCs and regeneration the DZA-NCs adsorbent were performed four times using 0.002 M HNO_3 to study the reusability of the prepared nanoadsorbent. Then,the DZA-NCs adsorbent was separated using filter papers and washed four times by deionized water and dried at 60^0C overnight for reuse. This process was repeated three times (Abdullah *et al.*, 2017).

RESULTS AND DISCUSSION

Characterization of doped zeolite A nanocomposites (DZA-NCs)

The nanocomposites synthesized was characterized using SEM,BET,FT-IR, XRD, UV –vis and

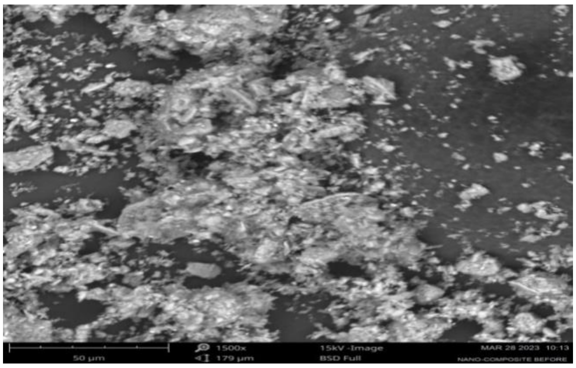

Figure 2a: SEM image of doped ZeoliteA nanocomposite (DZA-NCs)before adsorption.

Upon the incorporation of the zinc/iron/silver nanoparticles into the zeolite framework, it was observed from Figure 2 that there is a distortion of the original cubical /pointed structure of the zeoliteA. This indicates a bonding interaction between the zeoliteA and the silver/iron/zinc nanoparticles leading to morphological structural changes as observed in figure 3a, revealing that the DZA-NCs are well dispersed on the pointed shape of ZANPs as shown by the porous patches on its surface. The pointed patches suggest the porous nature of ZANPs which is expected to increase the porosity of the DZA-NCs.

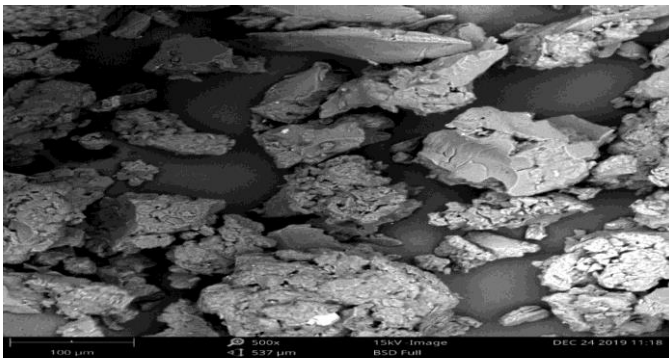

Figure 2(b): SEM Image of DZA-NCs after Adsorption

The morphology and the textural properties of the DZA-NCs after adsorption as revealed by SEM micrographs is shown in Figure2 (b) shows perfect cubic crystals with sharp edges depicting the well-defined crystalline phase of zeolite A which is in good agreement with XRD, which reveals that the adsorbate are well dispersed on the pointed shape of DZA-NCs as shown by the porous patches on its surface. The porous patches suggest the nature of DZA-NCs which is expected to increase the porosity of the DZA-NCs.

