



Simultaneous Removal of Phenanthrene and Ni(II) Co-contaminants from Sandy Soil Column by Triton X-100 and Citric Acid Flushing

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ABSTRACT

The remediation of soils co-contaminated with heavy metals (HMs) and hydrophobic organic compounds (HOCs) is urgent. In this paper, the simultaneous removal of phenanthrene and Ni(II) co-contaminants from sandy soil column by 3250 mg/L of Triton X-100 (TX100) and 0.1 mol/L of citric acid (CA) flushing was conducted. The removal effects were compared and discussed when CA after TX100 (TX100/CA), TX100 after CA (CA/TX100), and a mixture of TX100 and CA (TX100-CA) were used as flushing agents. The maximum concentrations of phenanthrene in effluent solutions appeared when the pore volume number (PVN) of influent was 3, 17.5 and 4 while those of Ni(II) occurred at 12.5, 2 and 2.5 of PVN during TX100/CA, CA/TX100 and TX100-CA flushing, respectively. The total removal efficiencies of phenanthrene were up to 93.7%, 94.5%, and 93.1%, while those of Ni(II) were 80.2%, 80.4% and 80.7% due to TX100/CA, CA/TX100 and TX100-CA flushing, respectively. Larger PVN was required for TX100/CA and CA/TX100 to clean phenanthrene and Ni(II) efficiently. The removal efficiencies of contaminants increased with PVN in Sigmoidal Model. The results showed that flushing using nonionic surfactant and organic acid is promising for *in-situ* remediation of soils contaminated with HMs and HOCs.

INTRODUCTION

Soil contamination with a mixture of substances is more frequent than with a single substance in many sites. Co-contaminated soils are commonly found (Amaraneni 2006, Tang et al. 2010). It was reported that the soils contain two types of volatile organic, heavy metal and semi-volatile organic contaminants at approximately 25% of the national list sites and all three types at 41% of the sites in USA (US EPA 1997). In China, heavy metals (HMs) and hydrophobic organic compounds (HOCs) (such as PAHs, PCBs, etc.) are not only two major chemical groups that cause soil pollution, but also often coexist together (Huang et al. 2011, Sun et al. 2011, Yang et al. 2011, Wu et al. 2012, Zhu et al. 2012). Both HMs and PAHs contaminated soils have been recognised as a widespread environmental problem (Ahtiainen et al. 2002, Sun et al. 2011, Yang et al. 2011). The combined harmful effects of HMs and PAHs on ecological system and human health were even synergistic (Shen et al. 2006, Soltani et al. 2015). Therefore, the remediation of soils co-contaminated with HMs and PAHs is urgent.

Chemical flushing/washing is considered as an effective approach for remediation of soils contaminated with HMs or HOCs, due to its higher efficiency and less time cost. The selection of flushing/washing agent is very im-

portant because the remediation efficiency depends much upon the interaction between agent and contaminant. Surfactants are often used as flushing/washing agents to remove HOCs from soils (Paria 2008, Laha et al. 2009). However, weak electrostatic attraction and coordination between HM species and surfactant molecules resulted in much less removal of HMs by surfactant (Mulligan et al. 1999, Zhao et al. 2009, Zhao et al. 2010, Khalil et al. 2015). Chelating agents, such as EDTA, EDDS and organic acids, are often used to remove HMs from soils (Dermont et al. 2008, Lestan et al. 2008, Udovic & Lestan 2009, Yip et al. 2010, Yan & Lo 2012, Luciano et al. 2013, Khalil et al. 2015). However, it is ineffective to remove HOCs by chelant washing/flushing because the chelants and HOCs are very different in physical and chemical properties.

Therefore, surfactant and chelating agents as admixture or as sequential individuals were used to remove HMs and HOCs simultaneously from soils through batch extraction (Khodadoust et al. 2005, Ehsan et al. 2006a, Ehsan et al. 2006b, Zhang et al. 2007, Maturi et al. 2008, Zhang et al. 2008, Yuan et al. 2010, Rivero-Huguet & Marshall 2011, Wen & Marshall 2011, Cao et al. 2013). Much attention was paid to the selection of surfactant and chelating agent, optimization of concentration of extractants, sequence of different extractants, cycle of extraction, reuse of extractant

and treatment of waste in washing solution, and interaction between surfactant and chelating agent. The results showed that the combination of surfactant and chelant could be a potential approach for *ex-situ* remediation of soils contaminated with HMs and HOCs. However, up to date, there are few studies which were conducted on the simultaneous removal of co-contaminants by column flushing using surfactant and chelant (Giannisa et al. 2012, Yun et al. 2015), to our knowledge. Thus, the references about *in-situ* remediation of co-contaminated soils by flushing method are somewhat limited.

