

PHENOL removal in refinery wastewater using mixed oxides prepared by green synthesis

DOI : 10.36909/jer.13917

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ABSTRACT

Mixed solid oxides are known for their excellent catalytic property and applications in environmental remediation. This study presents a green-synthesis route for magnesium oxide–titanium oxide, a mixed oxide here demonstrated to possess high performance of phenol removal from hydrocarbon refinery process wastewater. Mixed oxide (MgO-TiO₂) was prepared by using the whole extract from leaves of *Piliostigma Thonningii* as reducing agent. A structural attribute of the mixed oxide was investigated using X-ray Diffractometer, High-Resolution Scanning Electronic Microscopy and Energy Dispersive X-ray. Petroleum refinery raw wastewater having phenol concentration of 19.961 mg/L was treated using the green-synthesized mixed oxide. Adsorptive phenols removal up to 99.5% was achieved with a dosage of 0.04 g/100 mL at temperature of 35 °C, and contact time of 1.167 h. By this, the treated water meets the standard acceptable phenol concentration (0.1 mg/L) in wastewater of hydrocarbon refinery.

Keywords: green synthesis; magnesium oxide; mixed oxide; phenol; process wastewater; titanium oxide.

INTRODUCTION

The environmental problem caused by organic pollutants especially the phenolic compounds, and their contributions to water pollution has been widely reported in the literature (Vasudevan, 2014; Gupta & Balomajumder, 2015). It has been estimated that globally, over one billion people do not have access to safe drinking water, meanwhile, pollutants majorly due to industrialization have continually contaminated the available water sources through the introduction of such substances (such as phenol) into the water bodies (Jinxia *et al.*, 2019; Mais *et al.*, 2019).

Phenolic compounds have generally been found to be one of the most dangerous organic pollutants in wastewater from the refinery. A very low amount of phenolic compounds in water still makes it extremely toxic for human consumption (Mohamadi *et al.*, 2015). In natural waters, the presence of phenol allows the formation of other toxic compounds through oxidation processes. In addition, the several methods used for the removal of phenols from wastewater have been observed to be confined because they often involve high capital and operational costs. Such existing methods include electrocoagulation, extraction, volatilization, hot gas or steam stripping, ion exchange, microbial degradation, membrane separation, solvent extraction, polymerization and many others (Tasic & Antonijevic, 2014).

Popular methods of phenol degradation that have continually gained interest are the adsorption technique and photocatalysis. Energy-saving and the vast opportunity to develop efficient adsorbents and photocatalytic semiconducting materials from abundant and cheap materials are major motivating factors that have favoured the interest in the two methods. Particularly, mixed solid oxides such as MgO-SiO₂, Al₂O₃-SiO₂, TiO₂-SiO₂, and ZrO₂-SiO₂ systems have long been studied due to their excellent catalytic activity resulting from the acid or basic

properties (Itoh *et al.*, 1974). In recent times, the development of mixed metal oxides as adsorbents for wastewater treatment has attracted the attention of researchers due to their synergistic effect and enhanced adsorption capability (Chen *et al.*, 2018).

More recently, Khan *et al.* (2021) employed (Fe-Mg) binary metal oxide in removing arsenic from contaminated water. The adsorbent showed promising results in terms of high arsenic uptake. In another study, Mustapha *et al.* (2021) prepared silver and titanium oxides-doped activated carbon as adsorbents for the removal of phenols from pharmaceutical wastewater. The reducing activity of whole extracts of Shea butter leaves on the nitrate salts of silver and titanium was illustrated towards the preparation of silver and titanium oxides, and an activated carbon doped with the oxides was found suitable for adsorptive removal of total phenols from pharmaceutical wastewater. Due to its environmentally benign principles and the potential to produce novel bespoke materials, green synthesis has proved to be one of the best synthesis processes for synthesizing metal oxide nanoparticles.

