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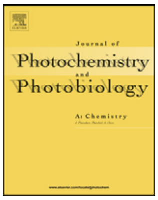

Elimination of estrogen and its estrogenicity by heterogeneous photo-Fenton catalyst β-FeOOH/resin

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ABSTRACT

β-FeOOH loaded resin (β-FeOOH/resin) was synthesized through in situ hydrolysis of Fe(III)-exchanged resin and its physiochemical properties were characterized. The typical environmental endocrine disruptor, natural hormone 17β-estradiol (E2) was removed by heterogeneous photo-Fenton reaction in presence of β-FeOOH/resin and H_2O_2 under weak UV irradiation. E2 degradation was effectively achieved by hydroxyl radicals that were generated in the heterogeneous photo-Fenton process. pH was an important factor that affected efficiency of E2 degradation and catalyst's surface activity which were determined by X-ray photoelectron spectrum (XPS). The mechanical stability and photo activity of β-FeOOH/resin were tested by several cycles of photo catalytic degradation and FTIR. The reduction of estrogenicity of E2 would be very important to the safety of treated water so as to avoid secondary pollution. It seems that the heterogeneous Fenton oxidation would be a promising method to eliminate the steroid estrogenic compounds.

1. Introduction

Endocrine disrupting chemicals (EDCs) are defined as exogenous agents that interfere with the synthesis, secretion, transport, binding, action or elimination of natural hormones in the body. The natural water and wastewater represents their significant exposure pathways [1]. The environmental concentration level EDCs in the public drinking water supply can cause adverse effects on humans and wildlife via interactions with the endocrine systems [2,3]. As such, it is important to understand and reduce EDC levels in the environment. For example, 17β-estradiol (E2) is a steroid hormone and releases from humans and domestic animals into the environmental water and usually causes suspected adverse effects in aquatic organisms at concentrations above 0.03 nmol/L [4]. E2 contributes a large part of the estrogenicity in environmental waters thus it was chosen as model compound in this study. The effective removal of EDCs becomes a challenging task due to its high toxicity for microorganisms and poor biodegradability. In some cases, the traditional activated sludge process was now assumed to generate EDCs in the form of free estrogens which are the result of incomplete degradation of respective parent compounds [5]. For these reasons, advanced oxidation processes (AOPs) have emerged as available and promising alternatives for conventional water treatment systems [6,7]. Among AOPs, Fenton reaction was also used to degrade EDCs [8]. The acceleration of decomposition of organic compounds is believed to be photolysis of iron aqua complex, $Fe(OH)^{2+}$, to provide a new importance source of $^{\bullet}OH$ radicals. Furthermore, the $Fe(OH)^{2+}$ can absorb light at wavelengths up to ca. 410 nm. Therefore, the photo-Fenton process can be expected to an efficient and inexpensive method for water treatment and promotes the rate of degradation of various organic pollutants. To overcome the drawbacks of conventional Fenton reactions, various modified Fenton systems have been developed due to their many advantages such as facile recovery, higher catalytic activity, lower level leaching of iron [9–14], etc. These characters must be the expectation quality of future novel Fenton catalysts. The mechanisms and the kinetics of heterogeneous Fenton systems are very sensitive towards almost any experimental variables, i.e. the oxidation state of metal ion, which can be rapidly changed at the beginning of the experiment [15]. Thus, attention must be paid to the possible competition or factors that would affect hydroxyl radicals receiving between substrates and competitors in Fenton-like degradation. In order to decrease the iron leaching and improve catalyst's stability and catalytic efficiency within a wide pH range, it's anticipated to prepare alternative highly effective catalyst.

The potential estrogenicity of EDCs was also focused during water treatment. The technology could thus be applied to water treatment is required effectively remove EDCs without producing biologically active intermediates or potential estrogenic substances