In this study, TX100 and CA were used to be the representatives of nonionic surfactants and organic acids, while phenanthrene and Ni(II) were chosen as the representatives of PAHs and HMs. The objectives are to investigate the pattern of column flushing and to assess the efficiency of simultaneous removal of PAHs and HMs from co-contaminated sandy soil using nonionic surfactant and organic acid either as admixture or as sequential individuals. The results could supply an implication for *in-situ* flushing remediation of soils co-contaminated with HMs and PAHs.

MATERIALS AND METHODS

All reagents were of analytical grade and used without further purification. TX100 ($C_8H_{17}C_6H_4(OCH_2CH_2)_{9.5}OH$, molar weight 625 g/mol, the critical micellar concentration (CMC) 118.75 mg/L) was obtained from Acros Organics, USA. CA ($C_6H_8O_7$, molar weight 192.14 g/mol, dissociation constants $K_{a1} 7.4 \times 10^{-4}$, $K_{a2} 1.7 \times 10^{-5}$ and $K_{a3} 4.0 \times 10^{-7}$, stabilization constant $\log K 14.3$ at 0.5 mol/L of ionic strength) was purchased from Yantai Shuangshuang Chemical Co., China. Phenanthrene ($C_{14}H_{10}$, molecular weight 178.17 g/mol, water solubility 1.18 mg/L at 25 °C) was obtained from Aldrich Chemical Co., USA. $NiSO_4 \cdot 6H_2O$ was purchased from Tianjin Kaitong Chemical Co., China. Deionized water was used in all experiments.

The soil was sampled from Wuwei, Gansu Province, China. It was air-dried and sieved through a 0.28 mm mesh. The organic matter, water content and pH value of the soil were determined as 0.12%, 0.47% and 7.28 (1:2.5), respectively (Bao 2000). The texture of soil consisted of 89.7% sand, 10% silt and 0.3% clay. The soil was firstly spiked with $NiSO_4$ solution and then spiked with phenanthrene in petroleum ether solution as described by Song et al. (2008). This slurry was mixed thoroughly and the solvent was allowed to evaporate under a hood. The final concentrations of phenanthrene and Ni(II) in soil were 100 and 1000 mg/kg.

The apparatus and process of column flushing were the same as those in our previous reports (Zhao et al. 2010). The glass column was with 5 cm diameter and 36 cm height. At

the bottom of the column, there was a gravel bed and a sheet of glass fibre, which were used to prevent leakage of fine soil particles. A 400 g portion of the contaminated soil was packed in the column in batches and the column was slightly knocked, in order to keep the same porosity and compaction at large. Glass fibre and gravel were placed upon soil in order to distribute influent uniformly to the soil surface. At the top, the column was equipped with plunger piston that had a control valve in order to keep the speed of influent. The pore volume of the soil was calculated by the difference between the weight of soil column (W_1) and the weight of soil column saturated with deionized water (W_2), together with water density. The calculated pore volume of soil was 90–100 mL in the following experiment.

The influent solutions were prepared as CA after TX100 (TX100/CA), TX100 after CA (CA/TX100), and a mixture of TX100 and CA (TX100-CA), in which the concentrations of TX100 and CA were kept as 3250 mg/L and 0.1 mol/L. The previous study showed that high removal efficiencies were obtained when 3250 mg/L of TX100 and 0.1 mol/L of CA were used for flushing phenanthrene and Ni(II) (Zhao et al. 2010). Meanwhile, 0.01% of NaN_3 was added in the influent solution to inhibit biodegradation of phenanthrene. The influent discharge was conducted at 1 L/min by adjusting the valves. The effluents were collected and determined for phenanthrene and Ni(II) at the interval of 0.5 pore volume. In the flushing procedure using TX100-CA, the flushing was stopped when the concentrations of both phenanthrene and Ni(II) in effluent could not be detected, respectively. In the flushing procedure using TX100/CA or CA/TX100, TX100 or CA was fed first. After phenanthrene or Ni(II) in effluent could not be detected, CA or TX100 was then introduced. The flushing was stopped when Ni(II) or phenanthrene could not be detected, respectively.