In the present study, the green synthesis method was utilized to develop a mixed oxide of MgO-TiO₂ using leaves extract of *Piliostigma thonningii* and applied in an adsorption process (non-photocatalytic) towards the removal of phenol from process water sourced from petroleum refinery

METHODOLOGY

Materials

Process wastewater was obtained from an indigenous Petroleum Refining and Petrochemical Company in Nigeria. Analytical grade magnesium nitrate hexahydrate (99%, Sigma Aldrich) and titanium nitrate tetrahydrate (99.9%, Sigma Aldrich) were used. Camel's foot leaf (*Piliostigma Thonningii*) was gotten from Ilorin, Nigeria. The leaves were sun-dried for 3 days, chopped into small pieces and then mortar and pestle were used to reduce it to powdery form. Dried powdered camel's foot leaves (4g) was introduced into the conical flask containing

100mL of distilled water. It was magnetically stirred (MS-H280-Pro digital magnetic hotplate stirrer) at 80°C for 50 min. Filtration of the extract yielded the filtrate that was used in the preparation of mixed oxide. Fourier transform infrared spectrum of the extract from *Piliostigma Thonningii* was acquired using a Bruker Vertex 70 spectrometer (Bruker Optics, Billerica, MA, USA) to identify the presence of functional groups. Also, phenolic content in the refinery process water was estimated using Folin-Ciocalteu method (Folin, 1927).

Mixed oxide preparation and characterization

In a 400 mL conical flask, 5.75 g of titanium nitrate was dissolved in distilled water (15.63 mL) and stirred for 2 h to obtain 1M aqueous solution. In another flask, 15.9 g of magnesium nitrate was dissolved in distilled water (62 mL) and agitated for 2 h to obtain 1M aqueous solution. The two solutions were mixed, and 7.76 mL of leaf extract was added. It was centrifuged at 4000 rpm for 4 h and filtered. The filtrate was dried at 90 °C for 2 h and calcined at 500 °C for 3 h. Mixed oxide MgO-TiO₂ was then stored in a sample bottle until use. Structural characterization of the mixed oxide was carried out using X-ray diffraction (Bruker AXS D8 Advance, USA), high resolution scanning electron microscopy and Energy-dispersive X-ray spectroscopy (Zeiss Auriga, USA). The XRD pattern was acquired at room temperature (25°C) with Cu K α radiation ($\lambda=1.5406$ m). The spectra ranged from 15 to 80° at a step of 0.034°.

Phenol degradation using mixed oxide MgO-TiO₂

Batch adsorption experiments were carried out using Mixed Oxide (MgO-TiO₂) to study the percentage phenol removal. Adsorption conditions were varied for adsorbent dosage, contact time, and temperature as shown in Table 1.

Table 1 Batch adsorption parameters

Variable	Dosage (g)	Contact time (min)	Temperature (°C)
(+)	0.1	80	50
(-)	0.02	10	35

In a typical experiment, a measured quantity of the mixed oxide (0.02 g) was added to 50 mL of the refinery wastewater, followed by shaking of the mixture in an orbital shaker at the desired temperature for a given period. Total phenol removal and the adsorption capacity were obtained from Equations (1) and (2) respectively;

$$\% \text{ Removal} = (C_0 - C_e) \times 100 / C_0. \quad (1)$$

The terms, C_0 and C_e are the initial concentration (mg/L), and the final concentration of phenol at equilibrium (mg/L) respectively.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

Symbols represents, adsorption capacity (q_e), the volume of solution ($V(L)$), and the mass of adsorbent ($W(g)$). Three kinetic models were used to examine the experimental data acquired from the adsorption process to describe the mechanism controlling the adsorption process. These are presented in Equations (3) – (5) respectively for pseudo-first order, pseudo-second order, and intra-particle diffusion models;

