

Co²⁺-Exchanged Titanate Nanotubes as a Novel Heterogeneous Catalyst for Peroxymonosulfate Activation and Degradation of Organic Pollutants

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Keywords: Advanced oxidation processes, Sulfate radical, Titanate nanotubes, Co²⁺ exchange, Peroxymonosulfate.

Abstract. We have successfully obtained highly isolated Co²⁺ active sites on the surface of titanate nanotubes (TNTs) by a simple ion-exchange process. The as-prepared Co-TNTs were applied in heterogeneous catalysis to generate powerful radicals from peroxydisulfate (PDS) for the removal of recalcitrant pollutant. Under the same conditions, Co-TNTs exhibited better degradation efficiency of Rhodamine B (RhB) than conventional CoFe₂O₄ and Co₃O₄. Some potential influential factors and recycling application were systematically investigated. We believe Co-TNTs may be an efficient and green heterogeneous catalyst for the degradation of organic pollutants, and this study provides insights into the rational design and development of alternative catalysts for wastewater treatment.

Introduction

It is of great importance to remove various trace organic contaminants in aqueous solution due to their considerable toxicity for the environment and human health. Over the past decades, advanced oxidation processes (AOPs), employing the excellent reactivity of hydroxyl radical ($\cdot\text{OH}$), have emerged as a powerful and attractive strategy to degrade a wide range of organic compounds in aqueous media [1]. However, hydroxyl radicals, no matter how they were generated (e.g. ozone, Fenton/Fenton-like process), suffered from many limitations in practical application, such as sophisticated and cost-intensive radical generation processes, pH adjustments and potential sludge generation [2].

Recently, sulfate-radical based advanced oxidation processes (SR-AOPs) have received more and more research interests, because sulfate radical, as an alternative to hydroxyl radical, could not only compensate some critical inadequacies of hydroxyl radicals, but also provide higher standard reduction potential (2.5-3.1 V) than hydroxyl radicals (1.8-2.7 V), which resulted in their superior reactivity and selectivity for oxidation processes [3]. Although sulfate radical can be easily released from peroxydisulfate (PDS) or peroxydisulfate (PMS) with heating, UV irradiation, ultrasound, or alkaline activation, these high-energy inputs and high alkaline dosing are not applicable for real water treatment [4]. Anipsitakis et al. reported that some transition metal ions could work for persulfate activation, especially Co²⁺ coupled PMS system demonstrated significant reactivity toward organic pollutants [5]. To avoid the secondary pollution caused by homogeneous transition metal ions, various heterogeneous catalysts, particularly some Co-containing candidates, e.g. Co₃O₄, Co₃O₄/TiO₂, CoFe₂O₄, Co/zeolite, have been extensively investigated [6-8]. Unfortunately, these heterogeneous catalysts will lose the characteristic of single active site and present much inferior activities as compared with homogeneous ions. Therefore, it still remains a challenge to develop novel heterogeneous catalysts with highly dispersed active sites in order to improve their catalytic activities.

Since the discovery of titanate nanotubes (TNTs), they have shown potential applications in many fields, including photocatalysis, catalyst support, batteries, absorption, gas sensing, and hydrogen

storage, due to their high surface area, large pore volume, stable one-dimensional nanostructures, wideband gap semiconductor properties, and excellent ion-exchange ability [9]. It is worth noting that the unique ion-exchange ability of TNTs opens up a simple avenue for the location of various isolated metal ions, so that the resultant products may promise highly catalytic activity in many reactions. For example, Tang et al. found that the incorporation of metal ions was able to extend the light absorption of TNTs to the visible-light region, thus making TNTs exhibit the visible-light photoactivity toward selective oxidation of alcohols [10]; our group previously prepared Fe³⁺-exchanged TNTs by ion-exchange method, and the obtained Fe-TNTs showed considerable activity in Friedel-Crafts type benzylation [11]. Following this direction, we reported herein the preparation of Co²⁺-exchanged TNTs and its catalytic performance in PMS oxidation of Rhodamine B (RhB) for the first time. Moreover, potential influential factors, including the dosages of catalyst and PMS, temperature, and pH value have also been investigated in terms of the catalytic performance of Co-TNTs.