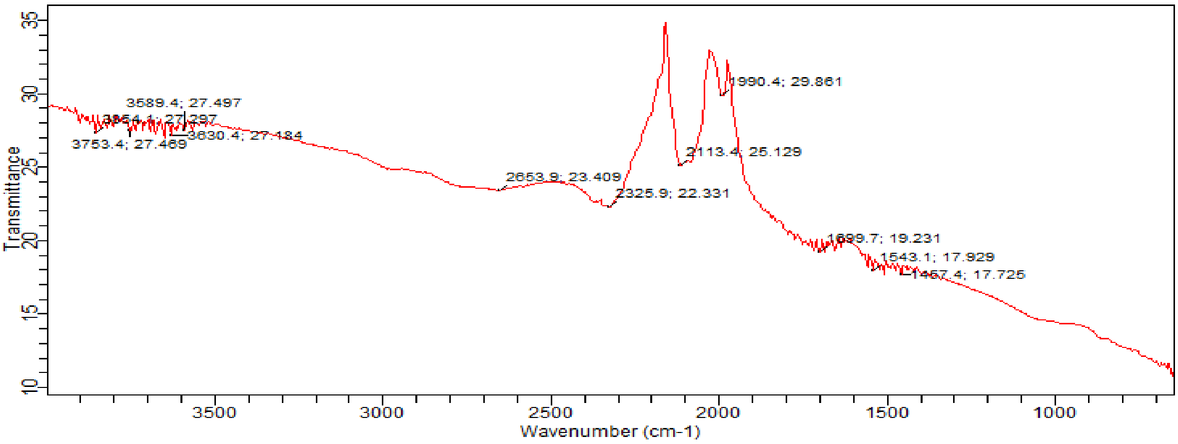

Figure 3:FT-IR of DZA-NCs

The FT-IR of DZA-NCs were performed to study the effect of the synthesized nanoparticles as shown in Figure 3.The IR spectrum of DZA-NCs (Figure 3) reveals bands at 3753.4, 3630.4 and 3589.4cm^{-1} which is attributed to the hydroxyl group stretch of water molecules present in the pores of zeoliteA, while that at 2113.4cm^{-1} with the sharp and low intensity bands corresponding to the bending vibration of alkyne. The sharp peak around 1543.1cm^{-1} nitro compound corresponds to the asymmetric stretching vibrations of all zeolitic materials (Byrappa and Suresh Kumar, 2007; Sarsar et al., 2013). The absorption band at 1467.4 and 1689.7 cm^{-1} is associated with stretching of C-H bond vibrations and C-O stretch of zeoliteA framework which is in good agreement with 1693 cm^{-1} as reported by Gougazeh and Buhl (2014) for zeolite group.

Table 1 BET analysis of synthesized two main adsorbent

Adsorbent	surface Area(m^2/g)	Pore Diameter (nm)	Pore Volume (cc/g)
ZANPs	106.250	2.132	0.052
DZA-NCs	650.162	2.105	0.320

ZeoliteA/Zn,Fe/Ag NCs exhibited II isotherm adsorption behavior due to the presence of zeolitic micropores, (Abdallah *et al.*,2017) as well as mesopores formed by the aggregation of crystals (fig. 2a&b). In order to assess the effect of doping on the surface area of the synthesized DZA-NCs, BET analysis was conducted.The results shown in Table 1 indicates that the surface area and pore volume of the ZANPs increased from 106.250 m^2/g to 650.162 m^2/g almost sixfold higher surface area of the prepared nanocomposite and 0.052cc/g to 0.320 cc/g, and the pore diameter decreased from 2.132nm to 2.105 nm,respectively. The expanded surface area might be due to unblocked zeolite A channel after the incorporation of zinc, iron and silver nanoparticles into its frame work,this shows that the Zn,Fe and AgNPs phases formed a porous layer on the surface and in the channel of the zeolite structural. Further, the formed, Zn,Fe and Ag NPs layer, with a large surface area, provides a large number of functional groups that enhance the adsorption process (Mihajlovic.*et al.*,2014). On the other hand, the average pore diameter decreased from 2.132 nm for zeoliteA nanoparticles to 2.105 nm ZeoliteA/Zn/Fe/Ag NCs(DZA-NCs) as a result of filling of these pores with Zn,Fe and Ag nanoparticles (Copcia *et al.*,2012)