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad (4)$$

$$q_t = k_p t^{\frac{1}{2}} + C \quad (5)$$

Quantity of phenol adsorbed at time, t (q_t), and at equilibrium (mg/g) (q_e) respectively,

and k_1 (l/min), k_p , and k_2 (g/mg min) are the rate constants for pseudo-first order, diffusion of intra-particles and pseudo-second order for the adsorption process respectively. The constant C depicts the intra-particle diffusion, which indicates the boundary layer thickness. For this works, as presented in Equations (6) and (7), Langmuir and Freundlich's isotherms were respectively considered.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (6a)$$

$$R_L = \frac{1}{1+bC_0} \quad (6b)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

In Equation (6a), b denotes Langmuir constant which is associated with the adsorptive energy (L/mg) while the maximum adsorption capacity (mg/g) is represented as q_m . The dimensionless equilibrium parameter, R_L is a crucial feature of the Langmuir isotherm that indicates the type of the isotherm to be either linear ($R_L = 1$), favourable ($0 < R_L < 1$), irreversible ($R_L = 0$), or unfavourable ($R_L > 1$), and C_0 is the initial phenol concentration mg/L. From Equation (7), K_F and n are the Freundlich constants that provide information about the adsorption capacity and adsorption intensity respectively.

The thermodynamics of the adsorption process of phenol onto MgO-TiO₂ mixed oxide was described using adsorption isotherms. The ΔH and ΔS were determined from the slope and intercept of the linear form of Van't Hoff's Equation (8) by plotting $\ln K_C$ against $1/T$. The change in Gibbs free energy ΔG was determined at different temperatures from equation (9).

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

$$\Delta G = (\Delta H - T\Delta S) \quad (9)$$

In the equations, R is the universal gas constant, T is the absolute temperature in Kelvin, and K_C is equilibrium constant which represents the ratio of adsorption capacity to the amount of adsorbate in the solution at equilibrium ($K_C = Q_e/C_e$).

RESULTS AND DISCUSSION

Fourier transform infrared spectrum of *Piliostigma thonningii* leaves extract was obtained (Figure not shown). In the spectrum, peak due to N-H stretching bond or carboxylic acid (COOH) and aliphatic hydroxyl (OH) groups was observed at 3480 cm^{-1} . The wavenumber 707 cm^{-1} is due to C-S stretching bond, alkyl halides, or the double bond $-\text{CH}=\text{CH}-$. Aromatic rings, carbonyl group (C=O) vibration or ethylenic double bond (C=C) were observed at 1634 cm^{-1} . The peak as a result of the triple bond $\text{C} \equiv \text{C}$ stretching bond at 2052 cm^{-1} was also evident. The presence of amine groups in the *Piliostigma thonningii* leaves extract as observed in the FTIR result is indicative of the suitability of the leaves extract as a reducing agent for the biosynthesis of MgO-TiO₂ mixed oxide. Also, the existence of diverse bioactive molecules in the leaves extract of *Piliostigma Thonningii* will serve to reduce, cap/functionalize, or stabilize the mixed metal oxide nanoparticles in the course of synthesis. The amount of total phenols in the petroleum refinery process water was reported as 19.961 mg/L

X-ray diffraction pattern of the prepared MgO-TiO₂ mixed oxide is presented in Figure 1. The XRD peaks are mainly due to rutile and anatase phases of titanium oxide (rutile: JCPDS card no. 00-021-1276) and (anatase: JCPDS card no. 00-021-1272). Peaks due to magnesium oxide were not revealed perhaps because it is relatively less crystalline compared to the anatase and rutile polymorphs of TiO₂. Nonetheless, the presence of MgO has been supported by qualitative and quantitative EDX elemental compositions, and the high resolution scanning electron microscopy images.

