Study on the Efficiency of Ethylene Vinyl Acetate-Fly Ash Composites for the Uptake of Phenols from Synthetic Waste Water

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ABSTRACT: In this study, ethylene vinyl acetate–fly ash (EVA-FA) composites were prepared by the melt mixing technique using a rheomixer for the purpose of removing 2,4,6-trichlorophenol (TCP) and p-nitrophenol (PNP) from water. The fly ash was characterized by X-ray fluorescence spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD); the composites were characterized using SEM and XRD. Brunauer, Emmett, and Teller (BET) measurements revealed a surface area (S_{BET}) of 0.07110 m^2/g for the fly ash. The adsorption of TCP and PNP were monitored by UV–Vis spectrophotometer. The maximum adsorption of PNP was obtained at pH 5 after a contact period of 12 h, whereas that of the TCP was obtained at pH 4 after a period of 10 h has elapsed. The equilibrium adsorption data were evaluated using Langmuir and Freundlich adsorption isotherm models. The Langmuir adsorption model gave the better correlation coefficients for the equilibrium adsorption data. The kinetics data followed the pseudo-second-order model for both TCP and PNP. The theoretical maximum adsorption capacity (q_{max}) of the adsorbent used in the study was found to be 3.424 mg/g and 2.544 mg/g for TCP and PNP, respectively. The desorption of the phenols from the composites was performed using 0.2M NaOH. About 82.6% and 76.3% of TCP and PNP were recovered, respectively. The study showed that the pH of the solution and contact time play a significant role in the adsorption process. Furthermore, we have demonstrated that EVA-FA composites have the potential to adsorb phenols from acidic water solutions. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Phenols are common contaminants existing widely in wastewater discharged from industries such as paint, drug, pesticide, cosmetic, rubber, dye, and steel.[1–3] The amount of phenolic compounds in industrial wastewater is about 30–2000 mg/L, and it is higher than the standard limit (1.0 mg/L) set by the (US-EPA) Environmental protection agency.[4,5] The World Health Organization recommends a tolerable phenolic concentration of 0.001 mg/L in potable water.[6] Phenols are highly toxic, poorly biodegradable, and present carcinogenic properties. Chronic toxic effects due to phenols reported in humans include vomiting, difficulty in swallowing, liver and kidney damage, headache, diarrhea, fainting, mental disturbances, and cognitive necrosis (death of cells).[7]

There are many documented methods for the removal of phenols from wastewater, e.g., microbial degradation, chemical oxidation, precipitation, ion exchange, incineration, solvent extraction, and irradiation, but the most frequently used technique is adsorption onto a solid surface.[1,8] Activated carbon is the most widely used adsorbent in water treatment. It has a high affinity for organic compounds coupled with porosity but being highly expensive, its use is limited.[9,10] This limitation makes it imperative that less expensive and sustainable materials be used for the removal of contaminants such as phenols from water. Fly ash (FA) is no doubt a suitable alternative because it is cheap and widely available. Also, the use of FA, a waste material as an adsorbent for organic contaminants (phenols) from water is a strategic path for the development of sustainable processes and for reducing the environmental burden as only 5% of the FA is utilized in constructions and the rest is used for landfills.[11]

FA is one of the by-products generated in the combustion of pulverized coal in coal fired power stations. FA is composed mainly of calcium oxide (CaO), silicon oxide (SiO$_2$), and aluminum oxide (Al$_2$O$_3$). FA particles are generally spherical in shape and with size ranging from 0.5 to 100 μm in size.[12] The disadvantage of using FA for water treatment purposes is that trace amounts of heavy metals present in the FA has the tendency of leaching into the water, this cause a secondary pollution of the water.[13]

FA as an adsorbent for phenols has been earlier reported; however, limited work has been reported on the utilization of FA as

part of a composite for water treatment purposes. In this study, ethylene-vinyl acetate (EVA) and FA were used to fabricate EVA-FA composites for the removal of *p*-nitrophenol (PNP) and 2,4,6-trichlorophenol (TCP) from synthetic wastewater. The polymer (EVA) will serve as a supporting material for the FA to make it easier to recover of the adsorbent material from water after treatment.

EXPERIMENTAL

Materials

Ethylene vinyl acetate (EVA) was supplied by Du Pont, Elvex with the density of 0.930 g/cm^3 and the melting point of 95°C. The FA used in the study was an identified class obtained from Matla Power Station, Kriel, South Africa. The FA was sieved to a particle size of $\leq$ 38 µm before use. Hydrochloric acid (HCl) of 32% purity and sodium hydroxide (NaOH) (99% purity) were purchased from Merck Chemical, South Africa. *p*-Nitrophenol ($\geq$ 99% purity) and 2,4,6-trichlorophenol ($\geq$ 98% purity) were purchased from Sigma–Aldrich. All chemicals were used without further purification.