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higher than mother compounds. Recently, many papers reported the reduction of estrogenic activity by ozonation, chlorination, UV/H_2O_2, TiO_2 photocatalysis, etc. Some papers reported the estrogenicity of EDCs reduction during the oxidation, such as TiO_2 catalysis and ozonation, while some papers reported contrary results, such as chlorination. Ohko et al. [16,17] reported that the degradation of bisphenol A (BPA, 170 μM) and E2 (1 μM) in TiO_2 (Degussa P25) slurry by photocatalysis, respectively. Results showed that the estrogenic activity was almost lost concurrently with the initiation of the photocatalytic degradation by Yeast estrogen screen assay (YES). The estrogenic activity of E2 reduced by ozonation was studied. With an initial E2 concentration level of μM, the estrogenic activity rapidly decreased to below the detection limit with the two-hybrid method using recombinant yeast [18,19]. Otherwise, Hu et al. assessed the estrogenic activity potentially stemming from bisphenol A (BPA) and 4-nonylphenol (4-NP) chlorination in drinking water. Oxidation results suggested that the chlorinated BPA and 4-NP solution led to increased estrogenic activity [20,21]. Itoh et al. also found a 2–3-fold increase in estrogenic effect in lake water after it was chlorinated [22]. Several studies have reported and evaluated concerning results regarding UV/H_2O_2 AOPs oxidation of some EDCs (E2, EE2, BPA and 4-NP). Synergistic effects or remaining estrogenic activity were observed in examining oxidation of estrogenic activity associated with these EDCs via UV/H_2O_2 [23]. Rosenfeldt et al. suggested the presence of some oxidation by-products that may retain estrogenic activity since complete mineralization of EDCs to carbon dioxide and water is impractical [6]. While estrogenicity have been well studied by O_3, UV/TiO_2, UV/H_2O_2 and chlorination, it is necessary to establish how efficient the estrogenicity was removed by Fenton processes. The degradation of estrogen (such as, E2, BPA, etc.) by homogeneous photo-Fenton process or under ultrasound assisting homogeneous Fenton process has been reported [24]. However, the relationship of the dose-response of E2 during Fenton processes was not explored in detail. Hence, it is important to assess the efficiency of the heterogeneous Fenton reaction with regard to EDCs removal potential and the associated estrogenicity.

Akaganeite, β-FeOOH, is a commonly occurring ferric mineral in the environment and is a sorbent, ion exchanger, and catalyst. It is often fine-grained (nano phase) and frequently contains excess water. In this work, we synthesized a novel heterogeneous Fenton photocatalyst of β-FeOOH coated resin (β-FeOOH/resin) and explored the catalytic activity for the degradation of E2 in the presence of H_2O_2 under relatively weak irradiation. This paper intends to provide information of pH effect, the stability of the Fenton catalyst and reduction of estrogenicity during the photodegradation course of E2. For bioassays embody high sensitivity for detecting estrogenic activity of EDCs, YES was used to assess the reduction of estrogenic activity of E2 following this photo-Fenton process.

2. Experimental

2.1. Chemicals

17β-Estradiol (E2) (>98%; Sigma) was used without further purification. All the other chemicals used were analytical grade and all the solvents used were HPLC grade. The water employed was purified by a Milli-Q system with a resistivity higher than 18 MΩ/cm. The resin was Amberlite® 200 with matrix of styrene-divinylbenzene, Na^+-form, strongly acidic and particle size of 20–50 mesh (0.297–0.840 mm) (Fluka). 0.1 mM stock solution was prepared by dissolving desired amount of E2 into methanol and stored in 4 °C. Working solutions were followed by diluting stock solution with Milli-Q water to desired concentrations.

2.2. Preparation of photocatalyst β-FeOOH/resin

The catalyst was prepared by dissolving 5 g $FeCl_3{\cdot}6H_2O$ and 10 mL resin into 50 mL doubly distilled water and agitated 1 day at room temperature. 50 mL 1 M NaOH was slowly dropped into the above mixture at a rate of 10 mL/h under continuous stirring at room temperature and then allowed to grow on the surfaces of resin for 7 days. After repeated washing with doubly distilled water and alcohol, the formed β-FeOOH/resin was desiccated under ambient temperature and stored in polyethylene bottles for further use. The physiochemical parameters were characterized by X-ray diffraction (XRD-6000) and scanning electron microscopy (SEM). Phase composition and crystallization of the α-FeOOH/resin were examined by XRD using a Philips PW 1729 type X-ray diffractometer with Cu Kα radiation (Shimadzu, Japan). Surface morphology was observed by SEM, using a JEOL 6700F type field emission scanning electron microscope with magnification up to 650,000× and the resolution of 1 nm (JEOL, Japan). The iron content was determined by Shimadzu AAS-6700 (Shimadzu, Japan). XPS was performed in a Kratos AXIS Hsi, Mono Al Kα system, energy is 1486.71 eV (Kratos analytical, Japan).