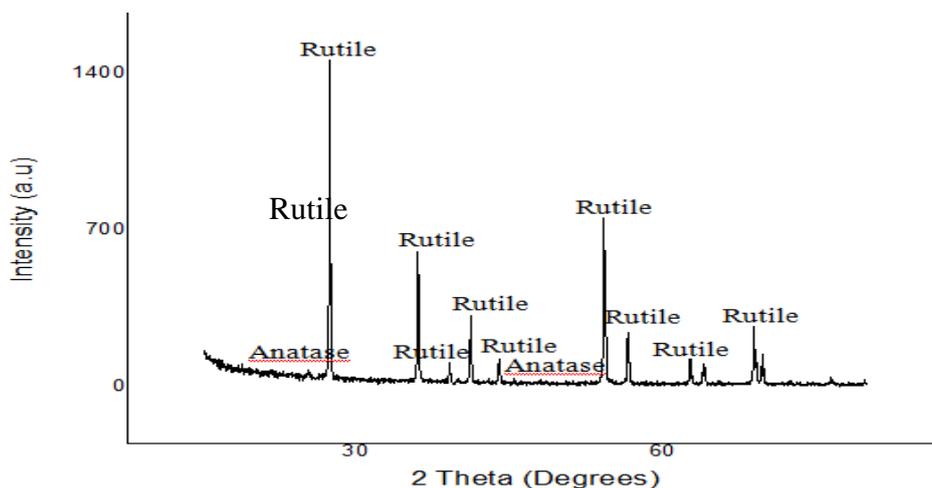


Figure 1 The XRD pattern of mixed oxide MgO-TiO₂

The EDX elemental analysis showed that both titanium and magnesium oxides were present in the sample as presented in Figure 2. In addition to Ti, Mg and O from the mixed oxide, other elements found in the mixture are: C, Al, and Si which were introduced by the leaves extract used in mixed oxide preparation. It was revealed in the EDX elemental composition that the elements were present in atomic% as C(8.23), O(70.63), Mg(0.87), Al(1.01), Si(0.65), and Ti(18.6). Analysis of both the XRD and EDX results imply that the formation of titanium and magnesium oxides from their corresponding nitrate salts was effective.

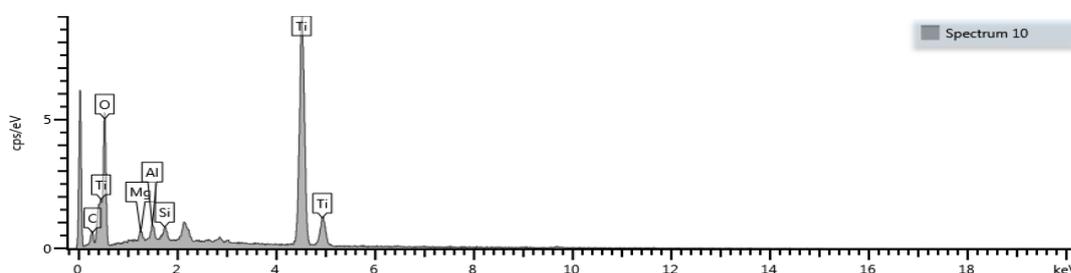


Figure 2 The EDX result of the MgO-TiO₂ mixed oxide

The rutile (tetrahedral, tetragonal) and anatase (octahedral) structures of the titanium oxide polymorphs present in the MgO-TiO₂ mixed oxide are confirmed by the HRSEM morphologies presented in Fig. 3(a) – (d). Calcination would have caused the phase transformation of the initially formed anatase into the rutile phase. Additional smaller structures appear on the surfaces of the well-defined crystalline titanium oxides and could be those of magnesium oxide.

In Fig. 3(b), micropores can be identified in the nanoparticles, a property indicating that the mixed oxide would possess sufficient active sites for surface adsorption. The BET surface area of the synthesized MgO-TiO₂ nanoparticles was 215.50 m²/g. A larger surface area provides more surface active sites for the adsorption of phenols from the refinery wastewater.