The phenanthrene and Ni(II)-free soil was packed in the column according to the process mentioned above. 3250 mg/L of TX100 and 0.1 mol/L of CA containing 0.01% of NaN_3 were fed at a discharge of 1 L/min. The effluents were collected and determined for TX100 or CA at the interval of 0.5 pore volume, which was stopped when the concentration of TX100 or CA in effluent was equal to that in influent.

Phenanthrene in effluent solution was quantified by petroleum ether extracted-ultraviolet spectrophotometric method (China NEPA 2002). The emulsification phenomenon was eliminated by adding 0.1 g of tannic acid (Zhu et al. 1996). Then absorbance of phenanthrene was detected on spectrophotometer (Model 752, Shanghai Spectrum Company, China) at 248 nm with 1 cm cell. Aqueous concentration of Ni(II) in effluent was quantified by dimethylglyoxime spectrophotometric method with 1 cm cell at 530

nm. The results from pre-experiments indicated that the influences of TX100, CA and the potential humic acids in effluent on determination of contaminants were negligible. TX100 was determined using UV spectrophotometric method at 210 nm with 1 cm quartz cell and CA was quantified using NaOH titration method. Each of the sampled effluents was analysed twice and the average value was used.

RESULTS AND DISCUSSION

The plots of phenanthrene concentrations in effluents versus PVN are shown in Fig. 1 when TX100/CA, CA/TX100 and TX100-CA were used as flushing agents. When TX100/CA was employed in flushing, the plots of phenanthrene concentrations versus PVN gave a peak. Before 1.5 h, the concentrations of phenanthrene were close to its water solubility. However, they increased sharply, peaked with 107.7 mg/L value at 3 PVN and then decreased dramatically with PVN. However, there was no obvious concentration enhancement of phenanthrene in effluents when CA was introduced sequentially, due to the weak interaction between CA and phenanthrene molecules. As CA/TX100 flushing was concerned, it took much time (17.5 PVN) to observe the peak concentration i.e. 109.7 mg/L of phenanthrene because CA was fed first. As for TX100-CA flushing system, the pattern of early flushing stage was almost the same as that by TX100/CA and the phenanthrene concentration achieved a peak with 102.7 mg/L at 4 PVN. However, the flushing could be stopped at 13 PVN rather than 24 PVN in TX100/CA in which flushing proceed.

Surfactant-enhanced remediation (SER) includes two main mechanisms, i.e. solubilization (solubility enhancement of HOCs in aqueous phase) and mobilization (reduction in interfacial tension between oil and water) (West & Harwell 1992). Anyhow, the later is generally effective for removal of liquid contaminants in ground water. It can be deduced that the removal of phenanthrene in soil column could be mainly attributed to the solubilization of phenanthrene by TX100. A few of data showed that TX100 is much capable of dissolving PAHs into aqueous phase from solid surface (Zhao et al. 2005, Chatterjee et al. 2010). Partitioning of PAH molecules into surfactant micelles results in the enhancement of apparent solubility of PAHs. According to the reference (Zhao et al. 2005), it can be estimated that 86.7 mg/L of apparent solubility of phenanthrene will be observed when 3250 mg/L of TX100 is used to solubilize phenanthrene, which is more than 80 times as the intrinsic solubility of phenanthrene (1.18 mg/L at 25 °C). Although some interaction may occur between CA and HOC molecules (Zhang & He 2013), no micelle of CA occurs in solution even if concentration of CA is much high, accordingly no significant apparent solubility of phenanthrene. Based

on our previous study, only 7.6×10^{-5} of solubilization ratio using CA to solubilize phenanthrene was found (Zhao et al. 2016) while that when using TX100, it was found to be 2.58×10^{-2} (Zhao et al. 2005). Thus, TX100 was much more capable than CA to desorb phenanthrene from soil. In the reported batch washing studies, regarding the effect of chelating agents on removal of HOCs, negligible desorption efficiencies were also achieved (Khodadoust et al. 2005, Cao et al. 2013).

