Reduction of nitrobenzene by steel convert slag with Fe(II) system: The role of calcium in steel slag

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ARTICLE INFO

ABSTRACT

Experiments were conducted to examine of nitrobenzene reduction by steel convert slag (SCS) with Fe(II) system. The results showed SCS with Fe(II) was an effective reductant for nitrobenzene at pH 5.5–6.5. Further analysis suggested Fe(II) was adsorbed by SCS through ion replacement with SCS-bound Ca(II). More than 81% of the total Ca(II) in SCS was replaced with dissolved Fe(II), indicating a high adsorption capacity for Fe(II) (more than 5.82 mmol Fe(II)/g SCS). A three step mechanism (replacement process, conversion process and electron transfer process) was proposed for nitrobenzene reduction by SCS with Fe(II) system. The amount of Ca(II) in SCS determined the adsorption capacity for Fe(II) and further determined the reduction capacity of SCS with Fe(II) system.

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1. Introduction

Steel convert slag (SCS) is a byproduct associated with steel manufacturing, which contains high amounts of calcium(Ca) and iron(Fe) [1]. SCS has been used to remove various heavy metals, such as Ni(II) [2], Cr(VI) [3], Cu(II) [4] and Pb(II) via adsorption [5]. SCS was used to remove phosphorus in wetlands or filter beds, due to strong adsorption and precipitation interactions [6–9].

SCS contains high quantities of iron oxides [1,10]. Iron oxides, such as magnetite, hematite and goethite are able to adsorb Fe(II) on surface active sites [11]. Research shows that iron oxides with adsorbed Fe(II) are a more reactive reductant than dissolved Fe(II) under anaerobic conditions, potentially able to reduce various organic pollutants, such as nitroaromatic compounds [12,13], poly-halogenated alkanes [14–16] and disinfection byproducts [17,18]. In previous studies [12,13,15,16,19,20], organic buffers are indispensable in iron oxides with Fe(II) system to buffer the acidity of Fe(II) solution. Calcium is the highest metal element in SCS [10], which could buffer the acidity of aqueous solution due to the fast hydration reaction [1,21]. Calcium in SCS may also dictate the reduction capacity of SCS with Fe(II) system.

Nitroaromatic compounds (NACs) are ubiquitous contaminants in soil and groundwater caused by the production of chemical intermediates, dyes, pesticides, and explosives [22]. The toxicity of NAC's towards humans and wildlife are due to mutagenic and carcinogenic effects [23,24]. Previous research [25] has demonstrated SCS with Fe(II) was capable of reducing chlorinated organics. However, reduction processes of NAC's by SCS with Fe(II) remains unknown.

The objective of this research was to explore the feasibility of SCS to reduce NAC's in the presence of Fe(II). Furthermore, experiments were conducted to evaluate the reduction mechanisms and the role of calcium. Nitrobenzene was chosen as a nitroaromatic model compound, which caused great environmental concern and was used in many redox reaction studies [19,26].

2. Materials and methods

2.1. Materials

SCS was obtained from a steel company (Baosteel Group Co. Ltd, Shanghai, China). Raw slag was received and finely ground to particle sizes less than 0.60 mm or 0.15 mm. Less than 0.60 mm SCS was used in all experiments unless otherwise stated. Nitrobenzene, nitrosobenzene, and aniline were reagent grade from Fluka. Ferrous chloride tetrahydrate was analytical grade from Fluka. All chemical stock solutions were prepared with oxygen-free deionized water.

2.2. Experimental procedures

All solutions were prepared by deoxygenated deionized water. 1 g SCS was stirred in 420 ml (2.38 g/L) deionized water for 4 h to analyze the leachate elements of SCS. Batch experiments were

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conducted in 42 mL Teflon-lined glass bottles in dark at 25 °C. Kinetic experiments were performed with 2.38 g/L SCS, 149 μM nitrobenzene, and various Fe(II) concentrations (2.38, 4.76 and 7.14 mM). Higher concentrations of nitrobenzene (298, 597 and 746 μM) were used to assess reduction capacity of SCS (2.38 g/L) with Fe(II) (4.76 mM) system. A series of control reactors were prepared concurrently: SCS with nitrobenzene or aniline system, and Fe(II) with nitrobenzene system.