Experimental Section

TNTs were synthesized by a modified hydrothermal method [11]. Briefly, 1.5 g of anatase TiO₂ powder was dispersed into 50 mL of NaOH aqueous solution (10 M) under magnetic stirring for 1 h. The suspension was transferred into a Teflon-lined autoclave, sealed and hydrothermally treated at 150 °C for 16 h. The white powder was re-dispersed into excessive 0.1 M HCl solution to neutralize the residual NaOH. Then, the product was collected by filtration, washed with distilled water until the pH value of the filtrate reached 7.0, and dried at 60 °C to obtain TNTs. 1.0 g of protonated TNTs was dispersed into 50 mL of CoCl₂ solution (0.10 M) and stirred for 24 h. Co²⁺-exchanged TNTs were collected by centrifugation and washed with distilled water until free Cl⁻ in solution could not be detected by AgNO₃ solution (1 M). Finally, the greyish-green powder was dried at 60 °C and denoted as Co-TNTs.

Powder X-ray diffraction (XRD) data were obtained on a Rigaku D/MAXRC X-ray diffractometer with a Cu K α radiation source (45.0 kV, 50.0 mA). Nitrogen adsorption/desorption isotherms were measured on a QUADRASORB SI-KR/MP (Quantachrome, USA). Transmission Electron Micrographs (TEM) images were recorded on JEM-3000F from JEOL. X-ray photoelectron spectroscopy (XPS) analysis was performed on PHI 5700 ESCA System (Physic Electronics, USA) with an Al K α 1486.6 eV radiation sources. Leaching cobalt ions were measured with Optima 8300 ICP-OES (PerkinElmer, USA).

The catalytic degradation of RhB was performed in a 100 mL conical flask at room temperature (25 °C). In a typical run, 2.5 mg of catalyst was firstly added into 50 mL of RhB solution (100 ppm) under constant stirring for about 30 minutes. Then, 65.0 mg of oxone (KHSO₅·0.5KHSO₄·0.5K₂SO₄, equivalent to [PMS]=0.64 g/L) was added to start the reaction. At given time interval, 1.0 mL of reaction solution was withdrawn and quenched by saturated Na₂S₂O₃. The degradation efficiency of RhB was determined using UV spectrophotometer.

Results and Discussion

Fig. 1a and 1b show TEM and optical images of TNTs and Co-TNTs. As observed, the as-prepared TNTs display typical tubular microstructure with an average inner diameter at 5 nm (Fig. 1a, inset), which is consistent with previous report [12]. The introduction of Co species causes an obvious color change from white to greyish-green (Fig. 1a and 1b, inset). It is well known that cobalt oxides and cobalt hydroxides always present black and roseate, respectively, and the distinguishable color may come from isolated Co²⁺ sites. However, the different chemical composition does not produce any impact on the microstructure, and Co-TNTs still give quite similar tubular morphology to that of TNTs. A closer look (Fig. 2b, inset) reveals that the external surface of Co-TNTs is very clean without any additional particles or amorphous coatings, again implying that Co species in Co-TNTs are highly dispersed.