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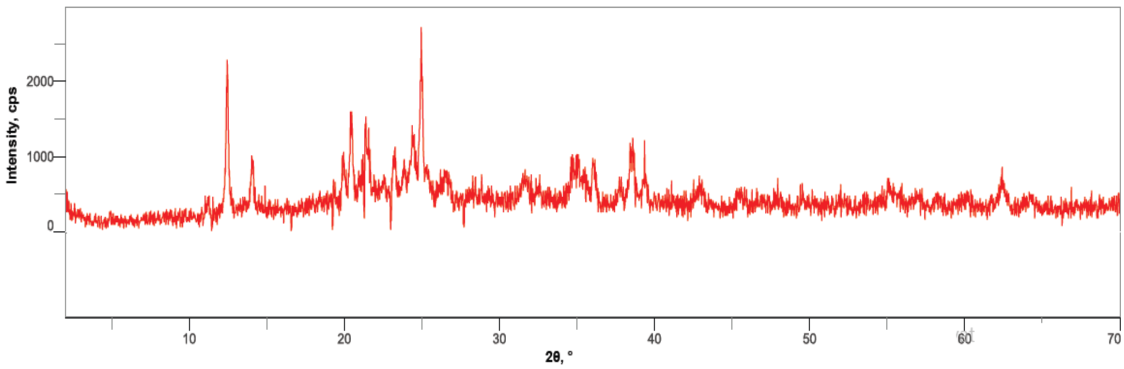


Figure 4: XRD Pattern of DZA-NCs

The XRD pattern of DZA-NCs (fig.4) presented higher peaks at 30°, 20° and10° at 2ϴ which depicted a crystalline adsorbent, it also shows a reduction in the intensity of peaks at 18.20⁰, 23.41⁰, 28.55⁰, and 29.22⁰. This is a suggestion that the incorporation of the zinc, iron and silver nanoparticles into the ZANPs framework, has led to a reduction in the intensity of these peaks. These results are in good agreement with literature (Kamyar *et al.,* 2011; Odutayo*et al.,* 2016).

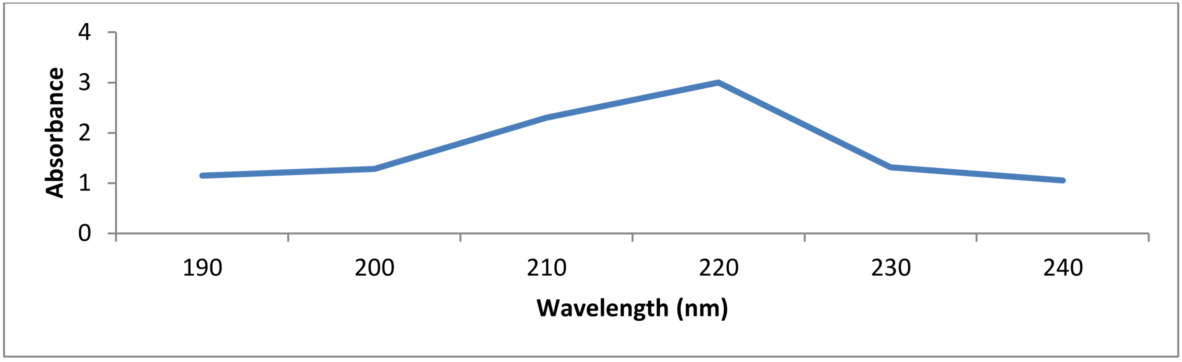
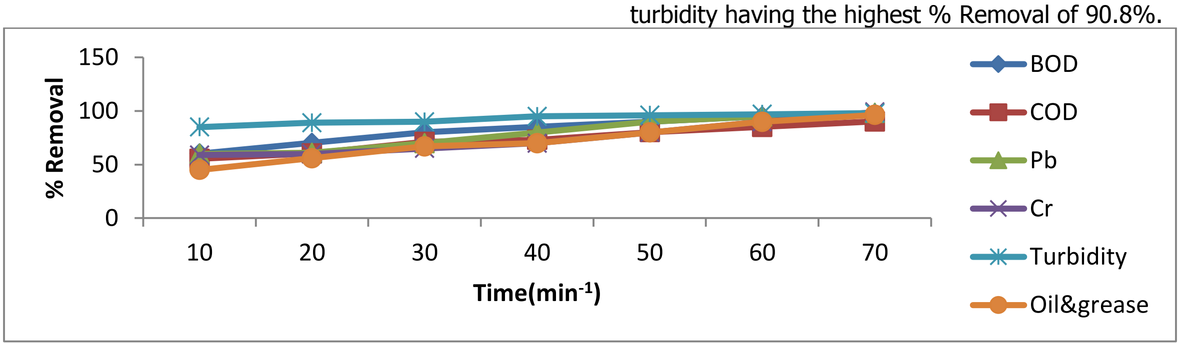


Figure 5: UV-Visible Specroscopy of doped Zeolite A nanocomposite(DZA-NCs).