2.3. Photo-Fenton degradation experiments

The photochemical reactor was made of open cylindrical Pyrex with diameter of 19 cm and height of 9 cm and equipped with a magnetic stirring bar. 1 L of desired concentration E2 aqueous solution was prepared without adjusting pH prior to addition of required amount of β-FeOOH/resin (5 g/L) and H_2O_2 (9.7 mM). The mixture was magnetically stirred at 200 rpm at 20 °C air-cooled room. The experiments conducted in open reactor, and the lamps were not immersed in the solution, while on top of the reactor. The irradiation was carried out with two 15 W black light lamps (Wuxing Co., Singapore) with the irradiation intensity at the center of the reactor of 0.3 mW/cm^2 (measured by a UV radiometer, IL700, International Light, USA.) and the main emission wavelength of 365 nm. For concentration of E2 is very low, the weak UV irradiation will avoid to waste light energy. The main aim of choosing weak UV365 nm will provide a promising technology using nature light to degrade 17β-estradiol in the future. The distance between light source and the surface of the solute was 5 cm. About 25 mL aliquot of the suspension was collected at regular intervals and analyzed for subsequent residual E2 concentrations and total dissolved iron with irradiation. The influence of pH was studied which was adjusted with 1 M HCl or 1 M NaOH. The recycling experiments were repeated 5 times under current experimental conditions. Photocatalyst samples were also analyzed by FTIR spectroscopy using a Jasco FTIR 430 spectrometer with accessory for diffuse reflectance measurements (Jasco Co., Japan). All the photodegradation samples were concentrated by solid phase extraction (SPE). The amount of E2 in the test solutions was determined using a Liquid chromatography/triple quadrupole tandem mass spectrometry, equipped with turbo ion spray interface (API2000 LC/MS/MS system, Applied Biosystems Asia Pte Ltd., USA) [25].

2.4. Evaluation of estrogenic activities for treated water

10 μL aliquots of the reaction mixture were sampled at frequent time intervals during the reactions, and were assayed for estrogenic activity in the recombinant yeast assay. Yeast colony (*S. cerevisiae* Strain BJ3505) was supplied by Gaido in USA. Transcriptional estrogenic activities in response to a recombinant yeast-based estrogen assay were evaluated for the treated water as reported [26].

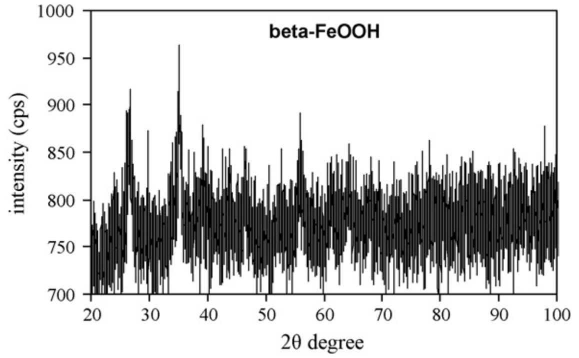


Fig. 1. XRD patterns of β-FeOOH/resin.

3. Results and discussion

3.1. Characterization of catalyst

Amberlite® 200, spherical macroporous cationic exchange resin of polystyrene matrix with sulfonic acid groups, was chosen as photocatalyst carriers. The synthesis of the catalyst was carried out in-situ hydrolysis Fe-exchange resin by 1 M NaOH, all which resulted in the formation of iron oxides nanocrystals. The crystalline of the loaded iron oxides on the resin was characterized by XRD in high angle range depicted in Fig. 1. Wide-angle XRD patterns of the sample gave the diffraction peaks that can be indexed well as the formation of iron oxyhydroxides of akaganeite (β-FeOOH) structure. The line broadening indicated that the samples were composed of small particles of several nanometers in size. The poor quality of Fig. 1 maybe ascribed to the presence of resin which made akaganeite's content to be lower. The morphology of surface of resin beads and surface of β-FeOOH entities was analyzed by SEM shown in Fig. 2. SEM confirmed the presence of β-FeOOH entities on the surface of resin comparing with non-coated resin. The size of β-FeOOH entities were mainly in nanometer range. The loaded β-FeOOH in the photocatalyst was digested by HNO_3-HCl and the iron content measured by AAS was 92 mg Fe/g catalyst. The loaded β-FeOOH content in polymer matrix could be comparable to DeMarco's work [27]. Ion exchange resin supporters showed higher chelating ability than that of inorganic carriers, such as zeolite, activated carbon, sand and silica whose iron loaded contents were less than 5 wt.% Fe and also not stable. Iron content and stability of the catalyst are very important factors to influence the activity of catalysts.

