

## Phenanthrene Sorption onto Kaolinite; Heavy Metals and Organic Matter Effects

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**ABSTRACT:** Several factors effect on sorption of polycyclic aromatic hydrocarbons (PAHs) in soil. Coexistence of metals and organic matter of soil are among important affecting factors on sorptive behavior of PAHs. This research investigated the effect of organic matter content and heavy metals (lead, nickel and zinc), on sorption of phenanthrene onto kaolinite. For this purpose, sorption of the organic matter to the kaolinite clay was investigated through batch experiments. Six types of soils in presence and absence of metals at different levels organic matter were prepared for assessment of phenanthrene sorption. Obtained data for phenanthrene sorption were well described by linear Freundlich isotherm. Making comparison between linear distribution coefficients ( $K_d$ ) of phenanthrene for six prepared soils showed that heavy metals and organic matter can increase the sorption of phenanthrene. Heavy metals coexisting with organic matter have a synergic effect on phenanthrene  $K_d$  increment. A model to predict the sorption of phenanthrene onto kaolinite was developed and verified using obtained experimental data.

**Key words:** Phenanthrene, Heavy metals, Organic matters, Sorption, Kaolinite

### INTRODUCTION

Over the past few decades, the contamination of groundwater and soil by hydrophobic organic compounds (HOCs) has become a major environmental issue around the world (Song et al., 2008). PAHs as a main group of HOCs, are persistent, toxic, and dominant pollutants among most contaminated sites (Connell, 2005, Luthy et al., 1994, Reddy and Cameselle, 2009). The sorption behavior of PAHs influences on their fate and transport in soil and groundwater system (Cheng and Wong, 2006, Kile et al., 1995). PAHs can be easily adsorbed onto soil and some factors such as soil type and minerals, organic matters, pH and co-pollutants like heavy metals can change their sorption behaviors. A better understanding affecting factors on PAHs sorption can contribute to achieve a better insight in PAHs fate and transport which consequently could lead to more effective decontamination of these compounds from soil (Weber et al., 2001).

It is widely accepted that the soil organic matter (SOM) can increase the sorption of HOCs in soil (Chiou et al., 1979, Karickhoff et al., 1979). Presence of hydrophobic sites on SOM increases the sorption of PAHs through hydrophobic interactions (Stumm and J. Morgan, 1996). SOM can also change some fe-

atures of the soil, such as porosity and specific surface area, and thereby enhance the sorption of PAHs such as phenanthrene in soil (Wu et al., 2011). Polubesova et al. (2009) found that if montmorillonite is coated with the humic acid, the aromatic moieties in the humic acid is capable for forming  $\pi$ - $\pi$  interaction with phenanthrene and pyrene (Polubesova et al., 2009). It is noteworthy that, dissolve organic matters (DOMs) can facilitate the transportation of PAHs in soil-water system and have a negative impact on the PAHs sorption onto soil (Liu and Amy, 1993, Newman et al., 1993). Zhang et al. (2016) found that the release of the SOM from sediment into the aqueous phase decreases the sorption of phenanthrene. The presence of heavy metals can also affect the PAHs sorption in soil through changing some of the physiochemical features of organic matter in soil-water system (Gao et al., 2006, Zhang et al., 2011b). Gao et al. (2006) found that the existence of heavy metals in soil, via two mechanisms, can promote the sorption of phenanthrene in soil (Gao et al., 2006). The first mechanism is that the heavy metals can bond with dissolved organic matters and reduce them. In the second mechanism heavy metals can increase SOM content via acting as a cation bridge between DOMs

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and soil particles and thereby increase phenanthrene sorption onto the soil. Liang et al. (2016) estimated the binding energy between PAHs and heavy metals in aqueous solution and found that the cation- $\pi$  bonding between electron-rich aromatic structure (phenanthrene, naphthalene and pyrene) and heavy metals ions plays an important role in increasing the sorption capacity and nonlinearity of the PAHs in soil. Hundal et al. (2001) found that the cation- $\pi$  bond between the PAHs rings and cations accumulated on the surface of the soil can be formed. The cation- $\pi$  bond strength in the presence of soft cations is stronger than hard cations based on Lewis acids-bases (Zhu et al., 2004). Zhang et al. (2011) investigated the sorption of phenanthrene in both kaolinite and bentonite with coexisting lead ( $\text{Pb}^{2+}$ ) or cadmium ( $\text{Cd}^{2+}$ ). According to their study, adsorption of lead on kaolin clay and consequently creation of new sorption sites for cation- $\pi$  binding between phenanthrene and lead are the possible reasons for enhancement of phenanthrene adsorption on soil. Thus, it can be postulated that presence of heavy metals and organic matter influence on the PAHs sorption behavior by soils.