EVA-FA Composites

The composites were synthesized via the melt mixing technique in a rheomixer using EVA and FA as a filler at 10% filler loading. The rheomixer was operated at 120°C, rotational speed of 60 rpm for the duration of 30 min. The composites formed were then extruded to obtain strips with the average width of 50 mm and 0.5 mm in thickness. The masses (in grams) of EVA and FA were calculated using the formula below:

$$m = D \times V \times Fr \times W\%$$

where *D* the density of either the EVA or FA, *V* is the volume of the chamber, *Fr* is the filler rate with respect to the total volume of the chamber, and *W* is the weight in percentage of either the polymer or filler in the final product.

Characterization of FA and EVA-FA Composites

X-Ray Fluorescence. Elemental concentrations within the FA were analyzed by X-ray Fluorescence (XRF) spectroscopy. A total of 8 g of the FA was mixed with 4 g of cellulose ($C_6H_{10}O_5$). The sample was placed in an aluminum cup and hydrolytically pressed into a pellet under high pressure of 20 tons for 60 s. The analysis was carried out with Magi"X Pro XRF spectrophotometer operated at 40 kV and 40 mA.

X-Ray Diffraction. The phases and qualitative analysis of the minerals within the FA were carried out using X"Pert Diffractometer by PAnalytical operated at 40 kV and 40 mA for 60 min over 2θ angle range of 4–60°.

Scanning Electron Microscopy. The morphology of the FA and the composite were determined by a JOEL scanning electron microscopy (SEM) instrument with a field emission gun. The samples were deposited on a glass slide with a double sided scotch tape and carbon coated before viewing.

Brunauer, Emmett, and Teller Measurements. The surface area of the FA was determined using Micrometrics ASAP 2020 surface area analyzer by nitrogen (N_2) adsorption at −196°C. Samples were degassed at 200°C for 24 h before adsorption.

Table I. XRF Results of Fly Ash Used

Component	Concentration %
SiO_2	46
CaO	5.9
Al_2O_3	31
Fe_2O_3	2.4
MgO	1.4
TiO_2	1.5
K_2O	0.72
P_2O_5	1.0
Na_2O	0.60
Ba	0.16
Sr	0.23

Adsorption Studies. The studies were performed using TCP and PNP as the model pollutants. The effect of contact time and pH were investigated using 20 mL of the pollutants and preweighed EVA-FA composites with the average mass 0.5 g. All the experiments were performed at room temperature, the samples shaken using a shaker at a rotational speed of 160 rpm. The amount of TCP and PNP adsorbed were monitored by UV-VIS spectrophotometer (UV 2450 Shimadzu) at wavelength maxima (λ_{max}) of 274 nm and 317 nm, respectively. The pH of the solutions was adjusted with either dilute NaOH or HCl and measured with a pH meter (BT-600 pH meter-Boeco). The calibration plot of absorbance vs. concentration for all the standards (0, 5, 10, 15, 20, and 30 ppm) showed a linear relationship with the correlation coefficient of $\geq$ 0.99. The amount of TCP and PNP adsorbed at any particular time (q) was calculated using the formula:

$$q = \frac{C_0 - C_t \times V(L)}{w(g)}$$

where C_0 is the initial adsorbate concentration (mg/L), C_t is adsorbate concentration at time t (mg/L), V is the volume of the solution (L), and w is the mass of the adsorbent (g).

RESULTS AND DISCUSSION

XRF Analysis and BET Results of FA

The elemental analysis was performed using XRF; the results obtained are shown in Table I. The FA is composed mainly of SiO_2, Al_2O_3, and CaO. The low % of CaO (<10%) implies that the FA originates from the combustion of bituminous coal and it is classified as class F. For BET surface area analysis, the N_2 adsorption gave the specific surface area (S_{BET}) of 0.0711 m^2/g, pore volume of 5 $\times$ 10^{-5} cm^3/g, and pore size of 2.809 nm for the FA.