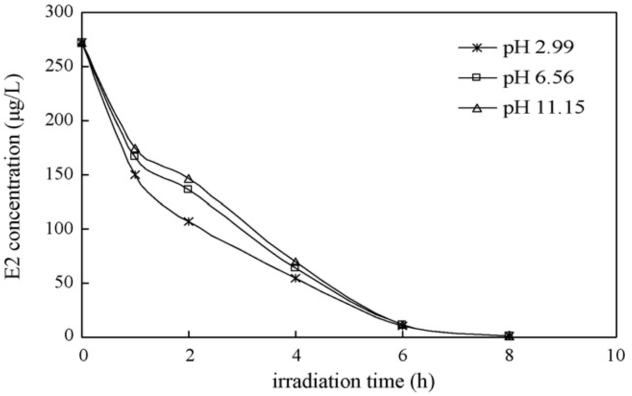
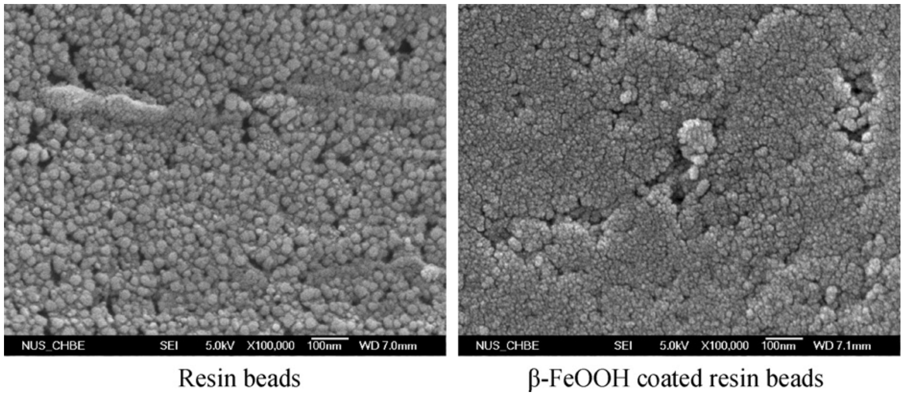


Fig. 3. Effect of pH on E2 photodegradation. [β-FeOOH/resin] = 5 g/L; [E2] = 272 μg/L; $[H_2O_2]$ = 9.7 mmol/L; T = 20 °C; pH 2.99, 6.56 and 11.15, respectively.

3.2. Effect of pH

The effects of pH on the removal of E2 with β-FeOOH/resin were determined with a pH range of 2.99–11.15 and results were presented in Fig. 3. In this study, the photodegradation process remained efficient and feasible from pH 2.99 to 11.15 with the photodegradation rate of E2 all above 99.5% within 8 h irradiation. The photodegradation of E2 over β-FeOOH/resin exhibited pseudo-first order reaction kinetics, i.e. 0.5899 h^{-1} (R^2 0.940) at pH 2.99, 0.5795 h^{-1} (R^2 0.920) at pH 6.56, 0.5771 h^{-1} (R^2 0.910) at pH 11.15, separately. Basically, the photodegradation efficiency of E2 slightly decreased with increase of pH. With the variation of pH, the surface species fraction of FeOOH changed due to the dissociation of FeOOH in water, i.e. $\equiv$Fe–$OH^+{}_2$, $\equiv$Fe–OH and $\equiv$Fe–O^- (the dissociation constant of FeOOH is K_{a1} = 5.3 and K_{a2} = 8.8, respectively) [28]. The different species maintains a different level of binding strength with H_2O_2 and E2 for the binding strength may be altered with pH [29]. β-FeOOH is positively charged at lower pH (i.e. at pH <5.3) and favors neutral molecules of E2 adsorption for the higher reaction rate constant of E2 should be due to an increment of the electron density on the phenyl ring because of an electron-donating group of cycloalkane. When pH is in the range of 5.3–8.8, β-FeOOH is presented in the neutral form. The binding strength of β-FeOOH with E2 decreases with the increase of pH. When pH >8.8, the surface of β-FeOOH is gradually deprotonated to the negative ions causing repulsion with E2 because E2 would be gradually ionized to the phenoxide, especially pH >10 (pK_a of E2) [30]. Many studies had reported that solution pH dramatically influence homogeneous Fenton reaction efficiency. At neutral pH the homogeneous photodegradation efficiency can nearly be neglected because of the iron precipitation. The activity of a heterogeneous catalyst is dependent