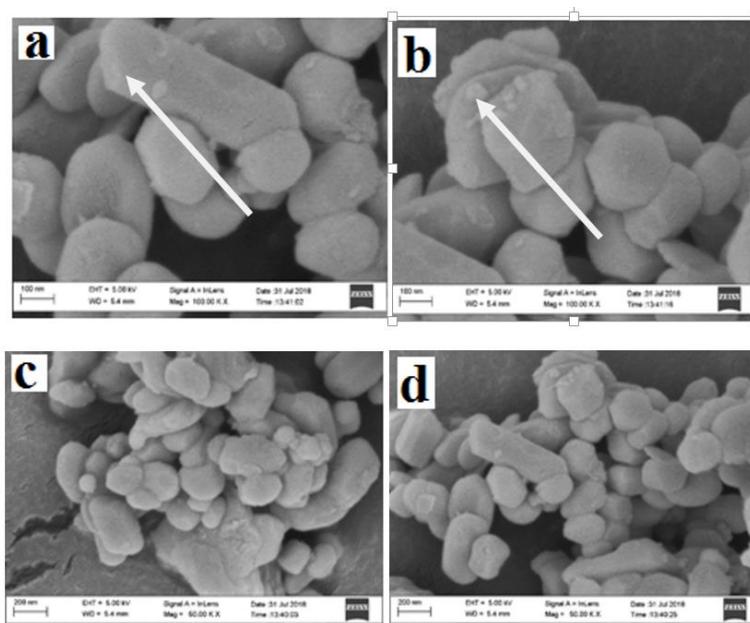


Figure 3 HRSEM Images of the MgO-TiO₂ mixed oxide nanoparticle (adsorbent) with rutile TiO₂ indicated (a), anatase TiO₂ indicated (b), and images in (a),(b) repeated at a different magnification (c),(d).

In the phenol adsorption studies using the mixed oxide, contact time, adsorption temperature, and the adsorbent loading had notable influence towards percentage removal of phenol, as revealed in Fig. 4(a) – (c). The optimal (most favourable) contact time was reached after 70 minutes after which the efficiency declined (Fig. 4a). The initial high rate of phenol uptake had been related to the greater vacancy on the adsorption active sites (mixed oxide surfaces). It was observed that the rate of phenol removal declined gradually after reaching the optimum at 70 minutes because most of the available sites have been occupied. It is shown in Fig. 4(b) that the percentage of phenol removal was best at 35 °C, which occurred at the optimum contact time of 70 minutes, and adsorbent dosage of 0.02 g. Presented in Fig. 4(c) is the relationship

between percentage phenol removal and adsorbent loading (dosage). An optimum point in percentage phenol removal was attained with 0.04 g of MgO-TiO₂ mixed oxide, occurring at 35 °C and time 70 minutes. This condition resulted in 99.5 % removal of phenol. An additional dose of adsorbent resulted in a saturated aqueous mixture and could therefore block active adsorption sites, thereby causing a reduction in phenol removal due to insufficient sites.