Fe(II) adsorption experiments were conducted at similar conditions as the kinetic experiments (SCS 2.38 g/L, Fe(II) 2.38, 4.76 and 7.14 mM) but in the absence of nitrobenzene. SCS was also presoaked in deionized water for 5 days to remove a certain amount of calcium and then dried. Presoaked SCS (2.38 g/L) with Fe(II) (4.76 mM) system was used to evaluate the role of calcium in SCS on adsorption of Fe(II). Furthermore, excess Fe(II) (23.43 mM) was used to determine the adsorption capacity of SCS (2.38 g/L, 0.15 mm). After reaction, samples were filtered through 0.45 μm pore diameter membrane for further analysis.

2.3. Analytical methods

The composition of SCS was determined by X-ray Fluorescence (SRS3400, Bruker) and X-ray diffraction (D/MAX 2550, Rigaku). Nitrobenzene, nitrosobenzene, and aniline were determined by HPLC analysis on a RP18 column (250 mm × 4.6 mm, Waters Xterra) connected to a pumping system (ProStar 230, Varian) and a diode array UV detector (ProStar 335, Varian). The mobile phase was CH_3CN/H_2O (2/3, v/v). The flow rate was typically set to 1 mL/min, and the injected volume was 20 μL. The detector wavelength was set to 280 and 254 nm [26].

Dissolved Fe(II) was determined photometrically after complexation with phenanthroline using a UV–vis spectrophotometer (UV-2550, Shimadzu) at 510 nm. Adsorbed Fe(II) was calculated as the difference between the concentration of dissolved Fe(II) at the beginning ($t = 0$) and dissolved Fe(II) at time t.

Dissolved Ca(II) and other leachate elements of SCS were measured with inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2100DV, PerkinElmer).

2.4. Data analysis

Pseudo-first-order reaction model was used to fit the nitrobenzene reduction data by SCS with Fe(II) [26]:

$$-\frac{d[NB]}{dt} = k_{red}[NB] \tag{1}$$

where [NB] was the nitrobenzene concentration at time t, and k_{red} was the reduction rate constant (h^{-1}). The reported errors were within 95% confidence intervals.

3. Results and discussion

3.1. Composition of SCS

Calcium and iron oxides were the major components and accounted for 40.5% and 27.7%, respectively according to the chemical composition measured by X-ray Fluorescence (Table 1). The iron oxide concentration of the SCS was consistent with previous research (26.3–27.9%) [10]; while the calcium concentration was less than previously reported (47.9–50.0%) [10]. X-ray diffraction patterns show that the mineralogy of calcium included CaO, Ca_2SiO_4 and Ca_3SiO_5, while Fe_2O_3 was the predominant iron mineral phase (Fig. 1).

The major elements in leachate were calcium and silicon, which were 58.10 mg/L and 13.82 mg/L, respectively. No heavy metals were detected in leachate (Table 2).
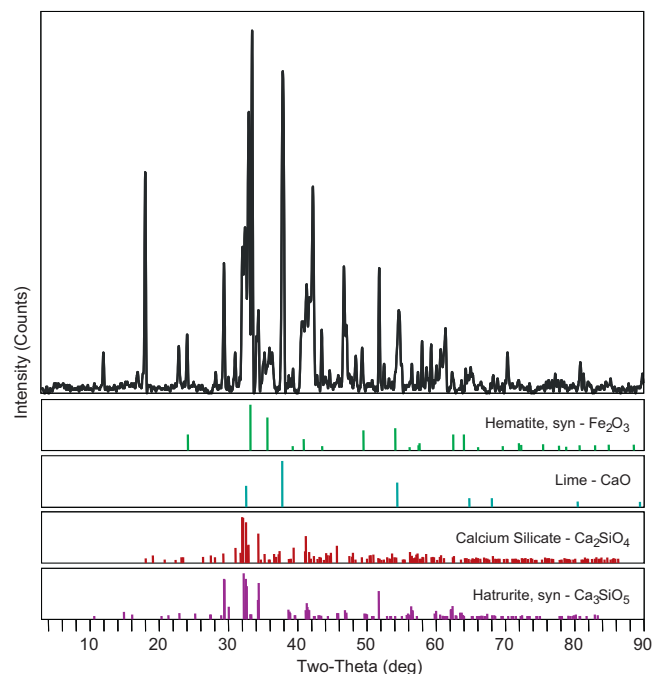