Resin beads β-FeOOH coated resin beads

Fig. 2. FESEM of the surface of resin beads and β-FeOOH/resin.

on the structure and composition of its surface – both of which can change in response to variations in the environment [31]. Generally, the pH change can have an obvious effect not only on the mode of adsorption of substrate on the catalyst but also on the selectivity of the photodegradation reaction on the catalyst surface. So the heterogeneous Fenton reactions might also be extensively influenced by pH. Neppolian reported that the p-CBA degradation by FeOOH/H_2O_2 indicated the 38% degradation at pH 3, 9% and 4% at pH 7 and 9 [32]. He et al. reported the effect of pH on the photodegradation of salicylic acid in H_2O_2/goethite system. The detrimental effect of pH was also obvious. The efficiency was decreased from about 95% to 45% with pH increasing from 6 to 11 [33]. Feng et al. reported that the pH can significantly influence the efficiency of Fenton catalytic processes. At pH 2.0, it needs about 120 min for the salicylic acid concentration to become zero while at pH 3.1, only 75 min are needed. The highest efficiency of the catalyst was observed at about pH 3. The results at pH 3.1 and 3.7 are almost the same [34]. The photodegradation efficiency of Methylene blue over iron oxide pillaring clay mineral within pH ranging from 3.0 to 6.0 was similar to those of the photo-Fenton assay performed at pH 3.0, suggesting a wide range of effectiveness for the heterogeneous process. Because the influence of pH may be attenuated in the heterogeneous system since immobilized Fe(III) species could not be transformed into less photoactive materials: $Fe^{3+}(H_2O)_6$ at lower pH and $Fe(OH)_3$ at higher pH. Further, the stabilization of iron oxide pillars may also be attributable to interactions with the clay sheet [11]. It is the same with this heterogeneous Fenton catalyst β-FeOOH/resin which can overcome the drawback of a narrow pH range of conventional Fenton reaction tended to be highest at around pH 3. The superiority of β-FeOOH/resin to other reported catalyst was mainly ascribed to the nature of surface construction of iron species and the role of the supporters which would in synergy enhance the catalytic ability of β-FeOOH within the resin [35].

The surface color of β-FeOOH/resin was changed which mean the iron oxide experienced redox reaction after the photodegradation of E2. The X-ray photoelectron spectrum (XPS) results of the β-FeOOH/resin samples before and after E2 photodegradation (presented in Table 1) disclosed the elemental changes of the catalysts. The results led to a few interesting observations and proved the photodegradation occurred on the surface of catalysts. The most interesting points are probably the presence of two oxidation states of surface iron species, two doublets of Fe 2p with an intensity ratio of 1.5:1, and a splitting energy of about 13.6 eV in samples before photodegradation. The major component is found to be Fe^{2+}, which contributes to 59.4% of the total iron surface atoms, while 40.6% of the total iron surface atoms are in the Fe^{3+} state. The 2p line of the β-FeOOH/resin is very broad and can be deconvoluted into two components with line position at 710.4 and 712.2 eV [36]. These two components correspond to the Fe^{2+} and Fe^{3+} species, respectively. The intensity ratio of Fe^{2+}/Fe^{3+} species was found to be 59:41, 61:39 and 59:41 for the sample after E2 degradation at pH 2.99, 6.56 and 11.15, respectively. Whereas, for the sample before E2 degradation, the intensity ratio of Fe^{2+}/Fe^{3+} species was found to be 59:41. Hence, the observation supports the conclusion that β-FeOOH participate in oxidation–reduction reaction during E2 photodegradation. The intensity of the surface hydroxyl signal is very high. Through these surface hydroxyl groups, E2 can interact with β-FeOOH and undergo photocatalytic decomposition. Otherwise, the surface of the β-FeOOH particle on the resin is more strongly dehydroxylated with the increase of the pH (as reflected in the OH-surface component observed at 531.3 eV). The less surface hydroxyl groups the lower E2 photodegradation rates were achieved. This result further proved E2 photodegradation efficiencies decreased with the increase of the pH.