X-Ray Diffraction Analysis

Figure 1 shows that FA consisted mainly of quartz (SiO_2), mullite (Al_2O_3 and SiO_2) with small amounts of hematite (Fe_2O_3), and lime (CaO). These results were similar to earlier reports on FA from Lethabo power station (South Africa) and Eastern India.[9,14] The intensity of quartz was very strong with mullite
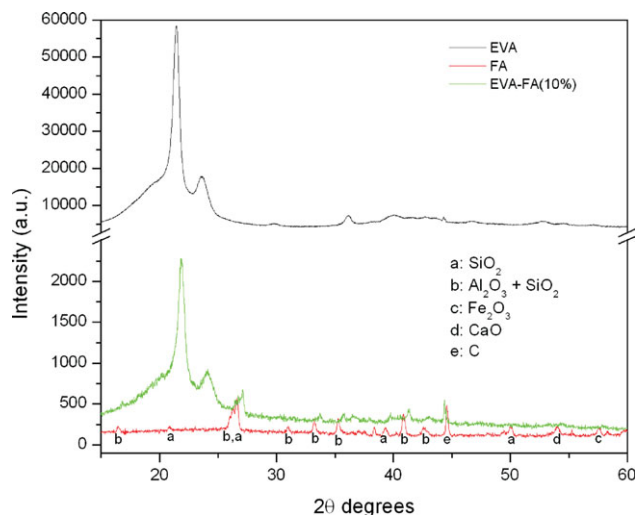
Figure 1. X-ray diffraction pattern of EVA, FA, and EVA-FA composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

forming a chemically stable surface layer. The peak for CaO had a low intensity indicating the presence of small amounts of CaO confirming that the FA belonged to Class F. The X-ray diffraction spectrum for the EVA-FA composite showed the disappearance of some of the low intensity peaks of the FA at $2\theta = 50$, 55, and 58°. The peaks associated with silica and mullite on the EVA-FA composite compared to that of the FA shifted slightly to a higher 2θ degree angle. According to Bragg's law equation of diffraction ($n\lambda = 2d \sin \theta$), an increase in the 2θ degree angle resulted in a decrease in the d-spacing, which suggested the delaminating of the silicate layers by the polymer.

SEM Analysis

Figure 2(a, b) shows the scanning electron micrograph of the FA particles and the EVA-FA composite. The FA particles are spherical in shape with a relatively smooth surface and they also vary in size. Previously, Matjie reported the spherical microparticles from South African coal FA generated from low rank bituminous South African coal.[15] Figure 2b shows the FA particles (white in color) distributed uniformly on the surface of the polymer matrix. The FA particles vary in size because the sieve used was of particle size ≤ 38 μm.
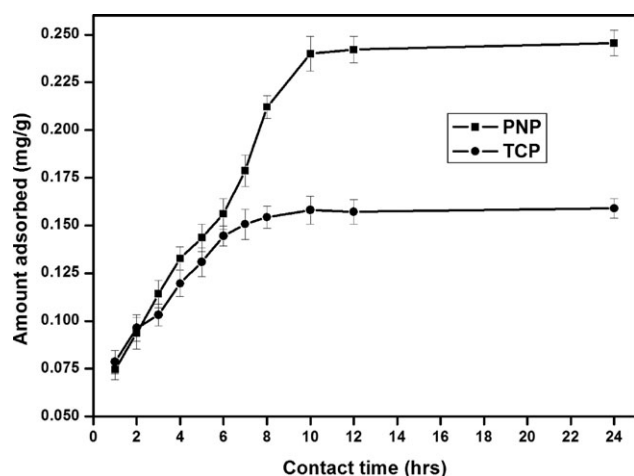
Adsorption Studies

Effect of Contact Time on the Adsorption TCP and PNP. Effect of contact time on the adsorption TCP and PNP onto EVA-FA composites was studied for a period of 24 h. The uptake of both phenols was rapid in the beginning; a rapid increase in adsorption in the initial time of contact might be due to high number of vacant adsorption sites available. As the number of vacant sites is filled, no further adsorption is observed. A maximum of 0.24 mg/g of PNP was adsorbed after a period of 10 h and about 0.15 mg/g of TCP was adsorbed onto EVA-FA composite after 8 h. Figure 3 shows that the uptake of PNP was more favorable when compared with that of TCP; the reason might be that it has a lower solubility in aqueous solution and also PNP being more acidic than TCP, it will be more attracted to the electron rich FA surface when compared with TCP.[9]