Fig. 1. X-ray diffraction patterns of steel convert slag (SCS) used in this study.

3.2. Reduction of nitrobenzene by SCS with Fe(II) system

The results demonstrate nitrobenzene was reduced to nitrosobenzene and aniline by 2.38 g/L SCS and 4.76 mM Fe(II) (Fig. 2). The intermediate product, nitrosobenzene, peaked at 2 h and was subsequently reduced to aniline stoichiometrically over the next 5 h (Fig. 2). Less than 1% of nitrobenzene and aniline were adsorbed by SCS and less than 1% of nitrobenzene was reduced only in the presence of SCS or Fe(II) (controls data not shown). In pure iron oxides with Fe(II) system, the reduction was a pH dependent process and almost no reduction occurred below pH 6.5 [26]. Our results showed SCS with Fe(II) was capable of reducing nitrobenzene even at a lower pH (5.5 ± 0.2) (Fig. 3). The reduction rate constant (k_{red}) increased with increasing pH (5.5 ± 0.2, 6.0 ± 0.2 and 6.5 ± 0.2) (Fig. 3), consistent with previous research [26]. Results suggested SCS with Fe(II) was an effective nitrobenzene reductant over a wider pH range than the pure iron oxides system.
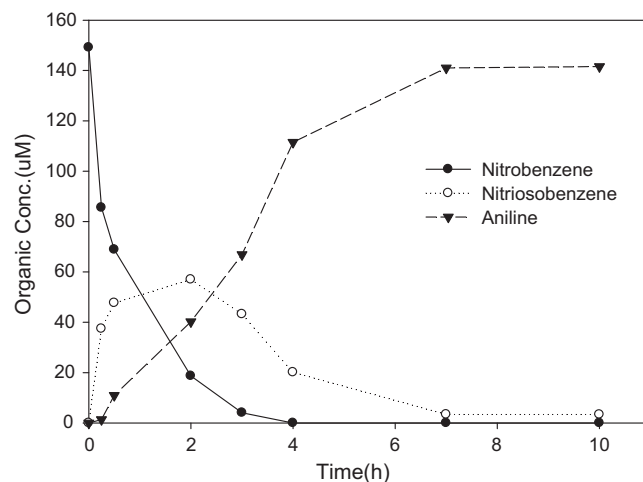

Fig. 2. Reduction of nitrobenzene by SCS with Fe(II): (Fe(II) 4.76 mM, SCS 2.38 g/L, nitrobenzene 149 μM, pH 6.0 ± 0.2).

Table 1
Chemical composition of SCS from Baosteel Group Co., Ltd.

Chemical composition	CaO	Fe$_2$O$_3$	SiO$_2$	MgO	MnO	P$_2$O$_5$	Al$_2$O$_3$	SO$_3$
Weight (%)	40.5	27.7	10.2	9.48	2.62	2.41	1.51	0.13

Table 2
The leachate elements concentration of SCS. 1 g SCS was stirred in 420 ml (2.38 g/L) deionized water for 4 h and the elements in leachate were analyzed by ICP-OES.
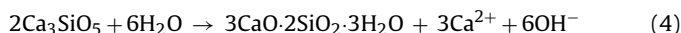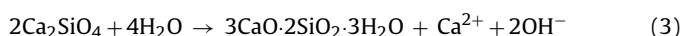
Leachate elements	Ca	Si	Mg	Al	Mn	Na	P	Fe	As	Zn	Pb	Cd	Ni
Concentration (mg/L)	58.10	13.82	0.469	0.218	0.012	0.742	0.009	-	-	-	-	-	-

-: Below detection limit.