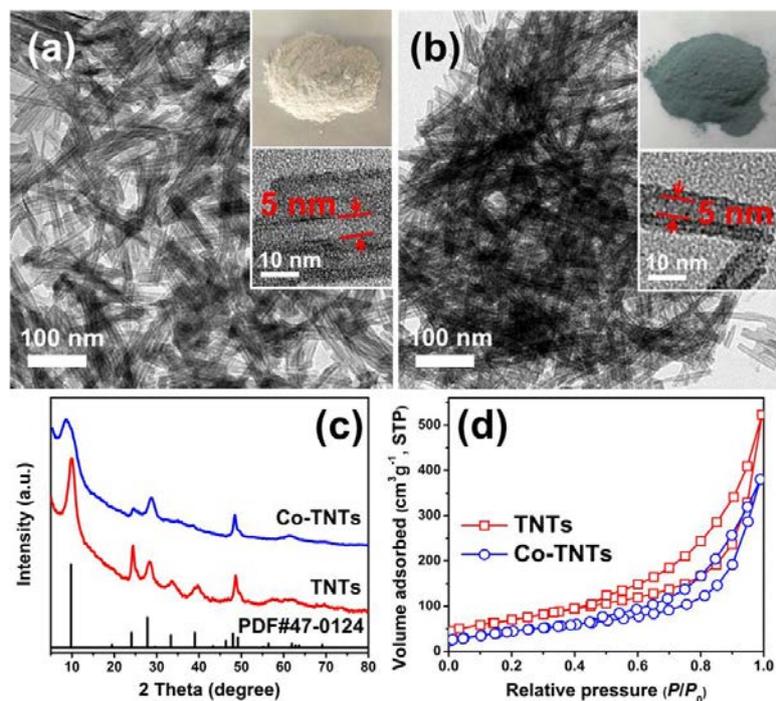


Figure 1 TEM images of TNTs (a) and Co-TNTs (b), and insets are their corresponding optical and HR-TEM images. XRD patterns (c) and N_2 adsorption/desorption of TNTs and Co-TNTs.

The crystalline phases of TNTs and Co-TNTs are identified by XRD, as shown in Fig. 1c. It is clear that TNTs exhibit six well-resolved diffraction peaks at $\sim 9.8^\circ$, 24.4° , 28.3° , 33.6° , 39.7° , and 48.6° , that can be indexed as the (200), (110), (310), (301), (501), and (020) planes of crystalline phase of $H_2Ti_2O_5 \cdot H_2O$ (JCPDS 47-0124), where H^+ is located in interlamination of zigzag ribbons of edge-sharing $[TiO_6]^{2-}$ octahedrons to keep the charge balance [12]. Compared with the as-prepared TNTs, the diffraction peaks in Co-TNTs are more or less weakened, while most of them are easily discerned, indicating that the basic structure of TNTs is well retained. Notably, the introduction of Co^{2+} causes a slight shift in peak of (200) plane to lower angle, because the atomic radius of Co^{2+} is much larger than that of substituted H^+ . In addition, there is no diffraction peak can be assigned to cobalt oxides/hydroxides, which is in agreement with TEM results. Fig. 1d shows the nitrogen adsorption/desorption isotherms of TNTs and Co-TNTs. Both of them give standard IV-type isotherms with a sharp capillary condensation step at relative pressure (P/P_0) from 0.4 to 1.0, indicating the presence of high-density mesopores in these two samples according to the IUPAC classification. However, one can also discover that the process of ion exchange produces a slight decrease in the adsorbed volume, and as a result, BET surface and total pore volume of Co-TNTs ($167 \text{ m}^2/\text{g}$ and $0.58 \text{ cm}^3/\text{g}$) are less than those of pristine TNTs ($255 \text{ m}^2/\text{g}$ and $0.63 \text{ cm}^3/\text{g}$).