Effect of pH. The effect of pH on the adsorption of TCP and PNP was studied over a pH range of 2–10 as shown in Figure 2. The results show that the adsorption of phenols is affected by the pH of the solution as the pH affects the surface charge of the adsorbent and the degree of ionization of the phenols.[6] The graph for TCP shows that the uptake remained almost constant in the pH range between 2 and 4, the adsorption decreased at pH above 4, the reason might be that TCP is a weak acid ($pK_a = 6.15$), its adsorption is not greatly affected in acidic medium. The adsorption of PNP decreased at low pH (below 5), the reason for this might be that a positive charge is developed on the oxides surface of the FA, this creates an unstable environment
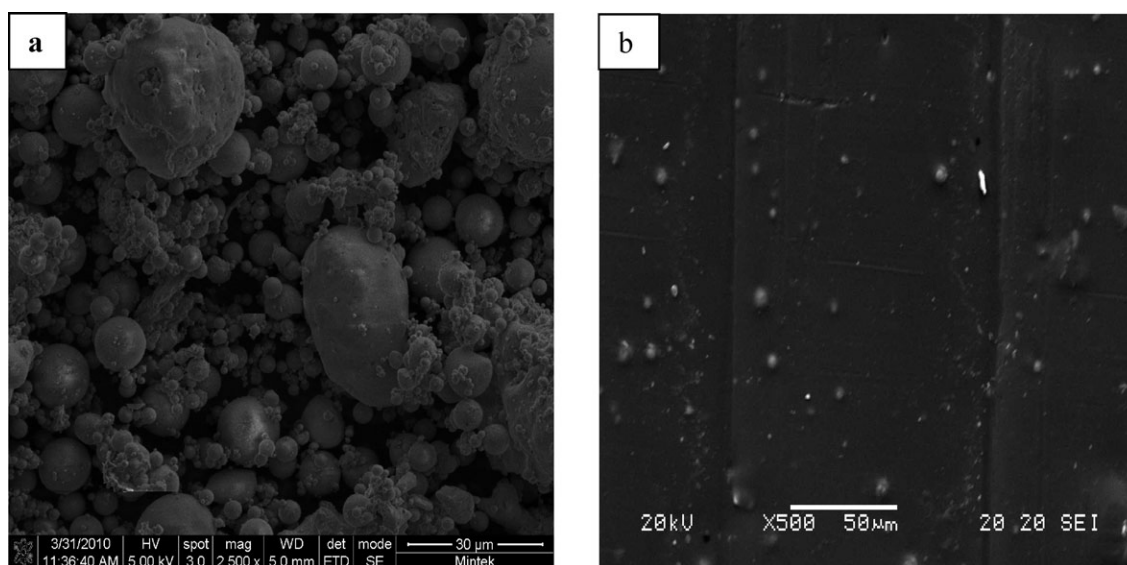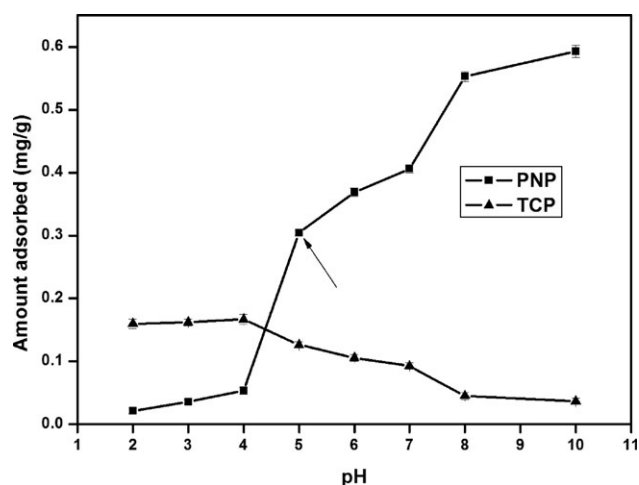

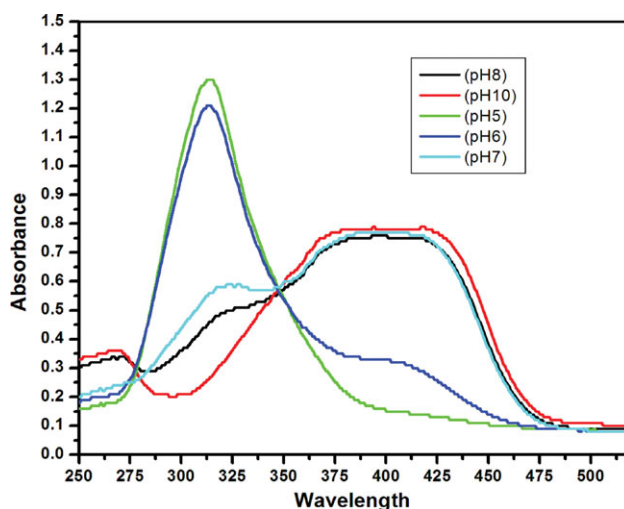**Figure 2.** SEM micrographs of (a) FA and (b) EVA-FA composite.

Figure 3. Effect of contact time on the adsorption of TCP and PNP by EVA-fly ash composites.