3.3. The role of calcium on nitrobenzene reduction in SCS with Fe(II) system

The mechanism of Fe(II) adsorption onto iron oxides, such as magnetite or hematite, was surface adsorption with surface hydroxyl group [11,27]. Klausen et al. [26] found that the adsorption of Fe(II) onto iron oxides increased with increasing pH. Our results showed SCS had strong adsorption capacity for Fe(II) and more than 2.2 mM Fe(II) was adsorbed in 4 h at different pH values (pH 5.5 ± 0.2, 6.0 ± 0.2 and 6.5 ± 0.2, Fig. 4A). Furthermore, Fe(II) adsorption processes were nearly pH independent (Fig. 4A), indicating a different adsorption mechanism from pure iron oxides system.

Calcium was the major leachate element from SCS (Table 2). Calcium in SCS, such as CaO, Ca$_2$SiO$_4$ and Ca$_3$SiO$_5$ could generate high concentrations of hydroxyl ions in aqueous solutions through hydration reactions, as follows [21]:

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \qquad (2)$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca^{2+} + 2OH^- \qquad (3)$$

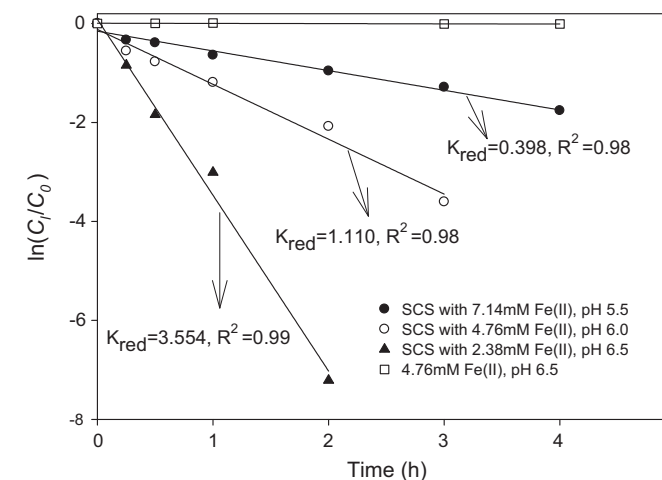$$2Ca_3SiO_5 + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca^{2+} + 6OH^- \qquad (4)$$

In SCS (2.38 g/L) with Fe(II) system, the pH of reaction solutions were well buffered due to the hydration reactions, which were 5.5 ± 0.2, 6.0 ± 0.2 and 6.5 ± 0.2 in the presence of 7.14 mM, 4.76 mM and 2.38 mM Fe(II), respectively. Therefore, no extra buffer was added contrasting previous research [12,13,15,16,19,20], which required organic buffers to buffer the acidity of Fe(II) in solution.