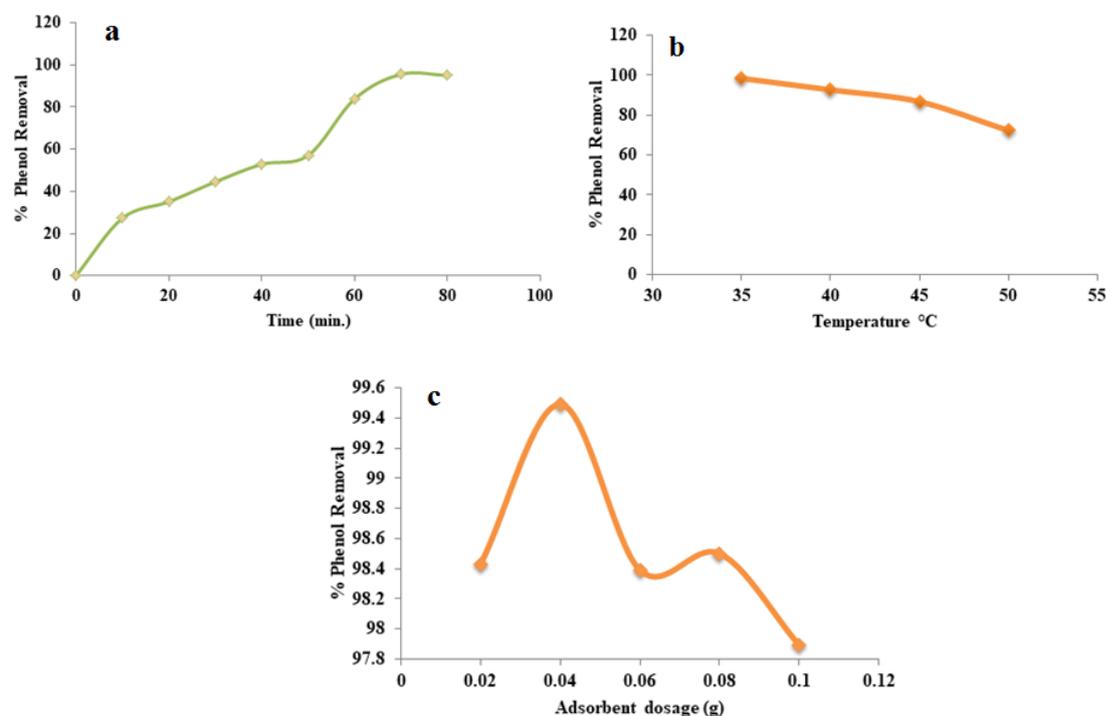


Figure 4(a) Time-dependent phenol removal by the mixed oxide **(b)** Temperature-dependent phenol removal by the mixed oxide **(c)** Adsorbent dosage-dependent phenol removal by the mixed oxide

Displayed as shown in Fig. 5(a) and (b) are the respective graphs of the kinetic models. Table 2 is a list of the pseudo-first order and pseudo-second order parameters as determined. The adsorptive phenol removal by the MgO-TiO₂ mixed oxide was better depicted by the model of pseudo-first order kinetic. It was found that both calculated q_e and experimental q_e agrees and followed the model of the pseudo-first order, and the (R^2) value was much closer to one (1.0) compared to that of the pseudo-second order kinetic model. Plotting of q_t against $t^{1/2}$ in Fig. 5(c) showed a linear graph which is due to the intra-particle diffusion of the adsorption process.

Such a linear graph that tends to deviate from the origin indicates that the rate-controlling step is not only controlled by the intra-particle diffusion but may also be as a result of some extent of boundary layers (Angin, 2014).