Despite all the attention on heavy metals and soil organic matter effects on PAHs sorption and describe the reasons, to our knowledge, there are few studies focusing on quantifying the impact of these factors and followed by the prediction of PAHs sorption in soil. Therefore, it is necessary to develop a model for the estimation of heavy metals and organic matter effects in a different concentration range onto a soil. The main objective of this study is: first, to investigate the effect of the SOM content and some heavy metals (Ni, Pb and Zn) and synergic effects of SOM and heavy metals on the sorption of phenanthrene as a representative of PAHs; second, develop a model to predict the phenanthrene sorption based on the initial concentration of phenanthrene in the soil-water system, heavy metals concentrations and organic matter contents of the soils. The results of this study can be used to predict the phenanthrene sorption in the soil-water system. However, the experimental condition and, type and amounts of heavy metals and organic matter can affect phenanthrene sorption in soil. Lead ( $\text{Pb}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ) were selected as co-existing metals because they have common emission sources as PAHs (Karlsruhe et al., 2000, Reddy et al., 2009). Kaolinite was selected because of being abundant in soils (Hassine et al., 2014).

## MATERIALS & METHODS

Phenanthrene was purchased from Sigma-Aldrich chemical Co., and lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and zinc nitrate tetrahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) we-

re purchased from Merck Co. Organic solvents used in the experiments were all purchased from Merck Co. (HPLC grade). Organic matter used in this study was Humax<sup>®</sup> which is extracted from Leonardite containing 80% humic acid and 15% fulvic acid, purchased from JH-Biotech Co. Kaolinite was purchased from international laboratory India (ILI).

Kaolinite mineral and chemical properties were determined using X-ray diffraction spectrometer (Philips PW 1800) and X-ray fluorescent spectrometer (Philips PW 1480). Infrared (IR) spectrum of the organic matter were taken using a Shimadzu FTIR model 8400S. Using the TOC analyzer SGE series II and a laser scattering particle size distribution analyzer LA950-Horiba Co., soil organic carbon (SOC) and soil particle size were quantified, respectively. Soils pH were determined in a 1:5 (soil:0.01 M  $\text{CaCl}_2$ ) by pH meter (Rayment and Higginson, 1992). Cation exchange capacity (CEC) of the soils were measured by using sodium acetate method (USEPA, 1986a). Soil was analyzed for  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and PAHs concentrations.  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  were extracted using EPA 3050B method and analyzed using EPA 7000B method (USEPA, 1996a, 2007). PAHs were extracted from soil by using EPA 3540C method and analyzed via EPA 8100 method (USEPA, 1986b, 1996b).

To scrutinize the effect of SOM content on sorption of phenanthrene, first, the sorption behavior of the organic matter on kaolinite was determined through batch experiments. In addition to the basic kaolinite soil ( $S_0$ ), two soils with mean and maximum absorbency of the organic matter were prepared by the organic matter sorption batch experiment (named  $S_1$ ,  $S_2$ ). To evaluate the effect of heavy metals on sorption of phenanthrene,  $S_0$ ,  $S_1$ , and  $S_2$  soils were spiked with  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  by applying batch experiments. Employing the isotherms were obtained from heavy metals batch experiments (data not shown), three soil samples with certain concentrations of heavy metals (5000 mg/kg for  $\text{Pb}^{2+}$  and equimolar for  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ ) were prepared (named  $S_{0M}$ ,  $S_{1M}$  and  $S_{2M}$ ). In order to reach the final concentration of 5000 mg/kg for  $\text{Pb}^{2+}$  in soils, specific initial concentrations of heavy metals were determined from isotherms and sorption experiments. Then sorption batch tests of heavy metals was repeated to produce adequate amount of soil contaminated with heavy metals. It is also noteworthy that soils with 5000 mg/kg of  $\text{Pb}^{2+}$  count as high risk for the human health and the environment (USEPA, 2014). Then, sorption of phenanthrene on  $S_0$ ,  $S_1$ ,  $S_2$ , and metals spiked soils ( $S_{0M}$ ,  $S_{1M}$  and  $S_{2M}$ ) was investigated. Sorbent to solution ratio of all batch experiments of organic matter, heavy metals, and phenanthrene sorption was 1:500(w/v). In the organic matter, heavy metals and ph-

phenanthrene batch experiments, the amounts of soil:background solution were 2 g:1000 mL, 0.2 g:100 mL and 0.1 g:50 mL respectively. This ratio was chosen due to the low solubility of phenanthrene (Zhang et al., 2011b). Moreover, this ratio is accepted by OECD guideline (OECD, 2000). All batch experiments were performed in glass bottles with screw cap. Initial amounts of the organic matter were 0.25, 0.5, 1, 1.5 and 2 g. Initial amounts of equimolar mixture of  $Pb^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  were 24, 48, 97, 193, 290, 386, 531 and 772  $\mu M$ . Specified amounts of phenanthrene were added to 50 mL screw cap glass bottles from stock solution (33 ppm of phenanthrene in dichloromethane) and then dichloromethane was allowed to evaporate (Yu et al., 2011). After adding the initial amounts of the organic matter, heavy metals and phenanthrene in appropriate bottles, soil and background solution were added. The samples pH were adjusted to 5.5 by HCl and NaOH to increase the organic matter sorption onto soil and minimize the pH effects in batch experiments (Shaker et al., 2012, Zhang et al., 2011b). All samples were shaken for 24 h at 300 rpm in gyratory shaker at room temperature in darkness. Studies have shown that 24 h is adequate time for sorption of the organic matter, heavy metals and phenanthrene (Bhattacharyya and Gupta, 2008, Shaker et al., 2012, Yu et al., 2011). The soil and solution were separated by centrifuging samples for 30 min at 4000 rpm which was calculated according to the kaolinite particles size and centrifuge device type (OECD, 2000). The background solution contained 0.01 M NaCl to maintain constant ionic strength and 100 mg/L  $NaN_3$  in order to inhibit bacterial growth.