In the presence of Fe(II), the concentration of leached Ca(II) and adsorbed Fe(II) increased with reaction time at different pH
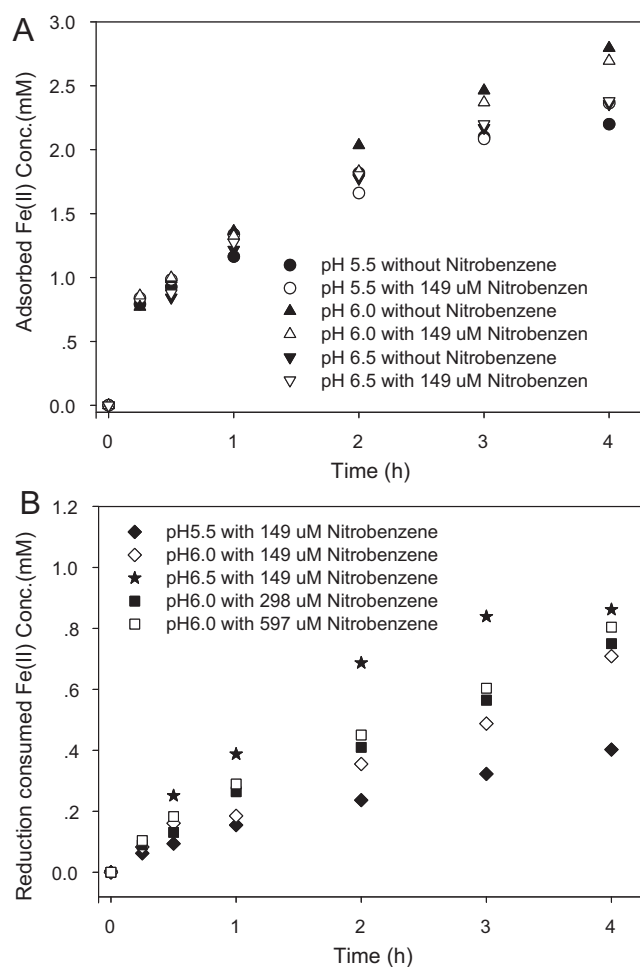
values (Fig. 5A and B). More important, the concentration of dissolved Ca(II) was nearly equal to the concentration of adsorbed Fe(II). On the basis of our results, a replacement process was proposed to account for the adsorption mechanism of Fe(II) onto SCS, which could be presented as:

$$Ca(II)\text{-SCS} + Fe(II) \rightarrow Fe(II)\text{-SCS} + Ca(II) \qquad (5)$$
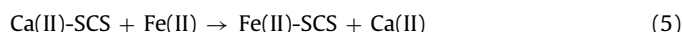
Heavy metals, such as Cu, Zn, and Ni ions, were found to be adsorbed on steel slag by ion replacement process [28–30]. Similarly, our results showed that Fe(II) adsorption by SCS was also a replacement process. To confirm this mechanism, SCS was presoaked in deionized water for 5 days to remove a certain amount of calcium in SCS through hydration reaction. After presoaking,

Fig. 4. Adsorbed Fe(II) onto SCS (A) and reduction consumed Fe(II) (B) at different pH values (SCS 2.38 g/L, pH 5.5 ± 0.2, 6.0 ± 0.2 and 6.5 ± 0.2 solutions containing 7.14, 4.76 and 2.38 mM Fe(II), respectively).

Fig. 3. Nitrobenzene reduction by SCS with Fe(II) system at different pH values (SCS 2.38 g/L, nitrobenzene 149 μM).
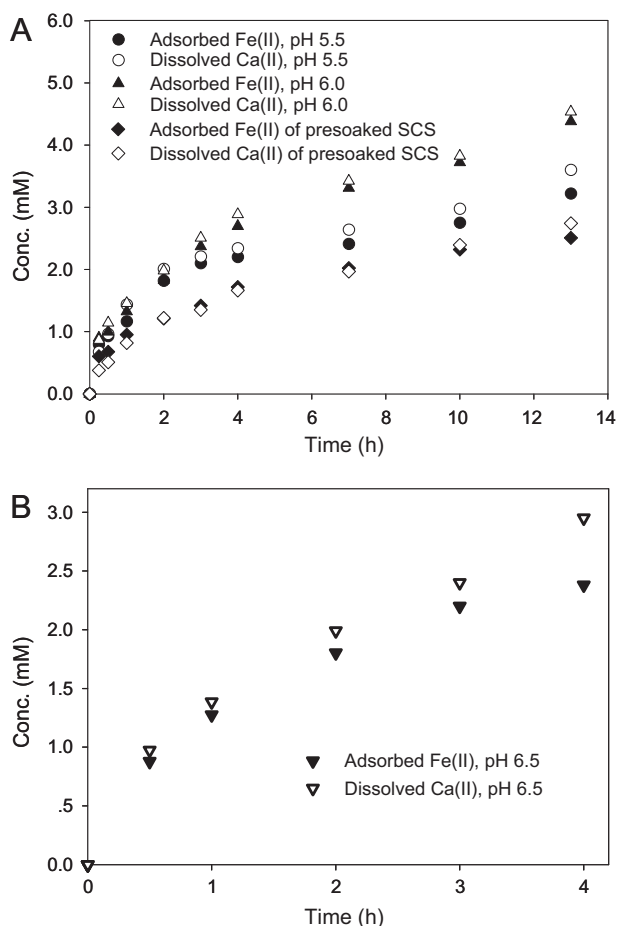
Fig. 5. Adsorbed Fe(II) concentration and dissolved Ca(II) concentration at different pH values and in presoaked SCS system. (A) pH 5.5 ± 0.2 system contained 2.38 g/L SCS and 7.14 mM Fe(II); pH 6.0 ± 0.2 system contained 2.38 g/L SCS and 4.76 mM Fe(II); presoaked SCS system contained 2.38 g/L SCS and 4.76 mM Fe(II); (B) pH 6.5 ± 0.2 solution contained 2.38 g/L SCS and 2.38 mM Fe(II).