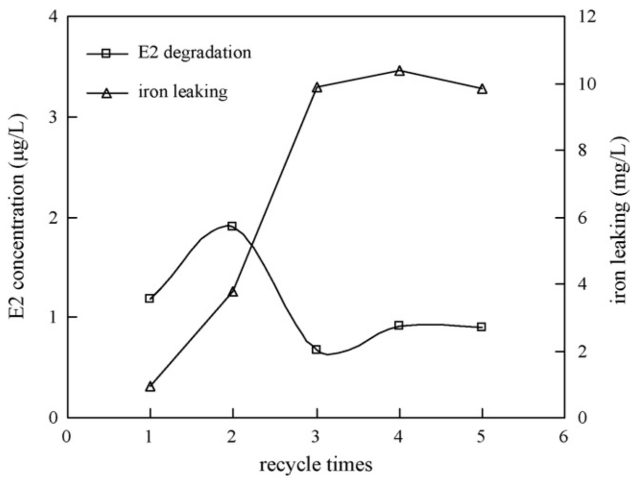


Fig. 4. E2 removal by β-FeOOH/resin after 5 times photodegradation cycles after 8 h irradiation. [β-FeOOH/resin] = 5 g/L; [E2] = 272 μg/L; [H_2O_2] = 9.7 mmol/L; T = 20 °C; pH 6.56; cycles: 5 times.

3.3. Recycles of the catalyst

A good photocatalyst, in addition to its broad pH range of application, high photocatalytic activity and easily separation property, must exhibit better capacity to use renewable and mechanical stability for multiple uses. In order to verify the activity of used catalyst and to check out its lifetime, five experiments of the photocatalytic regenerability of β-FeOOH/resin was conducted by a series of systematic experiments and results were showed in Fig. 4. After each photocatalytic cycle, β-FeOOH/resin was directly filtered and entered into the next photocatalytic cycle without any other post treatment. After experiencing 5 times photocatalytic cycles, the average residual E2 concentration was 1.11 μg/L and relative standard deviation of 0.48%. The iron leaching content increased with recycle times, the average iron leaching concentration was 6.9743 mg/L with relative standard deviation of 4.34%. The catalytic performance of β-FeOOH/resin basically remained the level of unused catalyst. The diffuse reflectance FTIR spectra of β-FeOOH/resin samples were illustrated in Fig. 5. A very strong IR band at 3470 cm^{-1} is due to the presence of surface OH-stretching of H_2O or to the envelope of hydrogen bonded surface OH groups. The typical bands of goethite at 902 cm^{-1} can be ascribed to Fe–O–H bending vibrations [37]. While the bands at lower wave numbers (such as less than 700 cm^{-1}) were assigned to Fe–O and Fe–OH

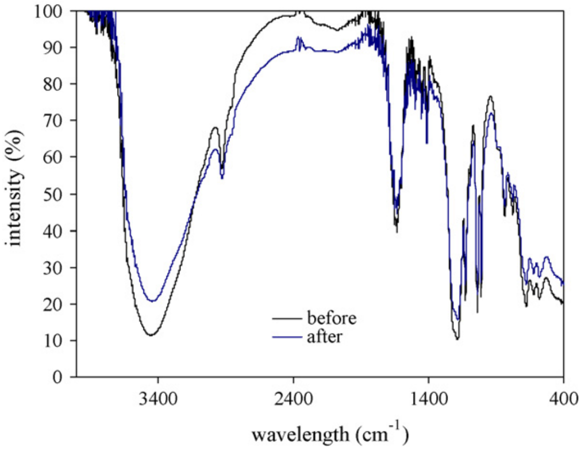


Fig. 5. FTIR of β-FeOOH/resin before or after 5 times photodegradation cycles. [β-FeOOH/resin] = 5 g/L; [E2] = 272 μg/L; [H_2O_2] = 9.7 mmol/L; T = 20 °C; pH 6.56.