Loss on ignition (LOI) was calculated as the weight difference between the soil heated at 110°C for 24 h and soil heated at 550°C for 1 h. The heavy metals concentrations in solution were measured by flame atomic absorption spectroscopy-wfx 210. Air-assisted liquid-liquid micro-extraction was used to extract phenanthrene from supernatant (Farajzadeh and Khoshmaram, 2013, Farajzadeh et al., 2013, Ghorbanpour et al., 2014). Briefly, 5mL of sample obtained from PAHs sorption batch experiment was transferred into 10mL glass tube with a conical bottom. Then 50  $\mu L$  carbon tetrachloride was added to the tube and the mixture was repeatedly sucked into 5 mL syringe and injected into tube for 10 times until a cloudy solution was formed. The mixture was centrifuged for 5 min at 4000 rpm. 1  $\mu L$  of the settled organic solution was removed using a 1  $\mu L$  GC micro-syringe and injected into the GC-FID 3420A for analysis. Phenanthrene was analyzed by using EPA 8100 method (USEPA, 1986b). The obtained experimental results were modeled by the Freundlich and Langmuir equation (Freundlich, 1906, Langmuir, 1918). The Freundlich equation is expressed as:

$$C_s = K_f C_w^{1/n} \quad (1)$$

Where  $C_s$  is the phenanthrene sorbed on solid phase at

equilibrium (mg/kg).  $C_w$  is the phenanthrene equilibrium concentration in liquid phase (mg/L),  $K_f$  is the Freundlich distribution coefficient and  $n$  is a constant that represents the degree of nonlinearity. When  $n=1$  the linear sorption model is expressed as:

$$C_s = K_d C_w \quad (2)$$

Where  $K_d$  is the linear distribution coefficient (L/kg). The Langmuir equation is expressed as:

$$C_w/C_s = 1/(K_l Q_m) + C_w/Q_m \quad (3)$$

Where  $K_l$  is the Langmuir constant (L/mg),  $Q_m$  is the sorption capacity (mg/kg).

All the glasswares used in the batch experiments were purchased as new. In all batch experiments, blank samples were prepared in the same way. Chemical analyses were performed at least in triplicate. Gas chromatography and flame atomic absorption spectroscopy were carefully calibrated in five different concentrations. The correlation coefficient of the calibration graph was close to one.

The ANOVA test was carried out to evaluate the significance of fitted models with experimental results. To evaluate the significant difference between the soils distribution coefficient, t-student test was carried out. A p-value of 0.05 was acceptable for the level of significance. To develop the model from the experimental data, Eureqa software, a scientific data mining software that can identify relationship between parameters in appropriate models, was used (Nanuam et al., 2012).

## RESULTS & DISCUSSION

The organic matter IR spectra in the 500–4000  $1/cm$  regions are shown in Fig.1. As shown in Fig.1 a broad peak was observed in 2400–3400 regions which are associated with carboxylic acids (hydroxide) and phenols.

Moreover, an absorption peak at 1570 region, which is associated with carbon-carbon stretches in the aromatic ring, was also observed. In addition, there is an absorption in the range of 1400 and 3000 which confirms the presence of aromatic rings (Pavia et al., 2008). The X-ray diffraction peaks showed that the basic soil ( $S_0$ ) was kaolinite and no other mineral peak was detected. The X-ray fluorescence result also revealed that the major elemental oxides of soil were  $SiO_2$  and  $Al_2O_3$ .  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$  and PAHs concentrations in the soil was negligible. Table 1, shows the characteristics of the  $S_0$ ,  $S_1$ , and  $S_2$  soils.

According to Table 1, after the addition of organic matter, CEC and pH value increased. Organic matter contains oxygen-containing group such as carboxyl and hydroxyl which can interact with cations (Kerndorff and Schnitzer, 1980). Presence of these functional groups increase pH and the CEC of soil. Arias et al. (2002) found that the soil CE-