Figure 5. Effect of pH on the λ_{max} of PNP on UV-Vis spectrophotometer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for the acidic PNP molecules. At pH above the zero point of charge of the adsorbent (pH above 5), a negative charge is developed on the surface of FA due to the presence of the hydroxyl anions present. The PNP completely ionizes at pH 7.08 forming phenolate ions which get repelled by the negatively charged FA surface. Above pH 7, the phenolate ion forms a bright yellow sodium salt with sodium hydroxide (NaOH). According to the results obtained as shown in Figure 4, the graph shows that the adsorption of PNP is favorable at pH above 6; this is not true because at basic medium the PNP ionizes and forms a compound with different absorption properties. The maximum adsorption can only be considered at pH 5. The sodium salt absorbs the electromagnetic radiation at the visible region of the spectrum with λ_{max} of 400 nm as shown in Figure 5.

Effect of Initial Concentration. The initial concentration of TCP and PNP was varied from 10 to 200 mg/L. The experi-

ments were conducted under the predetermined optimum conditions (contact time-12 hrs, pH 4–5). The initial concentration of the adsorbate plays an important role since a given mass of an adsorbent can adsorb a relative amount of a pollutant. If the solution contains high concentration of pollutants, a particular mass of an adsorbent will adsorb a smaller amount of pollutants compared to a less concentrated solution. Figures 6 shows that the maximum amount adsorbed for PNP is 1.9 mg/g and 2.6 mg/g for TCP. The results obtained reveal that the adsorbent performs better at higher phenol concentrations.

Adsorption Isotherms Studies. The equilibrium adsorption data were evaluated using both Langmuir and Freundlich adsorption isotherm models as shown in Figures 7 and 8 respectively. The Langmuir isotherm is based on the assumption that the surface of the adsorbent has finite number of

Figure 4. Effect of pH on the removal of TCP and PNP by EVA-fly ash composites.
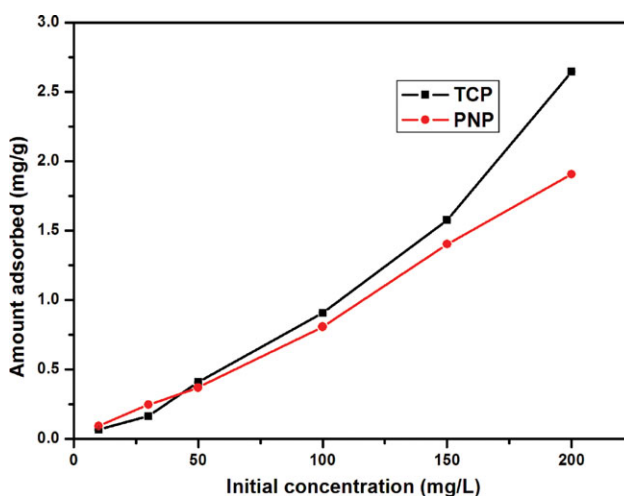
Figure 6. Effect of initial concentration on the uptake of TCP and PNP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
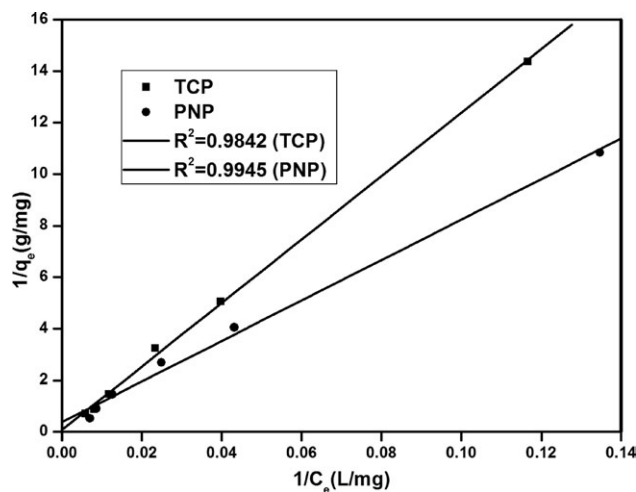
Figure 7. The linearized Langmuir isotherm model for the removal of TCP and PNP by EVA-FA composites.

Figure 8. The Freundlich isotherm model for the removal of TCP and PNP by EVA-FA composites.

adsorption sites, when the available adsorption sites are occupied, no adsorption will occur. This model is expressed in the linear form as:
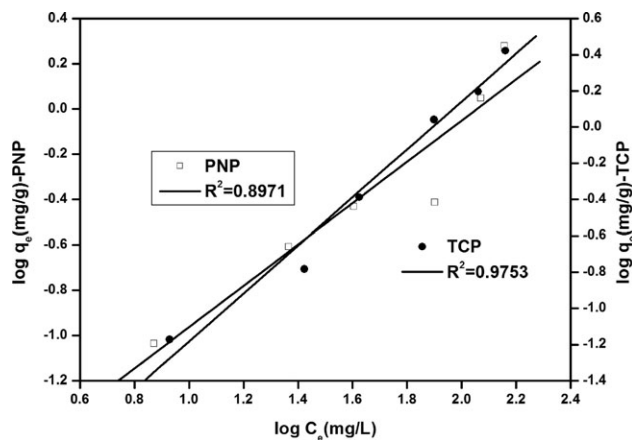
$$\frac{1}{q_e} = \left[\frac{1}{K_L q_{max}}\right]\frac{1}{C_e} + \frac{1}{q_{max}}$$

