Effect of surfactant on HCB dechlorination by Ag/Fe bimetal in polluted soil eluent

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Abstract

Washing is one of the common technologies in the chlorinated organic pollution site repair, surfactant adding would help washing more chlorinated organics pollution, but it also can be dissolved in eluent with the chlorinated organic together, and increase the difficulty of the eluent treatment. In this text, three surfactants, anionic surfactant (sodium dodecyl benzene sulfonate, SDBS), cationic surfactant (hexadecylpyridinium bromide hydrate, HBH), and nonionic surfactant (Triton X-100, TX-100), would be added in the polluted soil eluent, to study the effect on the dechlorination of HCB by Ag/Fe bimetal and the surface corrosion of Fe in the eluent. The experimental results showed that different surfactant and different surfactant concentration all affected the dechlorination. Nonionic surfactant would promoted the dechlorination significantly; Cationic surfactant promoted the dechlorination in lower concentration and impeded it in higher concentration; Anionic surfactant promoted the dechlorination only in higher concentration. Meanwhile, these three surfactants could not intensify the surface corrosion of Fe, and keep the reaction activity of the Ag/Fe bimetal for a long time. Hence, during the treatment for the eluent by Ag/Fe bimetal, the nonionic surfactant and the anionic surfactant would be recommended, and the cationic surfactant should try to be avoided.

1. Introduction

Organochlorine pesticides (OCPs), with high efficiency, low cost, and convenient use, were the highest yield, and the most widely using pesticides [1-2]. OCPs can easily be accumulated in the natural environment and threat to human health with high stability, low water soluble and high fat soluble.
characteristics. Along with the advancement of the Stockholm International Convention and the development of our country’s industrialization and urbanization, there appeared a large number of closed OCPs factories in China in recent years, waiting to move [3]. According to the official statistics, there had hundreds of OCPs contaminated sites in China, most of them faced functional conversion and secondary development.

Site remediation, has become the urgent problem need to be solved. Soil elution, is one of the commonly used technologies for organic pollution sites treatment, can make in-situ or ex-situ repair for polluted site. In the soil washing process, it is hard to dissolve the chlorinated organic pollution only by water solvent, especially for some saturated soil by organic pollution. So adding surfactants during washing process can effectively increase the solubility of the organic pollution, but the surfactants can blend in the eluent with the chlorinated organic together, increase the difficulty of the follow-up treatment for the eluent.

Zero-valent iron bimetal, with strong reductive ability, has common application in the organic wastewater processing [4-6]. The author had made degradation for chlorinated organic in liquid using zero-valent iron bimetal during the previous studies, and had got some ideal results. This paper will discuss that the surfactants affect the dechlorination of HCB by Ag/Fe in the polluted soil eluent, to summary the effect of surfactant on the dechlorination of HCB by comparing different types and different concentration of surfactants. Meanwhile, measure the iron corrosion current through amplify the electrochemical reduction system by Ag and Fe metal, to study the iron corrosion effecting by the adding surfactant. Then discuss the relationship between Ag/Fe reduction and the iron corrosion under the surfactants existence conditions. This study will provide a basis reference for surfactant application in polluted soil site elution.

2. Materials and method

2.1. Materials and instrument

Micro-Fe powers (99%+, 300 mesh), AgNO₃, HCl, all are pure analysis, nitrogen (99%+), HCB(99.8%, Sigma–Aldrich), diethyl ether, n-hexane, acetone, C₂₁H₃₈BrN.XH₂O (99%+), C₁₄H₂₂O(C₂H₄O)n (99%+), C₁₈H₂₉NaO₃S (99%+). Ag electrode, Fe electrode, Ag/AgCl reference electrode, glassy carbon electrode. HCB were dissolved in diethyl ether as standard samples. All aqueous solutions were prepared in deionized water.

Anaerobic box (60cm×90cm×60cm, customized), 40mL empty bottles with screw cover and 3 mm silica gel teflon gasket, electronic balance, constant temperature water-bath oscillator (THZ-28A, China), wave bed (HY-2, China), centrifugal machine (G10, China), Gas chromatograph (Agilent 6890, USA ), Electrochemical workstation (RST 5200, China)

2.2. Samples preparation

In the anaerobic box, Ag/Fe bimetallic particles were synthesized by adding 5 g of 300 mesh Fe powder to 20 ml of 0.22 mol/L AgNO₃ and 180ml deionized water. The Fe powder was washed twice each by HCl and deionized water. Ag was prepared by reductive on the Fe surface according to the following reaction: Ag⁺ + Fe₀ → Ag₀↓ + Fe²⁺. After 1 h of reaction, the Ag/Fe bimetal particles were filtered and blow dried using nitrogen.