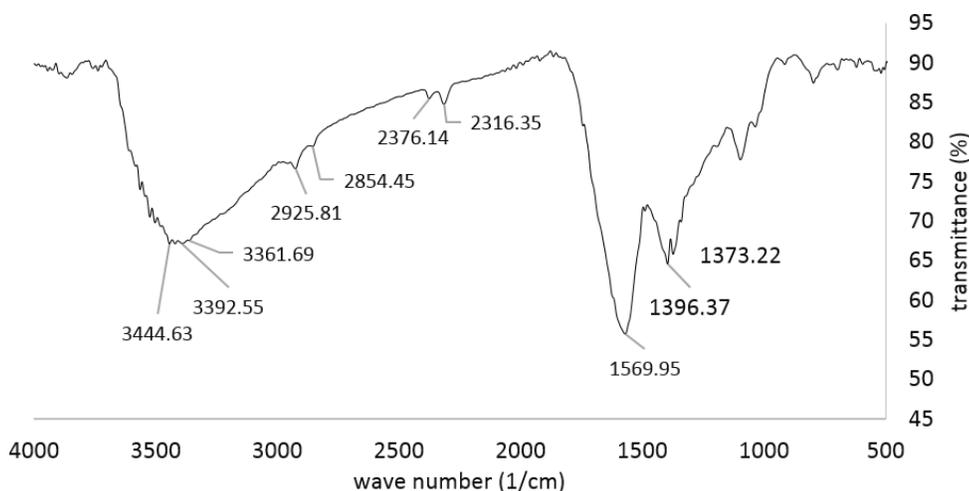


Fig. 1. IR-Spectra of the Humax

C increases with increasing SOM content (Arias et al., 2002). Moreover, Chorom et al. (2013) found that increasing organic matters could increase soil pH (Chorom et al., 2013). The sorption experiment results were fitted with the Freundlich and Langmuir equation (Table 2). The p-values were attained by regression analysis (ANOVA) to evaluate the meaningful of fitted isotherms from experimental results also are shown in Table 2.

The maximum Langmuir correlation coefficient ( $R^2$ ) among six soils is 0.528, which is very low, and the amount of p-value in soils is more than 0.05; therefore, the results are not well associated with the Langmuir equation (Table 2). In contrary, the Freundlich equation has a good association with the results. The  $R^2$  of the Freundlich equation is more than 0.993 and the amounts of p-values are acceptable ( $p$ -value < 0.05). Distribution coefficient is a simple and very common way to investigate the distribution of contaminants in the soil-water system that was used in many studies for comparing the tendency of the soil for the sorption of PAHs (Gao et al., 2006, Zhang et al., 2011b). Since the dimension of the  $K_f$  depends on the n value that changes from 0.914 to 1.004 for six soils of this study, accordingly, comparing the  $K_f$  is not possible. So the experimental results were fitted with linear Freundlich equation. According to the  $R^2$  and p-values of the linear Freundlich equation (Table 2), the results have a good correlation with linear Freundlich equation. Many studies have also shown that PAHs sorption behavior in the soil-water system are well described by a linear model (Gao et al., 2006, Wang et al., 2011, Zhang et al., 2011b). In this study the  $K_d$  is used to investigate the effects of heavy metals and SOM contents on phenanthrene sorption in the soils. It should be noted that the  $K_d$  differences between soils are significant ( $p < 0.05$ ). Table 3 shows the changes in the  $K_d$  of phenanthrene sorption in soils spiked with heavy metals.

As presented in Table 3, after the addition of heavy metals in soil, the  $K_d$  increased 11.36% in  $S_{0M}$ , 18.26% in  $S_{1M}$  and 16.23% in  $S_{2M}$ . Therefore it can be concluded that the presence the soil enhances phenanthrene sorption. The addition of heavy metals in kaolinite, causes to increase soil hydrophobicity and consequently hydrophobic attraction between clay and phenanthrene leads to the enhancement of phenanthrene sorption in soil (Zhang et al., 2011b). Furthermore, metal cations coexisting in the soil-water system can interact with PAHs via cation- $\pi$  bonding and thereby increase the phenanthrene sorption in soil that this interaction mostly concerns soft cations (Zhang et al., 2011b, Zhu et al., 2004). Therefore,  $Pb^{2+}$  which is a softer cation and exist in higher concentration in comparison to  $Zn^{2+}$  and  $Ni^{2+}$  in soils (Table 3), has a fundamental role in cation- $\pi$  bonding with PAHs. Fig. 2, shows changes in phenanthrene sorption onto the soils studied distribution coefficient based on changes in SOM.

Fig. 2, indicates that the phenanthrene sorption in the soils was increased with increasing SOM content with and without the presence of heavy metals. Studies conducted by Zhang et al. (2011) and Wijnja et al. (2004) have shown that the existence of aromatic ring moieties and phenol in organic matters structure can increase phenanthrene sorption (Wijnja et al., 2004, Zhang et al., 2011a). As seen in IR-Spectrum (Fig. 1), the organic matter used in this study having phenol and aromatic rings, could increase phenanthrene sorption in soils. Fig. 3, shows the changes in distribution coefficient of  $S_{1M}$  and  $S_{2M}$  in comparison to  $S_0$ .

The increment of  $K_d$  in  $S_1$  in comparison to  $S_0$  (Fig. 2) and  $S_{1M}$  to  $S_1$  (Table 3) are 40.92% and 18.26%, respectively, but in  $S_{1M}$  comparing to  $S_0$  is 66.65% (Figure 3) which is greater than the sum of 40.92% and 18.26%. Moreover, the  $K_d$  increment in  $S_2$

Table1. Basic characteristics of the S<sub>0</sub>, S<sub>1</sub>, and S<sub>2</sub> soils

Soil	Moisture(%)	pH	SOC (%)	LOI (%)	$(\frac{LOI_{S_1 \text{ or } S_2} - LOI_{S_0}}{LOI_{S_0}}) \times 100(\%)$	CEC (meq/100 g)
S <sub>0</sub>	1.07	5.5	0.22	13.3	-	17.2
S <sub>1</sub>	2.09	5.8	2.11	18.8	41.35	30.7
S <sub>2</sub>	5.83	6.0	4.22	24.5	84.21	44.2