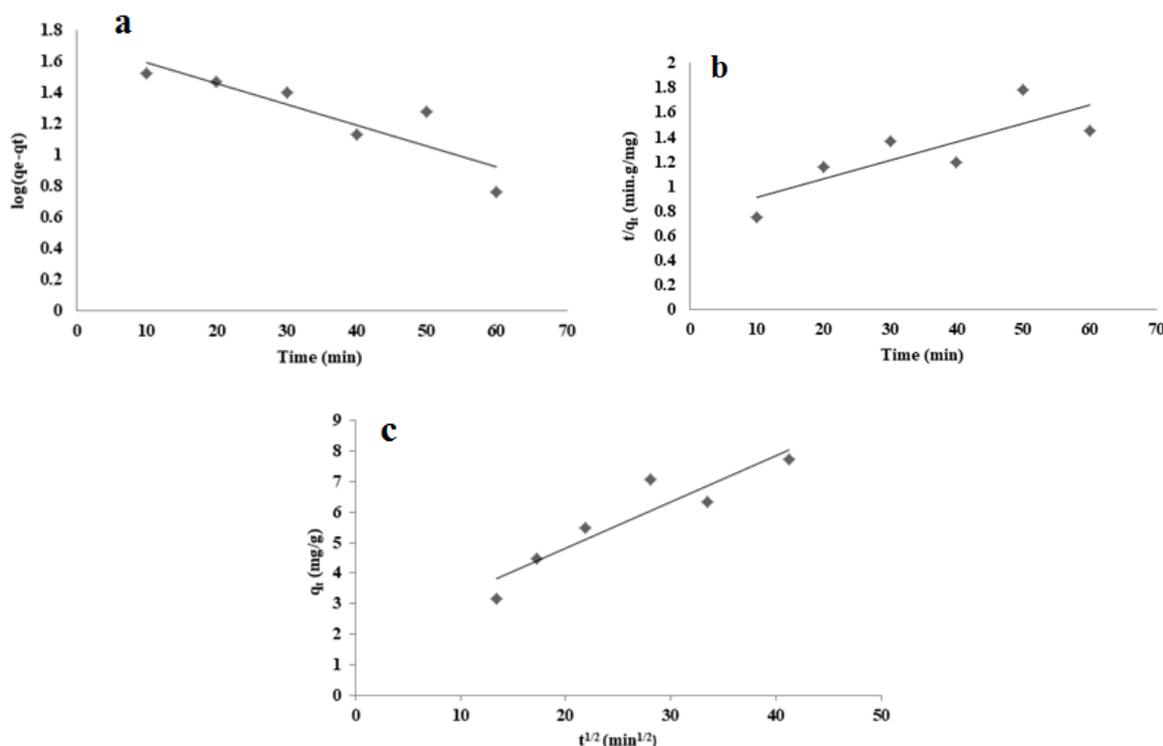


Figure 5 Fitting the phenol removal by MgO-TiO₂ mixed oxide to (a) pseudo-first order kinetics (b) pseudo-second order kinetics (c) intra-particle diffusion.

Table 2 Kinetics parameters for the phenol removal by the mixed oxide

Pseudo First order			Pseudo Second order			Diffusion of intra-particles			$q_e(Exp)$
R^2	K_1	$q_e(Cal)$	R^2	K_2	$q_e(Cal)$	R^2	K_p	C	
	min^{-1}	mg/g		$g/mg.min$	mg/g		$mg/g.min^{-\frac{1}{2}}$	mg/g	mg/g
0.7796	0.03086	53.80	0.6557	0.000292	67.11	0.861	0.151	1.796	47.03

The plot in Fig. 6(a) showed that Langmuir isotherm model fitted well to the experimental data having R-squares values of 1.0 when compared to the Freundlich isotherm with an R-square value of 0.9664. This simply means that the uptake process took place on a homogenous surface by a monolayer adsorption mechanism; all sites were occupied at once, and that the binding strength is attributed to the concentration of phenol at equilibrium. The ultimate adsorption capacity was found to be 48.077 mg/g and the R_L obtained was 1.008, indicating a linear model for the process of adsorption. The negative value of 'n' from the Freundlich isotherm plot in Fig. 6(b) suggests a chemical interface and an unfavourable adsorption route of phenol on the adsorbent. Also, the large value of K_f indicates a high adsorption capacity (Vasudevan, 2014). However, the adsorption process was well fitted into the Langmuir isotherm (Fig. 6a). Table 3 shows the summary of the obtained results.

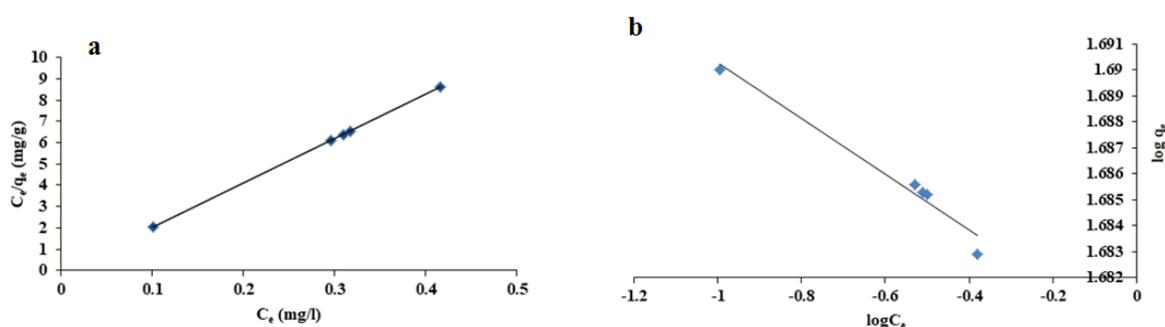


Figure 6 (a) Langmuir Isotherm for phenol adsorption onto MgO-TiO₂ **(b)** Freundlich Isotherm for phenol adsorption onto MgO-TiO₂