where q_e is the amount adsorbed at equilibrium (mg/g), q_{max} represent the theoretical maximum adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir affinity constant and C_e is the concentration of the pollutant in solution at equilibrium (mg/L). A plot of $\frac{1}{q_e}$ vs. $\frac{1}{C_e}$ should give a straight line for the adsorption data to conform to Langmuir assumptions.

The Freundlich adsorption isotherm describes heterogeneous surface energies by multilayer adsorption. It also predicts that the concentration of the adsorbate on the adsorbent will increase with an increase in initial concentration of the adsorbate. The Freundlich adsorption isotherm is expressed by the equation:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

where a plot of $\log q_e$ vs. $\log Ce$ should give a straight line for Freundlich adsorption model assumptions to be true. K_f is the Freundlich constant related to the adsorption capacity (mg/g) and n is related to the intensity of adsorption which varies with the heterogeneity of the adsorbent and hence the favorability of the adsorbent/adsorbate system. The adsorption data for TCP and PNP were evaluated, and the Langmuir and Freundlich constants are summarized in Table II. The correlation coeffi-

cients (R^2) show that the Langmuir isotherm model best fit the adsorption data for both the adsorbates indicating the monolayer adsorption. This implies that chemisorption was favorable.[16] The favorability of the adsorbent/adsorbate system was calculated using the Freundlich adsorption model; the value n was greater than 1(1.095) for the uptake of PNP which implies that the adsorption is unfavorable and the adsorption process is regarded as physisorption, whereas that of TCP was less than 1 (0.7547) which suggest that the adsorption was more favorable.

The maximum adsorption capacity (q_{max}) of the composite obtained was 3.424 mg/g (0.017 mol/g) and 2.544 mg/g (0.018 mol/g) for TCP and PNP, respectively. Potgieter et al. reported q_{max} of 2.70 mg/g for the uptake of 2,4-dimethyl phenol onto coal FA.[9] Ahmaruzzaman reported the adsorption capacity of 7.80–9.68 mg/g for the uptake of PNP.[6] Other chlorophenols have been well studied, the maximum adsorption capacity of 0.8–1.0 mg/g and 1.5–1.8 mg/g for orthochlorophenol and 2,4-dichlorophenol, respectively.[17] Other low cost adsorbents like rice husk ash, petroleum coke, and baggase FA have been studied and evaluated for the uptake of phenolic compounds were a q_{max} of 0.886 mg/g, 6.010 mg/g, and 7.80–9.68 mg/g was reported, respectively.[6,9]

Adsorption Kinetics. Kinetic studies are used to determine the rate of the adsorption process, and it is one of the important characteristics defining the effectiveness of the adsorbent. It was observed that the adsorption of TCP and PNP onto EVA-FA composites were rapid at the early stages up to 10 h after which the adsorption slowed down (Figure 3). The kinetics data obtained were modeled using pseudo-first-order and pseudo-second-order models. The first order equation is expressed as:

Table II. The Langmuir and Freundlich Adsorption Isotherm Parameters

Pollutant	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n (L/mg)	R^2
TCP	3.424	2.23×10^{-3}	0.9842	8.1×10^{-3}	0.7547	0.9755
PNP	2.544	5.01×10^{-3}	0.9945	1.5×10^{-3}	1.095	0.8970
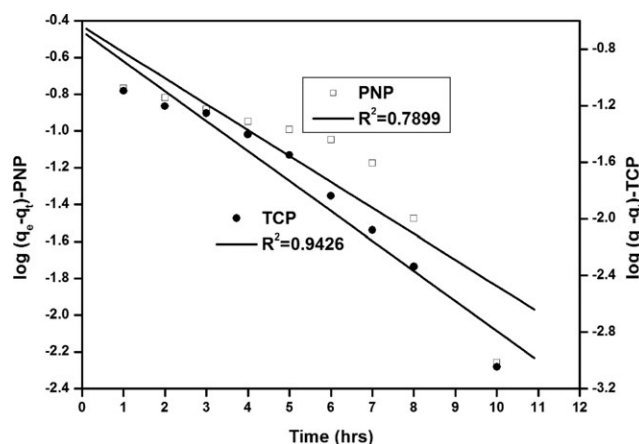
Figure 9. Pseudo-first-order kinetics for the adsorption of TCP and PNP onto EVA-FA composites.