The changes in phenanthrene concentrations in effluents are somewhat dependent upon the sorption of TX100 onto soil. Fig. 2 shows the breakthrough curve of TX100. About 2.5 PVN was needed for TX100 to saturate the soil. The concentrations of phenanthrene were very low at the beginning of flushing (Fig. 1) because TX100 was strongly adsorbed onto soil particles, e.g. before 1.5 PVN by TX100/CA, 15.5 PVN by CA/TX100 (2.5 PVN when only TX100 feeding was concerned) and 2.0 PVN by TX100-CA. After the soil was saturated with about 3 PVN of TX100, the phenanthrene concentrations in effluents sharply increased and peaked with PVN, e.g. peak at 3 PVN by TX100/CA, 17.5 PVN by CA/TX100 (4.5 PVN when only TX100 feeding was concerned) and 4.0 PVN by TX100-CA. With a stable TX100 concentration in column and the desorption of phenanthrene, the residual phenanthrene gradually decreased, and then the concentration of phenanthrene decreased in effluents.

Fig. 3 shows the plots of Ni(II) concentrations in effluents versus PVN when TX100/CA, CA/TX100 and TX100-CA were fed. There was no obvious Ni(II) concentration enhancement in effluent before CA was introduced in TX100/CA system, because of the weak interaction between TX100 molecules and Ni(II) ions. However, introducing CA caused the concentration of Ni(II) to increase and peak at 10 PVN and 12.5 PVN. During CA/TX100 flushing, a peak pattern of Ni(II) concentration versus PVN was observed before TX100 was introduced, where the Ni(II) concentration peaked with 1977 mg/L value at 2.5 PVN. After TX100 was introduced, no further Ni(II) concentration enhancement occurred because a large amount of Ni(II) in soil has already been removed by CA flushing, on the other hand, the weak interaction between TX100 molecules and Ni(II) ions occurred. As for TX100-CA system, its flushing pattern was somewhat similar to that in early half stage in CA/TX100 system. The maximum concentration appeared as 1646 mg/L at 2.5 PVN.

It can be predicted that desorption of Ni(II) by CA includes two mechanisms. The hydrogen ions resulted due to the dissociation of CA competed with Ni(II) ions on the exchange sites of soil surface and hence enhanced its

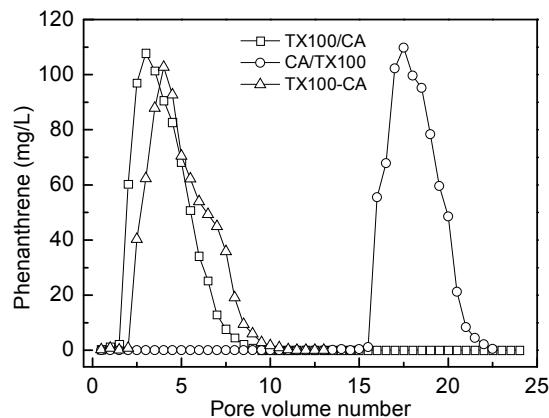


Fig. 1: Plots of phenanthrene concentrations in effluents versus PVN.

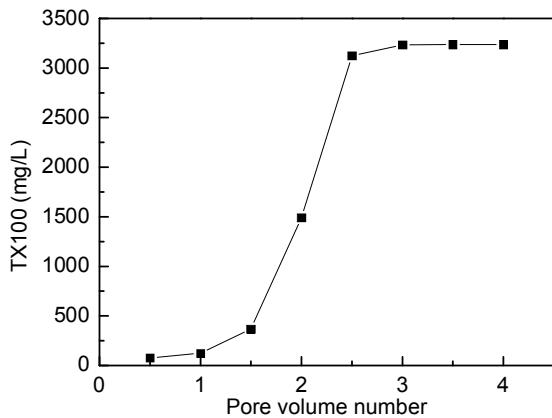


Fig. 2: Breakthrough curve of TX100.