Table 3 Langmuir and Freundlich constants for the adsorption of phenol onto MgO-TiO₂

Langmuir constants				Freundlich constants		
R_L	q_m (mg/g)	b (l/mg)	R^2	n	K_f (mg/g)	R^2
1.00	48.077	0.4069	1.0	-93.4577	47.8189	0.9664

The thermodynamic plot for the phenol adsorption in refinery process wastewater using the MgO-TiO₂ mixed oxide is shown in Figure 7. Enthalpy was found to be $\Delta H = -16.36195 \text{ KJ/mol}$ which means that the adsorption of phenol on MgO-TiO₂ is an exothermic reaction. The entropy $\Delta S = -53.05 \text{ J/mol K}$ suggests less randomness at the solid-solution interface and that the process of adsorption does not require much energy. The Gibb's free energy values were -0.023 kJ/mol, 0.240 kJ/mol, 0.510 kJ/mol and 0.770 kJ/mol at temperatures 308, 313, 318 and 323 K respectively. The negative sign of Gibb's free energy at the optimum temperature indicates spontaneous adsorption while the positive sign of Gibb's free energy above the optimum temperature indicates non-spontaneous adsorption (Djebbar *et al.*, 2012). Values are presented in Table 4.

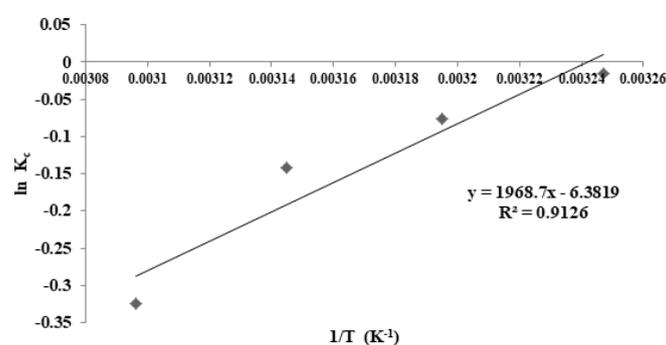


Figure 7 Thermodynamic curves for the phenol adsorption using the mixed oxide

Table 4 Thermodynamic parameters for phenol adsorption using the mixed oxide

		308K	313 K	318 K	323 K
ΔH (kJ/mol)	-16.36195	-	-	-	-
ΔS (kJ/mol)	-0.0531	-	-	-	-
ΔG (kJ/mol)		- 0.023	+ 0.240	+ 0.510	+ 0.770

CONCLUSION

The synthesized mixed oxide nanoparticles of MgO-TiO₂ was found suitable for adsorptive phenol removal from refinery process wastewater. The reducing activity of the whole extract of *Piliostigma thonningii* on the nitrates of magnesium and titanium was illustrated towards the

preparation of magnesium and titanium oxides. With an initial phenols concentration of 19.96 mg/L in the raw refinery wastewater, a maximum percentage removal of 99.50% was achieved using MgO-TiO₂ dosage of 0.04 g, contact time of 70 min and temperature of 35 °C. From the equilibrium and kinetic studies, Langmuir isotherm and pseudo-first order kinetic model defined the experimental adsorption data. It was found from the intra-particle diffusion model that the adsorption rate was not controlled only by intra-particles, but was also controlled by exterior mass transfer at the early stages of the process. It was also established that the process of adsorption was spontaneous and exothermic at the optimum temperature

ACKNOWLEDGEMENTS

The support of the Chemical Engineering Laboratory of the University of Ilorin, Ilorin Kwara state is greatly acknowledged.

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