Table 1
Binding energy of Fe 2p, O 1s and C 1s elements and atomic surface concentration of detected elements for β-FeOOH/resin catalysts.

	Fe $2p_{1/2}$	Fe $2p_{3/2}$	O 1s			C 1s
Binding energy (eV)						
Before	710.40	725.80	532.04	531.27	529.86	284.60
2.99	710.63	726.10	532.22	531.38	530.05	284.63
6.56	710.51	725.91	532.15	531.35	530.05	284.61
11.15	710.48	726.03	532.05	531.31	529.97	284.64
	Fe 2p		O			C
	Fe^{2+}	Fe^{3+}	H_2O_{ads}	OH_{surf}	O_{oxides}	
Atomic surface mass concentration (%)						
Before	8.46					
	59.4%	40.6%	6.96	20.09	3.84	60.65
2.99	9.35					
	59.4%	40.6%	8.04	19.29	3.85	59.48
6.56	11.09					
	60.7%	39.3%	7.79	17.91	5.41	57.80
11.15	7.56					
	59.3%	40.7%	7.54	17.81	4.92	62.17

stretching or lattice vibrations [38–41]. After 5 times photocatalytic cycles of β-FeOOH/resin, the FTIR of β-FeOOH/resin was the same with the original catalyst without appearance of other functional groups. The results showed that catalytic center β-FeOOH was still active. The skeleton of resin carriers were not attacked by hydroxyl radicals in solutions because of β-FeOOH entity compactly covering the whole surface of the resin. One study reported in the first trial, decomposition degree of phenol by TiO_2 was 76% while in the second trial decomposition degree was 32% and remained at about the same level during the third trial. And new absorption bands in the region of 1200–1800 cm^{-1} were also appeared on the spectra of photocatalyst used in the reaction of phenol photooxidation by TiO_2. These bands in the region of 1200–1800 cm^{-1} assigned to C═O, C–H, C–C, and aromatic ring vibrations, which were due to carbon deposits on the catalyst surface [42]. Comparing with TiO_2, β-FeOOH/resin showed better ability of reuse. This can make this treatment process cost-effective because the Fenton catalyst does not have to be replaced over a relatively long period of time.

3.4. *Elimination of estrogenic activity of E2*

The heterogeneous photo-Fenton technology needs to be assessed for their capability of removing estrogenicity in order to ensure a safe and cost-effective water supply. The reduction of transcriptional estrogenic activity of EDCs was quantitatively evaluated in response to hER in a yeast estrogen screen (Fig. 6). In single E2 system, the estrogenic activity of E2 photodegradation decreased from 1511 units to nearly zero with E2 concentration decreasing from 272 to 0.23 μg/L after 22 h irradiation over β-FeOOH/resin. It was found that the binding affinity of intermediates of E2 photodegradation with hER decreased with irradiation. The photodegradation rates and reduction of estrogenic activity for E2 can be determined from pseudo-first-order rate kinetics. The photodegradation of E2 over β-FeOOH/resin exhibited removal rate of 0.5795 h^{-1} (R^2 0.920) and elimination rate of estrogenic activity of 0.2821 h^{-1} (R^2 0.866). Ohko et al. [17] previously reported that the photocatalytic reaction with E2 started via oxidation of the phenol moiety, which was known to be critical for receptor binding and for conferral of estrogenicity to all steroid estrogens. It was likely that photocatalysis may quickly remove the ability of E2 to bind to estrogen receptors. It was found that many by-products were formed in the heterogeneous photo-Fenton degradation of E2 [25]. If one or more products of the photocatalytic degradation of E2 retained a similar level of estrogenic activity as the parent compound, the rate of estrogenic activity removal would be retarded compared to the photodegradation rate of the parent compound. However, there was no statistically significant difference between rate of oxidation and rate of reduction of estrogenic activity for E2. Therefore, it can be deduced that the observed degradation of parent compound corresponded directly with a reduction in estrogenic activity which was the same with that of Rosenfeldt' report [6]. The similarity between E2 removal rate and estrogenic activity removal rates implies that none of the oxidation by-products produced by β-FeOOH/resin were comparable with the parent compound in terms of estrogenic activity. The elimination of estrogenic activity of E2 is associated with the loss of chemical structure similarity with E2 that allows these intermediates not to bind to hER.