In the survey of XPS spectrum for Co-TNTs (Fig. 2a), a distinguishable signal in the range of 780–800 eV assigned to Co species can be observed, convincingly validating the introduction of Co species. The Co 2p spectrum of Co-TNTs (Fig. 2b) presents two typical peaks at 781.6 and 797.4 eV, as well as two corresponding shake-up peaks (787.5 and 803.9 eV) and one weak Auger peak (773.1 eV). The orbital splitting between $2p_{1/2}$ and $2p_{3/2}$ is 15.8 eV, which is close to that of Co^{2+} (16.0 eV) rather than Co^{3+} compounds (15.0 eV) [13]. Moreover, the binding energy of Co $2p_{3/2}$ for the Co-TNTs is similar to those of Co-NaX and Co-SBA-15 [13], and thus the cobalt species herein with such a binding energy can be indexed as isolated Co^{2+} sites. Considering the preparative system of Co-TNTs, Co^{2+} in final product can combine with $[TiO_6]^{2-}$ octahedron, OH^- , and Cl^- by electrostatic interaction. Cl^- is easily excluded due to the absence of typical XPS peaks (Fig. 2a), and thus $[TiO_6]^{2-}$ octahedron and OH^- may be responsible for the charge balance of Co-TNTs. It is worth noting that the molar ratio of Co/Ti deduced from the survey spectrum is about 0.335, less than the theoretical value of cobalt titanates [0.500, $CoTi_2O_5$] from complete ion exchange. The inferior Co/Ti molar ratio implies that a few exchangeable sites in titanates are still not accessible for Co^{2+} , and meanwhile, the

contribution of charge balance from OH^- is limited. This is because once considerable OH^- groups are involved into the final product, e.g. $\text{Co}(\text{OH})(\text{Ti}_2\text{O}_5)_{1/2}$ or $\text{Co}(\text{OH})_2$, the Co/Ti ratio will be markedly increased.

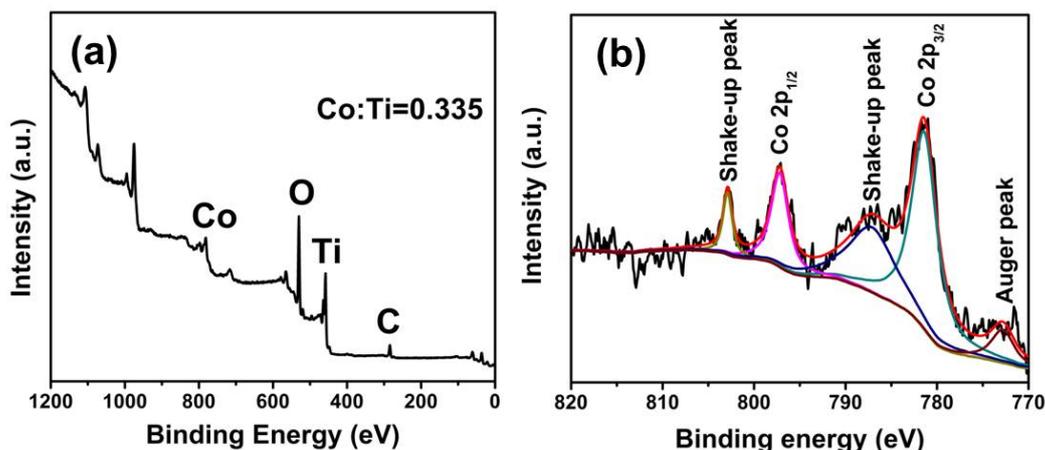


Figure 2 Survey (a) and Co 2p (b) XPS spectra of Co-TNTs.

Fig. 3a shows the degradation of RhB *via* catalytic oxidation process with different heterogeneous catalysts. As observed, sole PMS can work for the decoloration of dyes solution, and only 35.6% of RhB is removed after 40 min. In contrast, Co-TNTs cannot promise any RhB removal in the absence of PMS, suggesting that the contribution from simple physical adsorption is negligible. It is very interesting that the degradation of RhB can be substantially reinforced when PMS and Co-TNTs are coexisted in the reaction system, and a complete removal of RhB can be achieved in 30 min. To validate the catalytic activity of Co-TNTs, some conventional Co-containing catalysts, such as CoFe_2O_4 and Co_3O_4 , are also applied in the same system. It can be found that CoFe_2O_4 and Co_3O_4 present RhB degradations at 78.0% and 64.4% after 40 min, respectively, which are obviously inferior to that of Co-TNTs. In addition, the Co^{2+} leaching from various catalysts is further examined, as shown in Fig. 3b. Although Co-TNTs defends the best performance in RhB degradation, its Co^{2+} leaching ($129 \mu\text{g/L}$) is comparable to those from CoFe_2O_4 ($97.5 \mu\text{g/L}$) and Co_3O_4 ($141 \mu\text{g/L}$). It is worth noting that Co_3O_4 with the highest Co^{2+} leaching fails to produce the matching catalytic activity, indicating that homogeneous catalysis caused by the leaching Co^{2+} is not responsible for RhB degradation. Therefore, Co-TNTs may be taken as a promising heterogeneous catalyst in SR-AOPs.