Table 2. Isotherms parameters of phenanthrene sorption

Soil	Langmuir				Freundlich				Linear Freundlich		
	$K_L$ ( $\frac{L}{mg}$ )	$Q_m$ ( $\frac{mg}{kg}$ )	R <sup>2</sup>	P-value	$K_f$ ( $\frac{mg^{(1-1/n)}L^{1/n}}{kg}$ )	n	R <sup>2</sup>	P-value	$K_d$ ( $\frac{L}{kg}$ )	R <sup>2</sup>	P-value
S <sub>0</sub>	-5.06	-116.28	0.528	0.102	954.69	0.914	0.995	0.8E-05	713.39	0.995	1.1E-05
S <sub>0M</sub>	-0.61	-1250.00	0.018	0.799	735.55	1.009	0.996	0.5E-05	794.46	0.995	1.0E-05
S <sub>1</sub>	0.60	1666.67	0.006	0.883	1124.7	1.007	0.993	2.1E-05	1005.28	0.983	11.3E-05
S <sub>1M</sub>	-0.44	-2500.00	0.005	0.897	981.56	1.004	0.994	1.5E-05	1188.86	0.985	8.9E-05
S <sub>2</sub>	9.00	185.18	0.506	0.113	1033.9	1.080	0.993	1.9E-05	1309.70	0.985	8.4E-05
S <sub>2M</sub>	2.00	833.33	0.069	0.615	1554	1.004	0.996	0.7E-05	1522.15	0.990	4.0E-05

S<sub>0</sub>: Kaolinite, S<sub>0M</sub>: Kaolinite with heavy metals, S<sub>1</sub>: Kaolinite with middle level of organic matter, S<sub>1M</sub>: Kaolinite with heavy metals and middle level of organic matter, S<sub>2</sub>: Kaolinite with maximum level of organic matter, S<sub>2M</sub>: Kaolinite with heavy metals and maximum level of organic matter.

Table3. Effect of heavy metals on the K<sub>d</sub> values of phenanthrene sorption

Soil	Pb <sup>2+</sup> (mg/kg)	Ni <sup>2+</sup> (mg/kg)	Zn <sup>2+</sup> (mg/kg)	K <sub>d</sub> (L/kg)	$(\frac{K_{S_{NM}} - K_{S_N}}{K_{S_N}}) \times 100(\%)$
S <sub>0</sub>	-	-	-	713.39	-
S <sub>0M</sub>	4832	702	1023	794.46	11.36
S <sub>1</sub>	-	-	-	1005.30	-
S <sub>1M</sub>	4617	754	986	1188.90	18.26
S <sub>2</sub>	-	-	-	1309.70	-
S <sub>2M</sub>	4893	778	993	1522.20	16.23

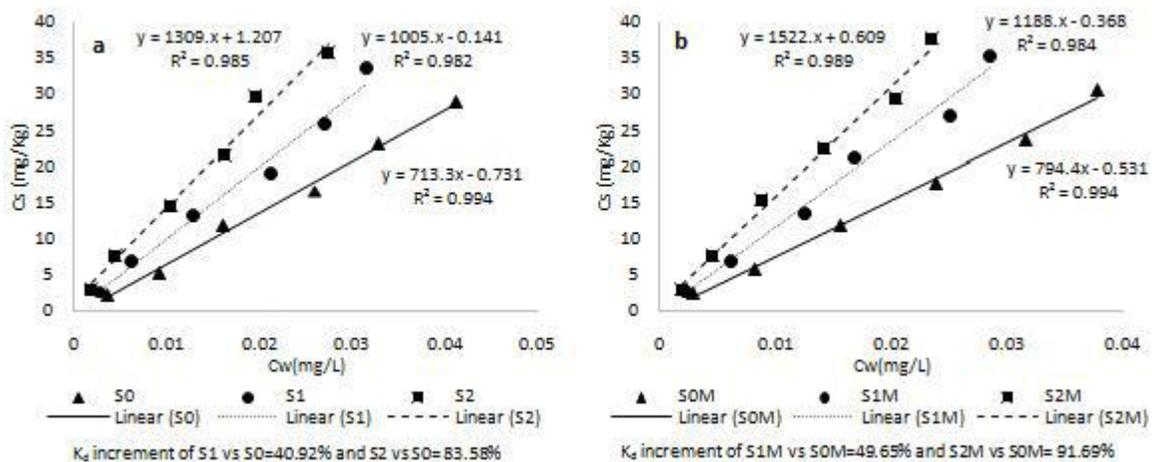


Fig. 2. Effect of SOM on the K<sub>d</sub> values of phenanthrene sorption, a) soil at different levels of OM, b) metals spiked soils at different levels of OM