Figure 10. Pseudo-second-order kinetics for the adsorption of TCP and PNP onto EVA-FA composites.

$$\frac{dq}{dt} = k_1(q_e - q_t)$$

where q_e and q_t are amount adsorbed in mg/g at equilibrium and at time t, respectively; k_1 is the rate constant of the pseudo-first-order adsorption model.[18] The integrated form becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

For the pseudo-first-order model to be applicable, a plot of $\log(q_e - q_t)$ against t should give a straight line. The plot of linearized form of the first order equation is shown in Figure 9; the pseudo-first-order rate constant, the amount of TCP and PNP adsorbed at equilibrium, and the correlation coefficient are tabulated in Table III. The value of R^2 is below the minimum value (0.9), and this implies that the kinetics data does not obey pseudo-first-order kinetics law, and the amount of TCP and PNP adsorbed (q_e, exp) does not correlate with the calculated value (q_e, cal) from the graph.
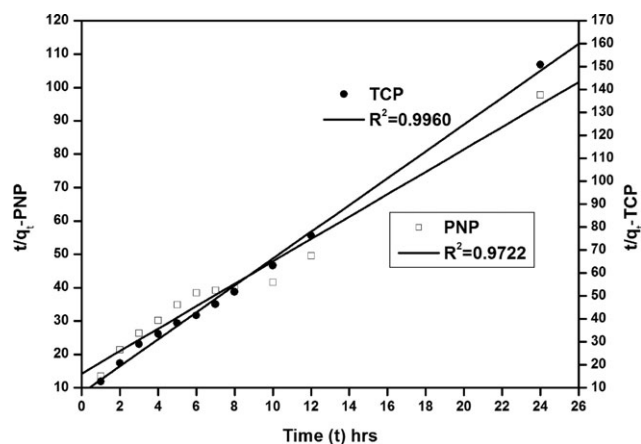
The second order kinetic equation is expressed as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2$$

where k_2 is the rate constant of the pseudo-second-order adsorption model.[19] The integrated equation becomes:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t,$$

a plot of $\frac{t}{q}$ against t should give a straight line.

The kinetics data fitted the second order adsorption model. A plot of linearized form of the pseudo second order equation is shown in Figure 10; the pseudo second order constants are tabulated in Table IV. The correlation coefficient obtained was above 0.9. The amount of both TCP and PNP adsorbed (q_e, exp) was comparable with the calculated value (q_e, cal). The pseudo-second-kinetic model fitted the kinetic adsorption data better than the pseudo-first-order-kinetics-model.

Desorption Studies. The desorption studies were performed to recover the phenols from EVA-FA composites. Sodium hydroxide (NaOH) solution with different concentrations ($0.1M$, $0.2M$, and $0.3M$) were used. Sodium hydroxide was used because it is known to be capable of forming sodium salts of phenol.[20,21] The composites were of average mass of 0.50 g; they were first saturated with about 5 mg/L of TCP and 7 mg/L of PNP. The results obtained as shown by Figure 11, show that a maximum of 76.3% PNP and 82.6% of TCP was recovered when $0.2M$ NaOH solution was used.

Adsorption Mechanism. The possible mechanism of interaction between phenols and EVA-FA composites is shown in Scheme 1.

The surface charge of the adsorbent (EVA-FA composite) and the charge on the pollutants play a crucial role in adsorption

Table III. Pseudo-First-Order Kinetics Constants for the Adsorption of PNP onto EVA-FA Composites

Pollutant	q_e, exp (mg/g)	q_e, cal (mg/g)	k_1 (min^{-1})	R^2
TCP	0.1590	0.5095	0.3252	0.9426
PNP	0.2846	0.6508	0.9891	0.7899

Table IV. Pseudo-Second-Order Constants for the Adsorption of TCP and PNP onto EVA-FA Composites

| Pollutant	q_e, exp (mg/g)	q_e, cal (mg/g)	k_1 (min^{-1})	R^2
TCP	0.1581	0.1706	4.486	0.9960
PNP	0.2846	0.2977	0.7937	0.9722
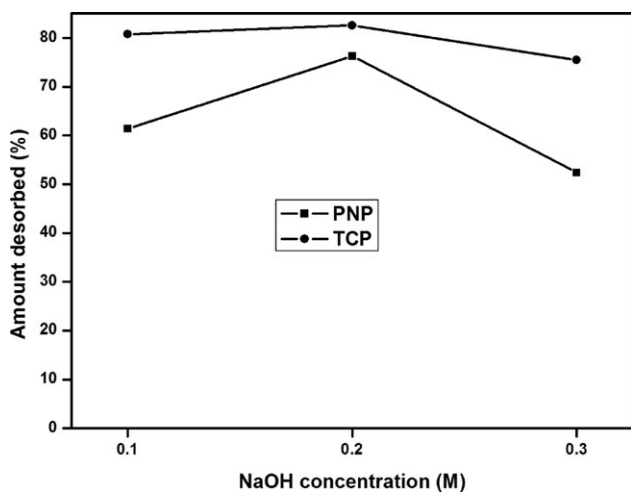
Figure 11. Fractions of TCP and PNP desorbed from EVA-fly ash composites by NaOH solutions.