The initial solution prepared as follow: 100 mg/L HCB dissolved in diethyl ether; 20, 50, 100, 200, and 400mg·L⁻¹ of SDBS, TX-100, HBH dissolved in deionized water, respectively. Dechlorination batch experiments were conducted in 40 ml vials containing 0.5 g Ag/Fe powder, 0.3 mL HCB initial solution,
and 10 ml deionized water under every surfactant concentration. Every concentration prepared two parallel samples. The finished samples reacted in a constant temperature water-bath oscillator about 40°C and 250 rpm/min for 20min, and then took out for detection.

2.3. Sample and intermediate analyses

The samples were extracted two times using an organic solvent mixture of n-hexane and acetone (1:1, v/v) for 30 min with constant shaking. The mixture was left undisturbed for 10 min, then through centrifugation and filter for analysis. The extracts were analyzed by gas chromatography (GC) using an Agilent 6890N GC column equipped with a micro-electron capture detector and a 30 m DB-5HT capillary column. The sample injection volume was 1 µL, and the temperature conditions were programmed as follows: oven temperature of 80 °C, injection port temperature of 260 °C, and detector temperature of 280 °C. Separation was performed with the following oven temperature program: initial 80 °C held for 1 min, ramped at 10 °C min⁻¹ to 200 °C held for 1 min, ramped at 5 °C min⁻¹ to 220 °C held for 1 min, and finally ramped at 10 °C min⁻¹ to 260 °C held for 3 min. Ultrapure nitrogen was used as the carrier gas for the GC at a flow rate of 1 mL min⁻¹.

The corrosion current of Fe under different conditions was measured using a Shiruisi RST5000 electrochemical workstation. Two pieces of Fe and Ag each with 3 cm² surface were used as working and auxiliary electrodes, respectively. The reference electrode was Ag/AgCl. The tafel polarization curves were obtained to calculate the Fe corrosion current at a scan rate of 40mV/s by RST 5200 (Zhengzhou Shiruisi Technology Co., Ltd).

The degradation rate (RHCB) of HCB was calculated as follows:

\[
R_{HCB} = \left[1 - \left(\frac{C}{C_0}\right)_{HCB}\right] \cdot 100\% \tag{1}
\]

Where \((C/C_0)_{HCB}\) is the observed rate of HCB in the samples, \(C\) is the residue concentration, \(C_0\) is the initial concentration.

3. Result and discuss

In this text, three surfactants, anionic surfactant (sodium dodecyl benzene sulfonate, SDBS), nonionic surfactant (Triton X-100, TX-100), and cationic surfactant (hexadecylpyridinium bromide hydrate, HBH), had been chosen to use in the eluent, to study the effect on the dechlorination of HCB by Ag/Fe bimetal and the surface corrosion of Fe in the polluted soil eluent.
Fig. 1. The effect of the three surfactants on the HCB dechlorination (Every value in the chart was the average value of the two parallel samples in the same condition)

3.1 The three surfactants effect on $R_{HCB}$

Fig.1 is the $R_{HCB}$ in different surfactants by reacting for 20min, The $R_{HCB}$ of the control sample was 59.5%, and the three surfactants really had different effect for HCB dechlorination by Ag/Fe. The detailed descriptions are as follow:

For anionic surfactant SDBS: There had no obvious influence to $R_{HCB}$ when adding little amount SDBS, the $R_{HCB}$ was 58.6% when added 20 mg·L$^{-1}$ of SDBS, closed to the control sample. The $R_{HCB}$ had a positive correlation with SDBS concentration ($C_{SDBS}$) increasing, HCB removal rate could reach 91.7% when $C_{SDBS}$ was 400mg·L$^{-1}$, far higher than that in the control sample. These showed that anionic surfactant have a promoted effect to HCB degradation by Ag/Fe bimetal.

For cationic surfactant HBH: The $R_{HCB}$ could achieved 88.6% when the concentration of HBH ($C_{HBH}$) was 20 mg·L$^{-1}$, indicated that small amount of HBH was able to produce great effect on the $R_{HCB}$, the largest HCB removal rate appeared when $C_{HBH}$ was 50mg·L$^{-1}$, then the $R_{HCB}$ dropped instead with $C_{HBH}$ increasing further. The $R_{HCB}$ was only 41.3% when $C_{HBH}$ at 400mg·L$^{-1}$. Hence, too much of cationic surfactants had certain inhibition for HCB degradation by Ag/Fe bimetal.