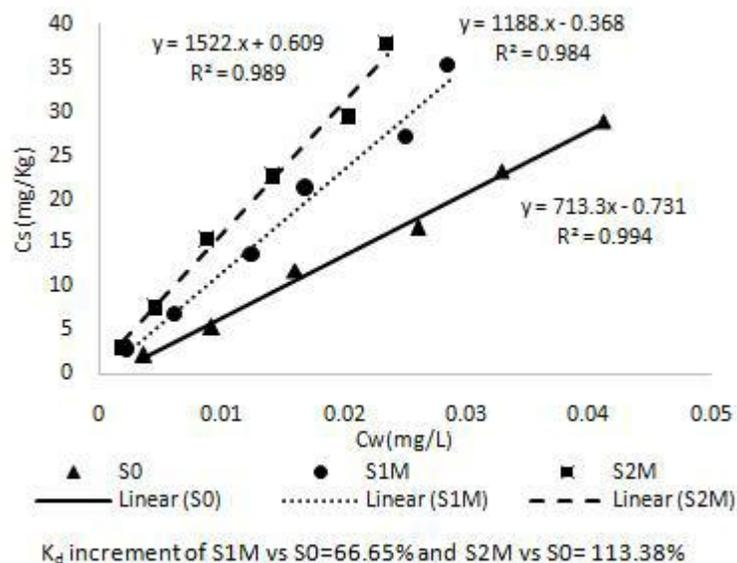


Fig. 3. Effect of the heavy metals and organic matter coexistence on phenanthrene sorption

Table 4. Sensitivity analysis over equation 4

Variable	Sensitivity	%Positive	Positive Magnitude	% Negative	Negative Magnitude
C <sub>0</sub>	0.924	100%	0.924	0%	0
SOC	0.110	100%	0.110	0%	0
SHM	0.027	100%	0.027	0%	0

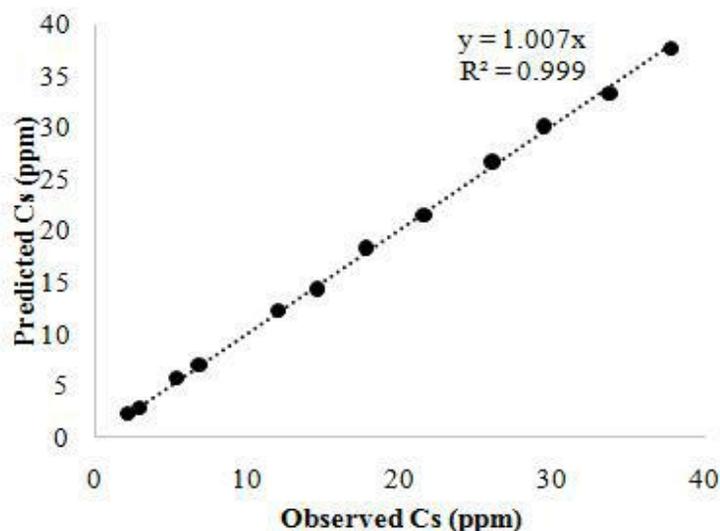


Fig. 4. Predicted and observed values of Cs (ppm) for phenanthrene sorption in the soils

in comparison to S<sub>0</sub> (Fig.2) and S<sub>2M</sub> to S<sub>2</sub>(Table 3) are 83.58% and 16.23%, respectively. The K<sub>d</sub> enhancement in S<sub>2M</sub> comparing to S<sub>0</sub> is 113.38% (Figure 3) which is greater than the sum of 83.58% and 18.26%. These results indicate that the heavy metals and organic matter coexistence have a synergic effect on phenanthrene sorption. In this study, we can conclude that a further increment of K<sub>d</sub> occurs in the coexistence of the heavy metals and organic matter in the soils. Heavy metals have the role as a bridge between PAHs and soil organic matter an-

d therefore prevent the dissolution of SOM as concluded in Zhang et al. (2011) and Gao et al. (2006) studies (Gao et al., 2006, Zhang et al., 2011b).

From 36 obtained data on phenanthrene sorption at different concentrations onto six soil types, 24 of them used to develop a prediction model and remained other 12 data points used for verification of the model. Eureka generated  $5.6 \times 10^5$  models that the stability and maturity of the final solution were 0.35% and 59.1%, respectively. Ultimately, between Eureka proposed solutions, one solution was selected which

after this equation, while the complexity increased, no significant change was observed in error. The solution is presented as follows: (4)

$$C_s = 0.00269 \times C_0 \times SHM + 402.5 \times C_0 \times \sin(6.197 + SOC)$$

Where  $C_s$  is the phenanthrene concentration sorbed onto kaolinite (ppm),  $C_0$  is the phenanthrene initial concentration (ppm), SHM is the soil heavy metals concentration (ppm) and SOC is the soil organic carbon concentration (ppm). Mean absolute error and correlation coefficient of this model are 0.3 and 0.998 respectively. Sensitivity analysis of equation 4 is shown in Table 4.

As shown in Table 4, the model is more sensitive to  $C_0$  (0.924) than SOC (0.110) and SHM (0.027). Results show that, the initial concentration of phenanthrene, soil organic carbon, and heavy metals contents have a positive impact on phenanthrene sorption onto kaolinite with magnitude of 0.924, 0.110 and 0.027, respectively. Fig.4, shows the predicted  $C_s$  values versus observed values using Equation 4.

As shown in Fig.4, fitted line between observed and predicted results have  $R=0.999$  ( $P<0.05$ ). The RMSE of measured and predicted results is 0.4. Moreover, Slope of fitted line in Fig.4 is 1.0076 which is close to 1. Therefore, the observed results have a good correlation with the model results. So it can be concluded that the model can be a good approximation of the phenanthrene sorption in kaolinite-water system with regard to the experimental condition, concentration range of phenanthrene, soil organic matter and heavy metals contents.