The characterization of UV –Spectrophotometer was carried out in the range of 190-250nm.The strong surface Plasmon resonance (SPR) band position at 220nm was observed for the DZA-NCs (fig. 5).The position of SPR is sensitive to particle shape, size and interaction with the medium and the particle (Ibrahim and Abdullahi 2017).The broad spectra indicate that there is a mixture of particles of the nanocomposite (Sosa *et al.,* 2003).

Effect of time

The result in Figure 6: below shows the extent of COD, BOD, Pb, Cr, turbidity, oil and grease removal by DZA-NCs, it was found to increase with increasing the contact time each a maximum value after 10 min. With turbidity having the highest % Removal of 90.8%.

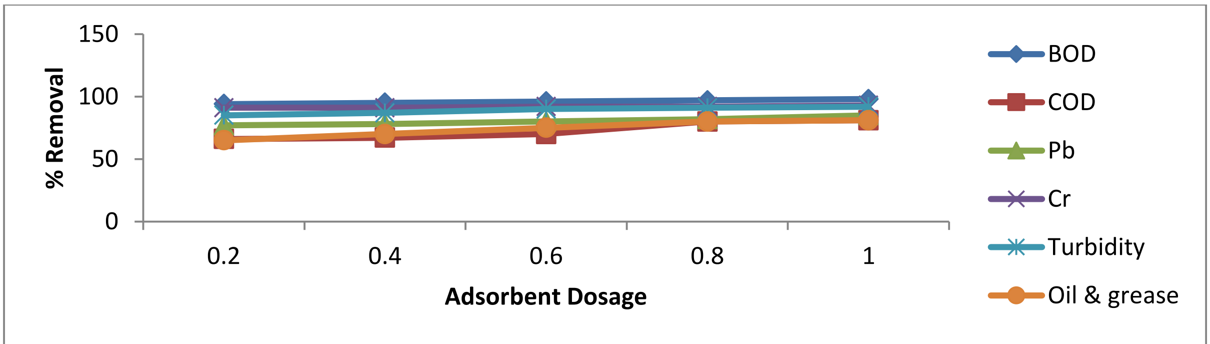


DZA-NCs

Figure 6:Result on effect of contact time on removal of chemical parameters on to doped zeolite A (temperature = 40⁰, speed 300rpm, and adsorbent dosage of 1.0 g/50ml).

Effect of adsorbent Dosage

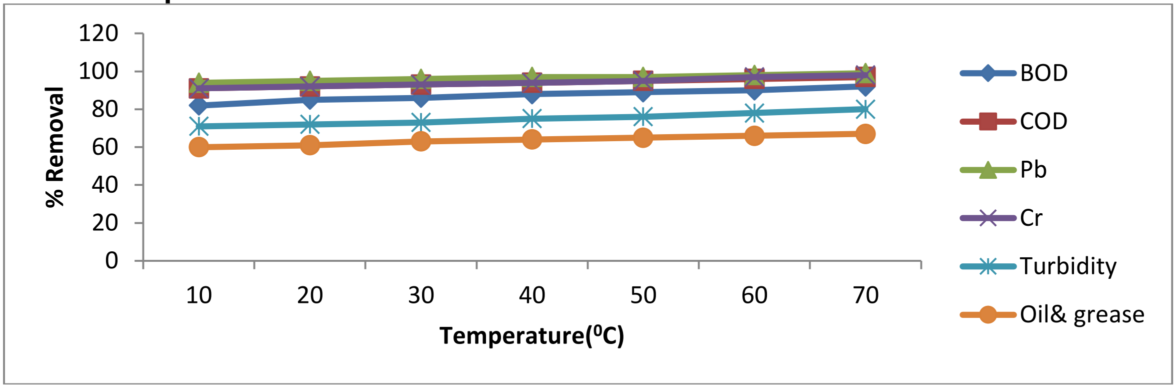
The amounts of COD, BOD, Pb, Cr, turbidity, oil and grease adsorbed by different amount of DZA-NCs adsorbent are shown in (Fig.7) below. The increase in adsorbent dosage from 0.2 to 1.0 g resulted in an increase in adsorptions percentage of COD, BOD, Pb, Cr, turbidity, oil and grease with BOD having the highest % Removal of 97.5%. The initial increase in adsorption capacity is attributed to the larger surface area and more adsorption sites that introduced by increasing the number of adsorbent particles results in more attachment of contaminant with the weight of adsorbent increasing (Mahdavi *et al.,*2013).