the concentration of dissolved Ca(II) in SCS (2.38 g/L) with Fe(II) (4.76 mM) system was lower than the un-presoaked SCS (Fig. 5A), while the concentration of dissolved Ca(II) was approximately equal to the concentration of adsorbed Fe(II) (Fig. 5A). Results suggested the sites in SCS lost Ca(II) during the presoak process, were ineffective for Fe(II) adsorption. This indicated that the Ca(II) dissolution and Fe(II) sorption occurred simultaneously, further confirming the replacement process between Fe(II) and Ca(II) in SCS with Fe(II) system.

It should be noted at pH 6.5 ± 0.2, dissolved Fe(II) (2.38 mM) was adsorbed completely by SCS after 3 h (Fig. 5B). In the absence of Fe(II), hydration reactions became the primary mechanism, resulting in the concentration of dissolved Ca(II) higher than adsorbed Fe(II) at 4 h (Fig. 5B).

A higher concentration of Fe(II) (23.43 mM) was used to study the adsorption capacity of SCS (2.38 g/L, 0.15 mm). After 30 days, the concentration of adsorbed Fe(II) onto SCS was 13.84 mM, and the dissolved Ca(II) reached 13.93 mM (data not shown), which accounted for 81% of total Ca(II) contents (17.22 mM) in SCS (2.38 g/L) analyzed by XRF. Results indicated the majority of Ca(II) in the SCS was active for replacement with dissolved Fe(II). Therefore, the high concentration of Ca(II) (40.5%) in SCS suggests a high adsorption capacity for Fe(II) (more than 5.82 mmol Fe(II)/g SCS).

3.4. Reduction process of nitrobenzene by SCS with Fe(II) system

Nitrobenzene reduction consumed Fe(II) at time t can be calculated according to the electron balances of reduction process [26].

$$[\text{Fe(II)}]_t^{\text{consumed}} = 2 \times [\text{NOB}]_t + 6 \times [\text{AN}]_t = [e^-]_t^{\text{transferred}} \quad (6)$$

where $[\text{Fe(II)}]_t^{\text{consumed}}$ was the concentration of reduction consumed Fe(II) at times t; [NOB] and [AN] were the concentration of nitrosobenzene and aniline at time t, respectively; $[e^-]_t^{\text{transferred}}$ was electrons transferred from Fe(II) to nitrobenzene to yield the corresponding nitrosobenzene and aniline.