## CONCLUSIONS

- Heavy metals and organic matter contents of the soils can affect the availability and mobility of phenanthrene in soil-water system at the contaminated sites.
- The increment of SOM content leads to increase the pH and CEC of the kaolinite and it also enhances phenanthrene sorption onto kaolinite.
- Presence of heavy metals in the kaolinite enhance phenanthrene sorption.
- The coexistence of heavy metals with organic matter in soils causes synergic effect on enhancing phenanthrene sorption in kaolinite.
- The equation was developed can accurately predict the sorption concentration of phenanthrene onto kaolinite with regard to the organic matter and heavy metals concentrations.
- Presence of metals and soil organic matter would lower the availability of phenanthrene in kaolinite soil, since they enhances its sorption greatly.

## REFERENCES

- Arias, M., Barral, M. and Mejuto, J. (2002). Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids. *Chemosphere*, **48(10)**, 1081-1088.
- Bhattacharyya, K.G and Gupta, S.S. (2008). Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Advances in Colloid and Interface Science*, **140(2)**, 114-131.
- Cheng, K. and Wong, J. (2006). Combined effect of nonionic surfactant Tween 80 and DOM on the behaviors of PAHs in soil-water system. *Chemosphere*, **62(11)**, 1907-1916.
- Chiou, C.T., Peters, L.J. and Freed, V.H. (1979). A physical concept of soil-water equilibria for nonionic organic compounds. *Science*, **206(4420)**, 831-832.
- Chrom, M., Mohammadzadeh Karkaragh, R. and Kaviani, B. (2013). Monometal and Competitive Adsorption of Cd, Ni, and Zn in Soil Treated with Different Contents of Cow Manure. *Applied and Environmental Soil Science*, 2013.
- Connell, D.W. (2005). *Basic concepts of environmental chemistry*, CRC Press.
- Farajzadeh, M.A. and Khoshmaram, L. (2013). Air-assisted liquid-liquid microextraction-gas chromatography-flame ionisation detection: A fast and simple method for the assessment of triazole pesticides residues in surface water, cucumber, tomato and grape juices samples. *Food chemistry*, **141(3)**, 1881-1887.
- Farajzadeh, M.A., Khosrowshahi, E.M. and Khorram, P. (2013). Simultaneous derivatization and air-assisted liquid-liquid microextraction of some parabens in personal care products and their determination by GC with flame ionization detection. *Journal of separation science*, **36(21-22)**, 3571-3578.
- Freundlich, H. (1906). Über die adsorption in lösungen. *Zeitschrift für Physikalische*.
- Gao, Y., Xiong, W., Ling, W. and Xu, J. (2006). Sorption of phenanthrene by soils contaminated with heavy metals. *Chemosphere*, **65(8)**, 1355-1361.
- Ghorbanpour, H., Yadeghari, A., Khoshmaram, L. and Farajzadeh, M.A. (2014). Air-assisted liquid-liquid microextraction for simultaneous derivatization, extraction, and preconcentration of some phenolic compounds. *Analytical Methods*, **6(19)**, 7733-7743.
- Hassine, A.B., Souli, H., Dubujet, P. and Trabelsi-Ayadi, M. (2014). On the use of electrokinetic in the kaolinite soil decontamination. *Journal of Materials and Environmental Science*, **5(S2)**, 2555-2559.
- Hundal, L.S., Thompson, M.L., Laird, D.A. and Carmo, A.M. (2001). Sorption of phenanthrene by reference smectites. *Environmental science & technology*, **35(17)**, 3456-3461.
- Karickhoff, S.W., Brown, D.S. and Scott, T.A. (1979). Sorption of hydrophobic pollutants on natural sediments. *Water Research*, **13(3)**, 241-248.
- Karlsruhe, F., Onderzoek, N.C.O.v.T.-N. and Leipzig-Halle, U. (2000). *Contaminated Soil 2000: Proceedings of the Sev-*