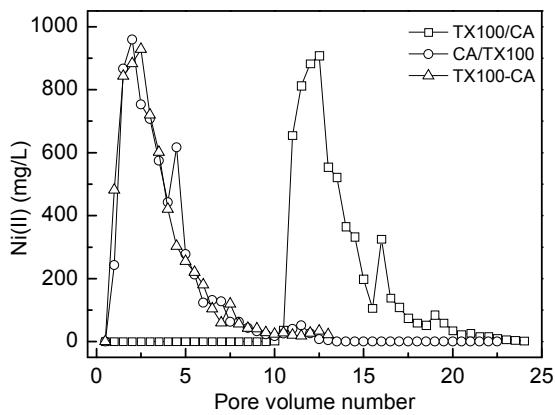


Fig. 3: Plots of Ni(II) concentrations in effluents versus PVN.

desorption from these sites. In addition, dissolution of some species of Ni(II) (e.g. hydroxides) at acid condition led to desorption of Ni(II). It has been proved that inorganic acids

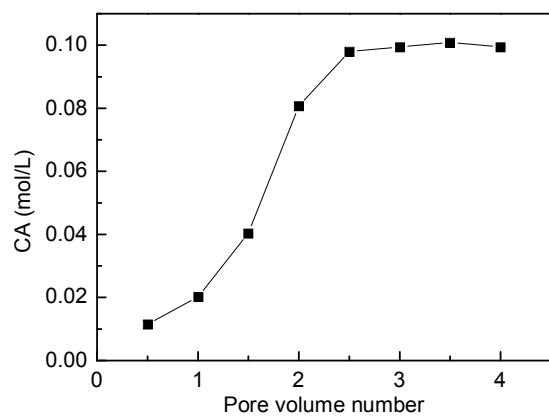


Fig. 4: Breakthrough curve of CA.

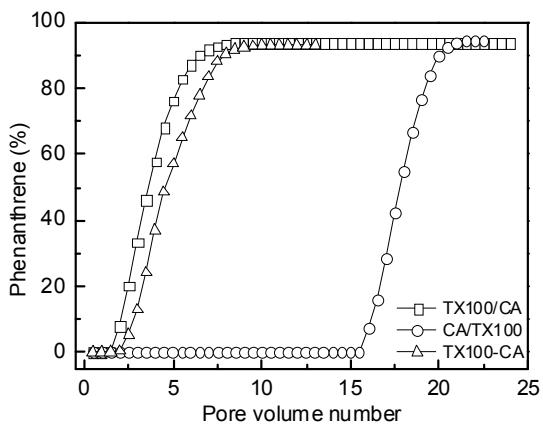


Fig. 5: Variations in total removal efficiencies of phenanthrene versus PVN.

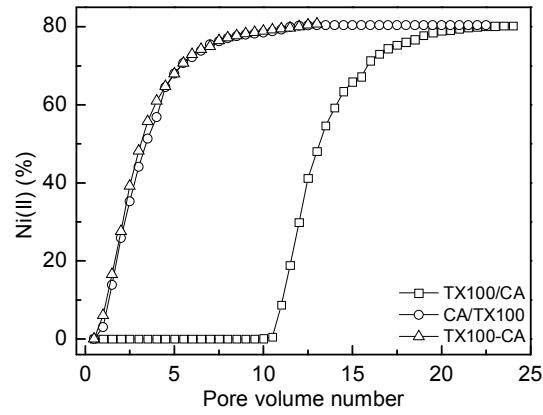


Fig. 6: Variations in total removal efficiencies of Ni(II) versus PVN.

are effective in removing HMs from soils, partly owing to better solubilization of metals in the soil at low pH conditions provided by the acids (Wasay et al. 2001. Khodadoust

Table 1: Regression results of Sigmoidal equation for removal efficiencies and PVN.