The concentrations of adsorbed Fe(II) were 4.9, 2.8 and 1.8 times higher than reduction consumed Fe(II) at pH 5.5 ± 0.2, 6.0 ± 0.2 and 6.5 ± 0.2 (4 h, Fig. 4A and B), respectively, indicating adsorbed Fe(II) accumulated in the system. Furthermore, the adsorption process of Fe(II) on SCS was similar between, with and without nitrobenzene reduction at pH 5.5 ± 0.2, 6.0 ± 0.2 and 6.5 ± 0.2 (Fig. 4A). Results demonstrated the replacement of Ca(II) by dissolved Fe(II) was a rapid process and was not the rate-limiting step in nitrobenzene reduction process. Considering adsorbed Fe(II) accumulated in system, the initial concentration of nitrobenzene was further increased from 149 μM to 298 and 597 μM in SCS (2.38 g/L) with Fe(II) (4.76 mM) system (pH 6.0 ± 0.2). However, the reduction consumed Fe(II) just slightly increased in 298 and 597 μM nitrobenzene systems compared with 149 μM nitrobenzene system (Fig. 4B). The possible explanation was the adsorbed Fe(II) on SCS may not be active for nitrobenzene reduction or recently formed SCS-Fe(II) species had a low activity for reduction. Subsequently, excess nitrobenzene (746 μM) in SCS (2.38 g/L) with Fe(II) (4.76 mM) system was used to examine the amount of adsorbed Fe(II) was active for nitrobenzene reduction. In this case, the concentration of nitrobenzene and aniline were not changing any more after 48 h (Fig. 6A), indicating the reduction capacity of system disappeared due to the exhaustion of active Fe(II). The following hydration reaction resulted in a sharp pH increase from 6.5 to 10.2. The reduction consumed Fe(II) was 4.04 mM at 48 h (Fig. 6B), showing the majority of adsorbed Fe(II) (84.9%) on SCS was active for nitrobenzene reduction. Therefore, the accumulation of adsorbed Fe(II) in Fig. 4 should be due to the low activity of newly formed SCS-Fe(II) species. Jeon et al. [27] observed that Fe(II) adsorption onto iron oxides formed outer-sphere (OS) complexes with a relatively fast rate. OS complexes then converted to inner-sphere (IS) complexes at a slower rate, suggesting the conversion was the rate limiting step of adsorption process. IS complexes were more effective for the reduction of organic pollutants [26,31]. We proposed that in SCS with Fe(II) system, the initial adsorbed Fe(II) on SCS also converted to more reactive species through further reaction such as OS-IS conversion.