process. Phenols are weak acids and they possess a partially positive charge. The pHZPC (pH of zero point of charge) for EVA-FA composites utilized in the study was found to be at pH 4–5. FA particles possess a negative charge as shown in Scheme 1(1). For the phenols to be adsorbed onto the FA surface, the surface charge of FA must be partially negative. The addition of

an appropriate concentration and amount of H$^+$ ions can reduce the density of the negative charge surrounding the surface of FA particles thus changing the surface to be partially negatively charged [Scheme 1(2)]. Phenols would then interact with FA particles thus resulting in adsorption.

CONCLUSIONS

The results obtained show that the adsorption of TCP and PNP onto EVA-FA composite were greatly affected by the pH of the solution, contact time, and the initial concentration of the pollutants. The maximum uptake was obtained at pH 5 up to 10 h for PNP and also between pH 2–4 up to 8 h for the uptake of TCP. The adsorption data for both adsorbents was better described by Langmuir adsorption isotherm than Freundlich isotherm, which suggested the monolayer coverage. The kinetics data were analyzed using pseudo-first-order and pseudo-second-order kinetics models; the pseudo-second-order kinetics model gave a better correlation for the adsorption data. About 76.3% of PNP and 82.6 of TCP was desorbed from the EVA-FA composite using 0.2M NaOH solution. This study has demonstrated that waste materials can be fabricated to afford cheap water treatment techniques. This adsorbent performed better than a low cost adsorbent, rice husk ash in terms of the adsorption capacity (q_{max}), but the results were comparable with other low cost adsorbents such as coal FA and baggase fly ash.
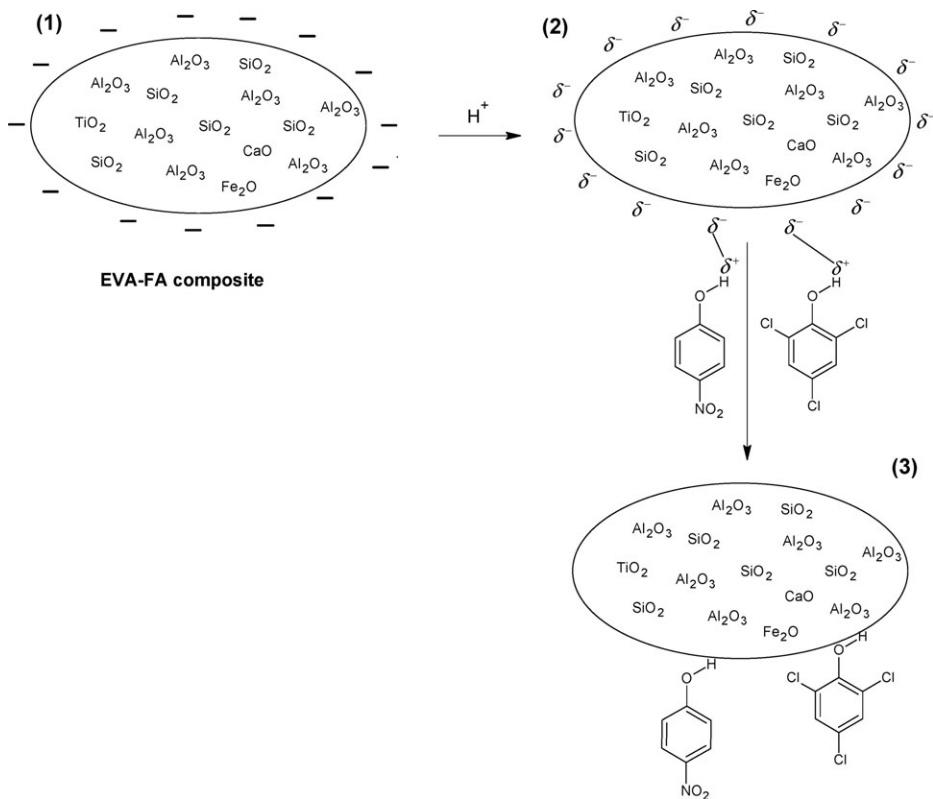
Scheme 1. Possible interaction mechanism of phenols and fly ash.

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