In E2 with coexisting EDCs system, the estrogenic activity firstly increased from 2236 to 3021 units then decreased from 3021 to 243 units with E2 concentration decreasing from 272 to 0 μg/L. This trend was not like that of single E2 estrogenic activity. Different estrogens will also interact in synergy thus make this system very complex. When the concentration of EDCs was too high (i.e. the concentration of mixture EDCs before 3 h irra-

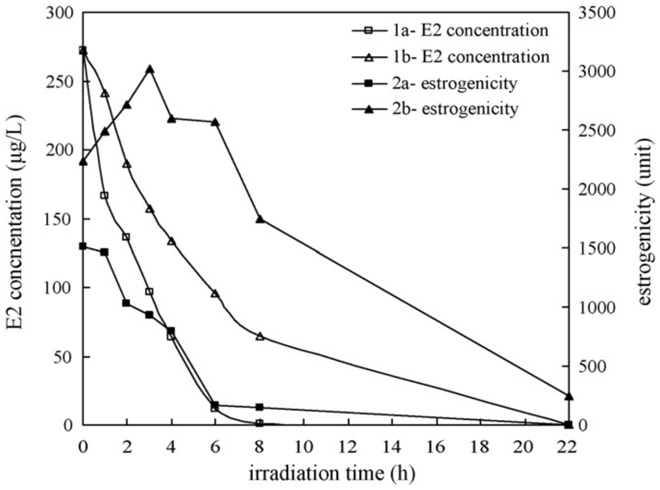


Fig. 6. Reduction of concentration and estrogenic activity of E2 during photo-Fenton process. (a) Single E2; (b) E2 with coexisting EDCs. [β-FeOOH/resin] = 5 g/L; [E2] = 272 μg/L; [H_2O_2] = 9.7 mmol/L; T = 20 °C; pH 6.56.

diation), EDCs would inhibit the express of yeast-based estrogen express. Until suitable estrogenic concentration reached after 3 h UV irradiation, EDCs would induce the change of yeast-based enzyme expressing. All the photodegradation of EDCs over β-FeOOH/resin exhibited pseudo-first order reaction kinetics, such as E1 (0.1657, R^2 0.995), E2 (0.1773, R^2 0.996), E3 (0.1391, R^2 0.986), EE2 (0.1633, R^2 0.967), BPA (0.1420, R^2 0.916). This trend should prove that EDCs experience almost the same photodegradation mechanisms, of phenol moiety of EDCs should be the starting point of photodegradation, so that the estrogenic activity of EDCs should almost lose concurrently with photodegradation. This is known to be critical for receptor binding and for conferral of estrogenic activity to all steroid estrogens [17]. As long as reaction time enough long, the estrogenic activity of EDCs mixture would be eliminated in the end. The result will be important to enable to estimate the interaction of combined estrogenic activity among mixture of EDCs. E2 is the most potent steroid among EDCs which suggests that estrogenic activities induced by degradation intermediates were much lower than that of E2 and thus would not elicit a potent estrogen receptor-mediated response. This means that there is no secondary risk to increase the estrogenic activity in treated water as a result of photocatalytic degradation of E2 by β-FeOOH/resin under weak UV irradiation.

4. Conclusions

Heterogeneous Fenton oxidation was tested to reduce E2 and its relative estrogen activities from water environment under relatively weak UV illumination in presence of β-FeOOH/resin and H_2O_2. The superiority of β-FeOOH/resin is a broad application of pH range, stable catalytically activity and completely reduction of the estrogenicity of E2 without any formation of estrogenic by-products. The estrogen activity derived from the E2 decreased with dose, which was estimated by the YES. On the other hands, estrogen activity of E2 with coexisting EDCs increased initially and then decreased. It would be of great promising for the application of Fenton catalyst like β-FeOOH/resin due to its highly photocatalytic stability and activity, little iron leaching, easy physical separation, capacity to use renewable, low cost.

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