Agent	Phenanthrene				R^2	Ni(II)				R^2
	A_1	A_2	A_3	A_4		A_1	A_2	A_3	A_4	
TX100/CA	-7.28	93.74	3.44	0.94	0.9989	-0.98	77.7	12.6	1.05	0.9948
CA/TX100	-0.31	94.60	17.7	0.79	0.9989	-39.8	80.1	1.74	1.54	0.9980
TX100-CA	-5.89	93.20	4.43	1.09	0.9975	-46.2	79.3	1.42	1.50	0.9979

et al. 2005). Also, the carboxyl and hydroxyl groups of CA can chelate Ni(II) and, therefore, enhance its desorption from soil. Moreover, the coordination compound of Ni-CA has much solubility and stability ($\log K = 14.3$). These properties facilitated desorption of Ni(II) from the soil. Also, the changes in Ni(II) concentrations in effluents should be related with the sorption of CA onto soil. Fig. 4 shows the breakthrough curve of CA. About 2.5 PVN was needed for CA to saturate the soil. Similarly, compared with the flushing proceed, it can be noticed that the PVN points at which the Ni(II) concentration began to increase and peak were corresponding to those at which CA concentration began to increase and to level off. However, the slight difference among these points could be due to the artificial heterogeneous nature of the column soils.

Fig. 5 shows the variations in total removal efficiencies of phenanthrene versus PVN when TX100/CA, CA/TX100 and TX100-CA were used as flushing agents. The influents exhibited the significant removal efficiencies for phenanthrene. The removal efficiencies by TX100/CA increased sharply between 2 and 8 PVN and then levelled off with PVN, recording ultimate removal efficiency about 93.7%. The effect of CA on phenanthrene removal could be negligible in TX100/CA system. As mentioned above, CA was not capable to solubilize or desorb phenanthrene from soil because it is of much affinity towards charged metals (Khodadoust et al. 2005). As for CA/TX100 system, the removal efficiency began to increase after TX100 input and 94.5% of total phenanthrene was removed after TX100 flushing. The removal efficiencies by TX100-CA were similar to those achieved by TX100/CA at early stage. The former resulted in a similar removal of phenanthrene (93.1%). However, it took only half the run of flushing of the later. The differences among the ultimate removal efficiencies might mainly be attributed to the heterogeneous nature of the column soils due to the artificial packing process.

The data from Fig. 6 show the variations in overall removal efficiencies of Ni(II) versus PVN when TX100/CA, CA/TX100 and TX100-CA were used as flushing agents. All the influents exhibited significant clean-up for Ni(II). In TX100/CA system, it could be noticed that negligible amount of Ni(II) was removed by TX100 in the first step and

the effective removal occurred after using CA in the second one. The efficiency achieved the highest value of 80.2%. As CA/TX100 system was concerned, the efficiencies of Ni(II) went up dramatically after 1 PVN, levelled off after 12 PVN and achieved the highest value of 80.4%. The efficiencies of TX100-CA on the removal of Ni(II) were almost similar to those of CA/TX100 flushing at early stage. The ultimate removal of Ni(II) was about 80.7%.

The removal data of phenanthrene and Ni(II) were analysed using OriginPro 8.0 software with fitting regression. They could be described with Sigmoidal equation:

$$R = A_2 + \frac{A_1 - A_2}{1 + \exp[(PVN - A_3)/A_4]} \quad \dots(1)$$

Where R (%) is the removal efficiency of contaminant; PVN is the pore volume number; A_1 , A_2 , A_3 and A_4 are the parameters of the model. The regression results are listed in Table 1.

CONCLUSIONS

The concentrations of phenanthrene in effluent solutions peaked at 3, 17.5 and 4 h while those of Ni(II) peaked at 12.5, 2 and 2.5 of PVN due to flushing the soil column with TX100/CA, CA/TX100 and TX100-CA, respectively. Solubilization and chelation are the main mechanisms suggested for phenanthrene and Ni(II) removal and the flushing process was related to sorption of TX100 and CA in column. The total removal efficiencies of phenanthrene were up to 93.7%, 94.5%, and 93.1% while those of Ni(II) were 80.2%, 80.4% and 80.7% after TX100/CA, CA/TX100 and TX100-CA flushing. However, a long run was needed for TX100/CA and CA/TX100 to remove both phenanthrene and Ni(II) efficiently. The removal efficiencies of contaminants increased with PVN in Sigmoidal model. The results implicated that the combination of nonionic surfactant and organic acid has a reasonable potentiality for *in-situ* remediation of the soils co-contaminated with HMs and HOCs.

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