DZA-NCs

Figure 7: Result on effect of dosage on removal of chemical parameters on to multiple doped zeolite A (temperature = 40⁰, speed 300rpm and contact time of 60minute)

Effect of Temperature



DZA-NCs

Figure8: Result on effect of temperature on removal of chemical parameters on to doped zeolite A (speed 300rpm, Adsorbent dosage of 1.0mg/L and contact time of 60minute)

The results obtained are presented in Figure 8. The figures revealed that the adsorption rate of the chemical parameters onto DZA-NCs increased with increase in temperature in all cases. This is attributed to immobility of the chemical parameters molecules as the temperature increased, which subsequently; resulted to formation of strong binding force between the contaminants and the zeolites A (Acemioglu, 2010; Al-Anber, 2011; Yusuf-Alaya, 2014; Bankole *et al.*, 2017). The result depict that Pb and COD has the highest percentage removal of 98.0% and 96% respectively. This is in agreement with the result reported by Sherifat *et al.* (2019).

Kinetics models, 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 3. Two isotherm models were tested and the parameters are shown in Table 2. From the results (Table 2), R^2 value of the Freudlich isotherm model was higher than Langmuir model, this explains that the experimental equilibrium data fits better by the Freundlich equation.

Table 2: Isotherms constants for the adsoption of chemical parameters/Heavy metals onto DZA – NCs at pH = 4

Adsorption Isotherms	BOD	COD	Turbidity	pb	Cr	Oil and grease
Langmuir						
qm (mg/g)	2.501	1.284	1.061	1.180	1.530	1.512
KL (L/g)	5.104	2.758	5.382	7.687	5.032	4.751
RL	0.021	0.098	0.020	0.014	0.022	0.053
R^2	0.934	0.975	0.960	0.983	0.960	0.936
Freudlich						
1/n	0.044	0.069	0.096	0.121	0.070	0.023
Kf(L/g)	0.286	0.542	0.149	0.284	0.456	0.538
R^2	0.875	0.897	0.677	0.999	0.959	0.903

Table 3: Kinetics constants for the adsorption of chemical parameters/Hearymetals onto DZA-NCs at pH = 4.

	Psendo-first order			Psendo-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**
BOD	0.389	0.070	0.973	0.384	0.019	0.012	0.999
COD	3.298	0.07	0.973	6.436	0.091	0.079	0.981
Turbidity	0.088	0.373	0.962	7.454	0.162	0.102	0.985
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
Oil and grease	0.256	0.010	0.977	0.213	0.092	0.072	0.954

CONCLUSION

This research work was conducted using doped zeoliteA nanocomposite. The adsorbents were characterized. The XRD results revealed well crystalline adsorbents and the surface area of the ZANPs and DZA-NCs were 119.98m²/g and 436.44m²/g, respectively. The adsorption of chemical parameters onto DZA-NCs was rapid removing 92.42–99.90%. It also showed that adsorption increased with contact time, adsorbent dosage and temperatures. Isothermal models indicated the suitability of the Freundlich model with R^2 = 0.999 contaminant which conforms to pseudo-second order kinetics with R^2 = 0.999.

From various analysis conducted therefore, it shows that the developed adsorbent is suitable for petroleum refinery wastewater treatments.

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