For non-ion surfactant TX-100: The $R_{HCB}$ was 94.1% when added 20 mg·L$^{-1}$ TX-100, far higher than the control sample and the other two surfactants. When continued to improve $C_{TX-100}$ to 100mg·L$^{-1}$, the $R_{HCB}$ improved to 98.5% accordingly, then almost inclined to stable with $C_{TX-100}$ increasing more.

Therefore, the optimal choice for the chlorinated organic pollution sites treatment is non-ion surfactant.

3.2 The surfactants effect on HCB diffusion

HCB, keeping sorption state in soil, usually be gathered in the surface or the internal pores of the soil particles. Surfactant can lower the surface tension and increase the solution in water phase, to increase the solubility and transfer speed of HCB in the aqueous phase. The previous literatures and our research foundation indicated that HCB diffusion and transfer was the control step in dechlorination reaction, dechlorination would happen only when HCB moved to the active site of bimetal. Fig.1 shows that different surfactant could give different effect to the dechlorination. These differences may be due to the different electric charges of the three kinds of surfactants in solution, lead to different HCB diffusion in the micro level in liquid. The three kinds of surfactants ionized in water situation are shown in Fig.2.

![Fig. 2. The dissociation of the different surfactants in solution (a SDBS; b HBH; c TX-100)](image)

SDBS will be dissociated to the negatively charge of dodecylbenzenesulfonic acid root and sodium ions in solution. The dodecylbenzenesulfonic acid root has surfactivity, as the hydrophilic group in solution. The bimetal system has negatively charge, too, so SDBS has certain rejection effect with the
same charge to the bimetal in liquid in low concentration, and produce a weak promoting of dechlorination, or even produce a certain block function for it. When $C_{SDBS}$ increase further, on the one hand, it could further improve the HCB migration ability, which has the advantage for HCB moving to the bimetal surface; On the other hand, SDBS with high concentration in the solution could form double adsorbed layers on the particle surface, and the out layer is hydrophobic group, which will be benefit for the HCB adsorption in the liquid phase.

HBH dissociate in solution to positively charge, opposite to the bimetal charge, lead to an improving move of HCB to the bimetal particles surface. The adsorption quantity of HCB would be improved when $C_{HBH}$ improving. In the low concentration, HBH form a single adsorption on bimetal particles, and the hydrophobic group point to the solution which is helpful for HCB diffusion. Whereas in the high concentration, HBH form a double adsorption on bimetal particles, and the hydrophilic group point to the solution and impede HCB diffusion.

TX-100 is non-ionic surfactant, none ionization in water, adding a little of it could produce great promoting for HCB degradation, and the promoting effect was significantly better than SDBS and HBH. Firstly, it doesn't make strong adsorption effect on the solid surface due to none ionization in solution. Meanwhile, non-ion surfactant has the characteristics of high surface activity, low surface tension and low critical micelle concentration, which all benefit for the diffusion. In addition, the increasing soluble areas of non-ionic surfactant will be happened on the micelle surface, different from ionic surfactant that are happened in micelle kernel or micelle kernel fence layers, is also benefit for HCB moving to the bimetal particles surface.

3.3 The surfactants effect on iron corrosion

Amin [7] discussed the influence of Trinton. X series surfactants (TX-100, TX-165, TX-305) on the iron corrosion in acid conditions (HCl concentration of 1 mg·L$^{-1}$), showed that surfactants could be adsorbed on iron surface and reduced the corrosion rate of iron. Fig.3 is the tafel polarization curves of iron in different surfactants with different concentration. The iron corrosion had small difference with the surfactant concentration changed from 0 to 200 mg·L$^{-1}$ in these three surfactants, indicated that surfactant had little effect on the iron corrosion. The iron corrosion mainly controlled by H$^+$ in the solution, the eluent with surfactants is a neutral condition and exist few H$^+$, so they all had little effect on the iron corrosion.
Fig. 3. The influence of iron corrosion by 3 kinds of surfactants (a SDBS; b HBH; c TX-100)

4. Conclusion

Surfactants were usually existed in eluent when washed the chlorinated organic polluted soil. Research in this text found that the surfactant’s type and the concentration are all affect the dechlorination of HCB. Non-ion surfactant has active effect for dechlorination; Cationic surfactant will promote $R_{HCB}$ in lower concentration, whereas restrain it in high concentration; Anionic surfactant will contribute to dechlorination only in high concentration. In addition, surfactants won’t aggravate the iron corrosion when using bimetal to treat the soil eluent. Hence, during the treatment for the eluent by Ag/Fe bimetal, the nonionic surfactant and the anionic surfactant would be recommended, and the cationic surfactant should try to be avoided.

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References