- enth International FZK/TNO Conference on Contaminated Soil, 18-22 September 2000, Leipzig, Germany, Thomas Telford Pub.
- Kerndorff, H. and Schnitzer, M. (1980). Sorption of metals on humic acid. *Geochimica et cosmochimica Acta*, **44**(11), 1701-1708.
- Kile, D.E., Chiou, C.T., Zhou, H., Li, H. and Xu, O. (1995). Partition of nonpolar organic pollutants from water to soil and sediment organic matters. *Environmental science & technology*, **29**(5), 1401-1406.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical society*, **40**(9), 1361-1403.
- Liang, X., Zhu, L. and Zhuang, S. (2016). Sorption of polycyclic aromatic hydrocarbons to soils enhanced by heavy metals: perspective of molecular interactions. *Journal of Soils and Sediments*, **16**(5), 1509-1518.
- Liu, H. and Amy, G (1993). Modeling partitioning and transport interactions between natural organic matter and polynuclear aromatic hydrocarbons in groundwater. *Environmental science & technology*, **27**(8), 1553-1562.
- Luthy, R.G., Dzombak, D.A., Peters, C.A., Roy, S.B., Ramaswami, A., Nakles, D.V. and Nott, B.R. (1994). Remediating tar-contaminated soils at manufactured gas plant sites. *Environmental science & technology*, **28**(6), 266A-276A.
- Nanuam, J., Sawangwong, P. and Pachana, K. (2012). The effects of varied pH on PAHs adsorption onto Thai clay minerals in synthetic sea water. *Journal of Science Technology and Humanities*, **9**(1), 1-7.
- Newman, M.E., Elzerman, A.W. and Looney, B.B. (1993). Facilitated transport of selected metals in aquifer material packed columns. *Journal of contaminant hydrology*, **14**(3), 233-246.
- OECD (2000). Adsorption - Desorption Using a Batch Equilibrium Method, OECD Guideline For The Testing of Chemicals.
- Pavia, D., Lampman, G., Kriz, G. and Vyvyan, J. (2008). *Introduction to spectroscopy*, Cengage Learning.
- Polubesova, T., Chen, Y., Stefan, C., Selle, M., Werner, P. and Chefetz, B. (2009). Sorption of polyaromatic compounds by organic matter-coated Ca<sup>2+</sup>- and Fe<sup>3+</sup>-montmorillonite. *Geoderma*, **154**(1), 36-41.
- Rayment, G and Higginson, F.R. (1992). *Australian laboratory handbook of soil and water chemical methods*, Inkata Press Pty Ltd.
- Reddy, K.R. and Cameselle, C. (2009). Electrochemical remediation technologies for polluted soils, sediments and groundwater, John Wiley & Sons.
- Reddy, K.R., Maturi, K. and Cameselle, C. (2009). Sequential electrokinetic remediation of mixed contaminants in low permeability soils. *Journal of Environmental Engineering*, **135**(10), 989-998.
- Shaker, A.M., Komy, Z.R., Heggy, S.E. and El-Sayed, M.E. (2012). Kinetic study for adsorption humic acid on soil minerals. *The Journal of Physical Chemistry A*, **116**(45), 10889-10896.
- Song, S., Zhu, L. and Zhou, W. (2008). Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponin, a plant-derived biosurfactant. *Environmental pollution*, **156**(3), 1368-1370.
- Stumm, W. and J. Morgan, J. (1996). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. 3rd ed.
- USEPA (1986a). Cation-exchange capacity of soils (sodium acetate), SW-846, United State Environmental Protection Agency.
- USEPA (1986b). Polynuclear aromatic hydrocarbons, SW-846, United States Environmental Protection Agency.
- USEPA (1996a). Acid digestion of sediments, sludges, and soils, SW-864, United States Environmental Protection Agency.
- USEPA (1996b). Soxhlet extraction SW-846, United States Environmental Protection Agency.
- USEPA (2007). Flame atomic absorption spectrophotometry, SW-846, United States Environmental Protection Agency.
- USEPA (2014). Technical review workgroup recommendations regarding gardening and reducing exposure to lead-contaminated soils.
- Wang, L., Yang, Z. and Niu, J. (2011). Temperature-dependent sorption of polycyclic aromatic hydrocarbons on natural and treated sediments. *Chemosphere*, **82**(6), 895-900.
- Weber, W.J., LeBoeuf, E.J., Young, T.M. and Huang, W. (2001). Contaminant interactions with geosorbent organic matter: insights drawn from polymer sciences. *Water research*, **35**(4), 853-868.
- Wijnja, H., Pignatello, J.J. and Malekani, K. (2004). Formation of  $\pi$ - $\pi$  complexes between phenanthrene and model  $\pi$ -acceptor humic subunits. *Journal of environmental quality*, **33**(1), 265-275.
- Wu, P., Tang, Y., Wang, W., Zhu, N., Li, P., Wu, J., Dang, Z. and Wang, X. (2011). Effect of dissolved organic matter from Guangzhou landfill leachate on sorption of phenanthrene by Montmorillonite. *Journal of colloid and interface science*, **361**(2), 618-627.
- Yu, H., Huang, G.H., An, C.J. and Wei, J. (2011). Combined effects of DOM extracted from site soil/compost and biosurfactant on the sorption and desorption of PAHs in a soil-water system. *J Hazard Mater*, **190**(1-3), 883-890.
- Zhang, L., Luo, L. and Zhang, S. (2011a). Adsorption of phenanthrene and 1, 3-dinitrobenzene on cation-modified clay minerals. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **377**(1), 278-283.
- Zhang, W., Zhuang, L., Yuan, Y., Tong, L. and Tsang, D.C. (2011b). Enhancement of phenanthrene adsorption on a clayey soil and clay minerals by coexisting lead or cadmium. *Chemosphere*, **83**(3), 302-310.
- Zhang, X., Wu, Y., Hu, S. and Li, T. (2016). Effects of the Release of Soil Organic Matter on Phenanthrene Sorption by Sediments. *Water Environment Research*, **88**(4), 346-354.
- Zhu, D., Herbert, B.E., Schlautman, M.A., Carraway, E.R. and Hur, J. (2004). Cation- $\pi$  Bonding. *Journal of environmental quality*, **33**(4), 1322-1330.