In this study, the concentration of adsorbed Fe(II) at pH 5.5 ± 0.2 was approximately equal to the Fe(II) concentration at 6.5 ± 0.2, and both were slightly lower than the Fe(II) concentration at pH 6.0 ± 0.2 (Fig. 4A). Meanwhile, k_{red} values of nitrobenzene reduction by SCS-Fe(II) increased with increasing pH values (Fig. 3). This implied adsorbed Fe(II) was more effective at higher pH values in SCS-Fe(II) system. One possibility was that the rate of conversion initial adsorbed Fe(II) species to active SCS-Fe(II) species increased with increasing pH. During iron oxides–Fe(II) interactions, adsorbed Fe(II) formed a $(\equiv\text{Fe}^{\text{III}}\text{OFe}^{\text{II}})^+$ surface complex at lower pH values, and formed a hydrolytic surface complex $(\equiv\text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH})$ at higher pH values. The latter $(\equiv\text{Fe}^{\text{III}}\text{OFe}^{\text{II}}\text{OH})$ is a more efficient reductant than the former $(\equiv\text{Fe}^{\text{III}}\text{OFe}^{\text{II}})^+$ [32,33]. Li et al. [34] confirmed that the peak oxidation potential of adsorbed Fe(II) onto γ-Al$_2$O$_3$ and TiO$_2$ decreased with increasing pH, which enhanced the reduction rate of pollutant. Therefore, another
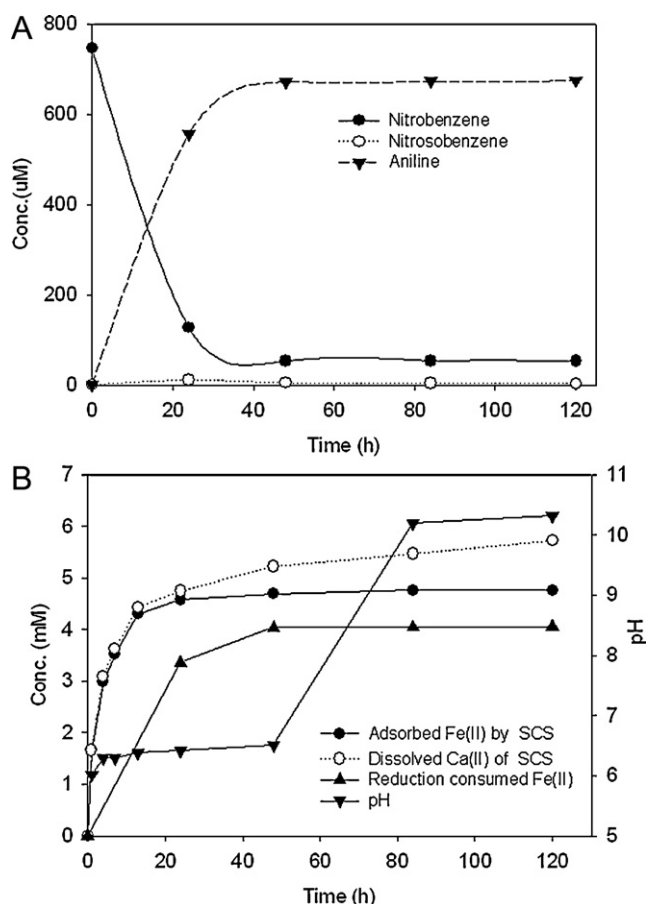
Fig. 6. Reduction of nitrobenzene by SCS with Fe(II) system in the presence of excess nitrobenzene (nitrobenzene 746 μM, Fe(II) 4.76 mM, SCS 2.38 g/L). (A) The concentration of nitrobenzene and aniline; (B) the concentration of adsorbed Fe(II), dissolved Ca(II) and reduction consumed Fe(II).
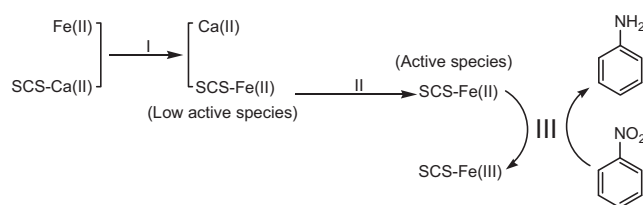
Fig. 7. The reduction process of nitrobenzene by SCS with Fe(II). Step I. Replacement process; Step II. Conversion process; Step III. Electron transfer process.

possibility was adsorbed Fe(II) in the SCS-Fe(II) species formed a more active hydrolytic surface complex at higher pH values.

The overall reduction process of nitrobenzene by SCS with Fe(II) was proposed as a three-step model in Fig. 7. In the fist replacement step, Fe(II) was adsorbed on SCS through fast ion replacement with Ca(II) and formed a low active SCS-Fe(II) species (Fig. 7, Step I); In the second conversion step, low active SCS-Fe(II) species further converted to an active SCS-Fe(II) species (Fig. 7, Step II); In the final electron transfer step, active SCS-Fe(II) species reduced nitrobenzene to the final reduction product, aniline (Fig. 7, Step III).

4. Conclusions

This study demonstrated the high capacity of SCS as a sorbent for Fe(II) through fast ion replacement with Ca(II) in SCS. Subsequently, formed SCS-Fe(II) species were capable of reducing nitrobenzene to

aniline without additional buffers. Our results suggested SCS could potentially be used as a substrate to transform nitroaromatic compounds in anoxic and anaerobic environments, where Fe(II) could be generated from iron oxide reduction facilitated by iron-reducing bacteria [35,36] and natural organic matter [37].

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