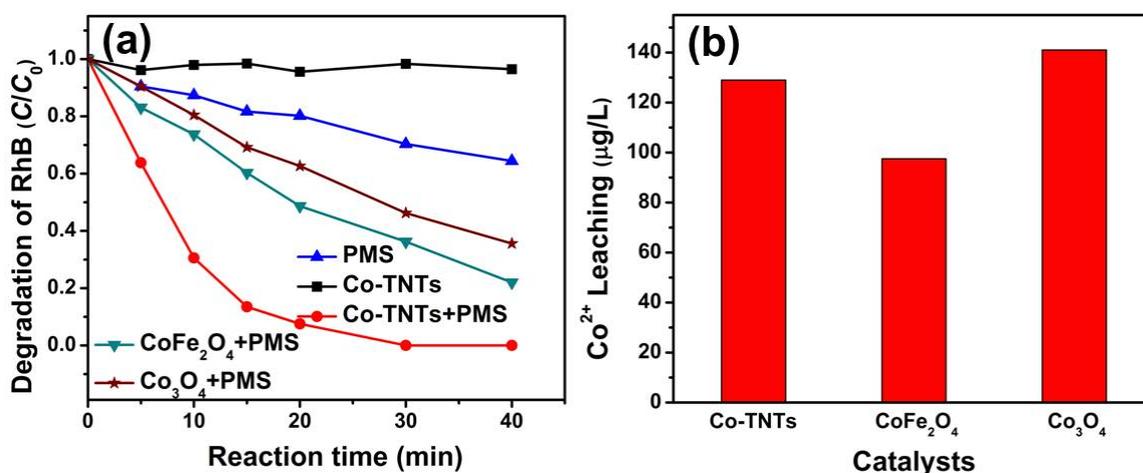


Figure 3 RhB degradations by various catalytic PMS systems (a) and corresponding Co^{2+} leaching (b).

Moreover, the effects of reaction temperature, catalyst dosage, PMS dosage, and pH value are further studied in Co-TNTs/PMS system. Reaction temperature is a critical operating parameter in AOPs. Data fitting (Fig. 4a) shows that the RhB degradation can be described by the first order kinetics, and reaction temperature can remarkably affect the degradation rate of RhB. The activation energy (E_a) of RhB degradation is evaluated by plotting $\ln k$ against $1/T$ based on the Arrhenius equation (Fig. 4b). It has to mention that the E_a is much higher than that of diffusion-controlled reactions (10-13 kJ/mol), indicating that the apparent reaction rate for this process is dominated by the rate of intrinsic chemical reactions on the surface of Co-TNTs [14]. With increasing the initial PMS concentration, RhB degradation can be enhanced significantly (Fig. 4c). However, when PMS concentration exceeds 1.28 g/L, RhB degradation will not be further promoted any more. It is reliable that the positive PMS effect can be attributed to the facilitation for the generation of radical species by attaching more HSO_5^- to the active sites of Co-TNTs, and the ineffective PMS consumption should be due to the limitation of the quantity of active sites for PMS activation. Interestingly, RhB degradation shows a similar dependence on the dosage of Co-TNTs (Fig. 4d), while its stimulation effect will be strongly restrained once the dosage of Co-TNTs is beyond 0.15 g/L. Although it is common that there are optimum dosages for different catalysts in previous reports, this value for Co-TNTs is rather low, which endows Co-TNTs with an attractive prospect in potential applications. In our opinion, this phenomenon may be linked with considerable catalytic activity resulted from the highly isolated Co^{2+} sites.

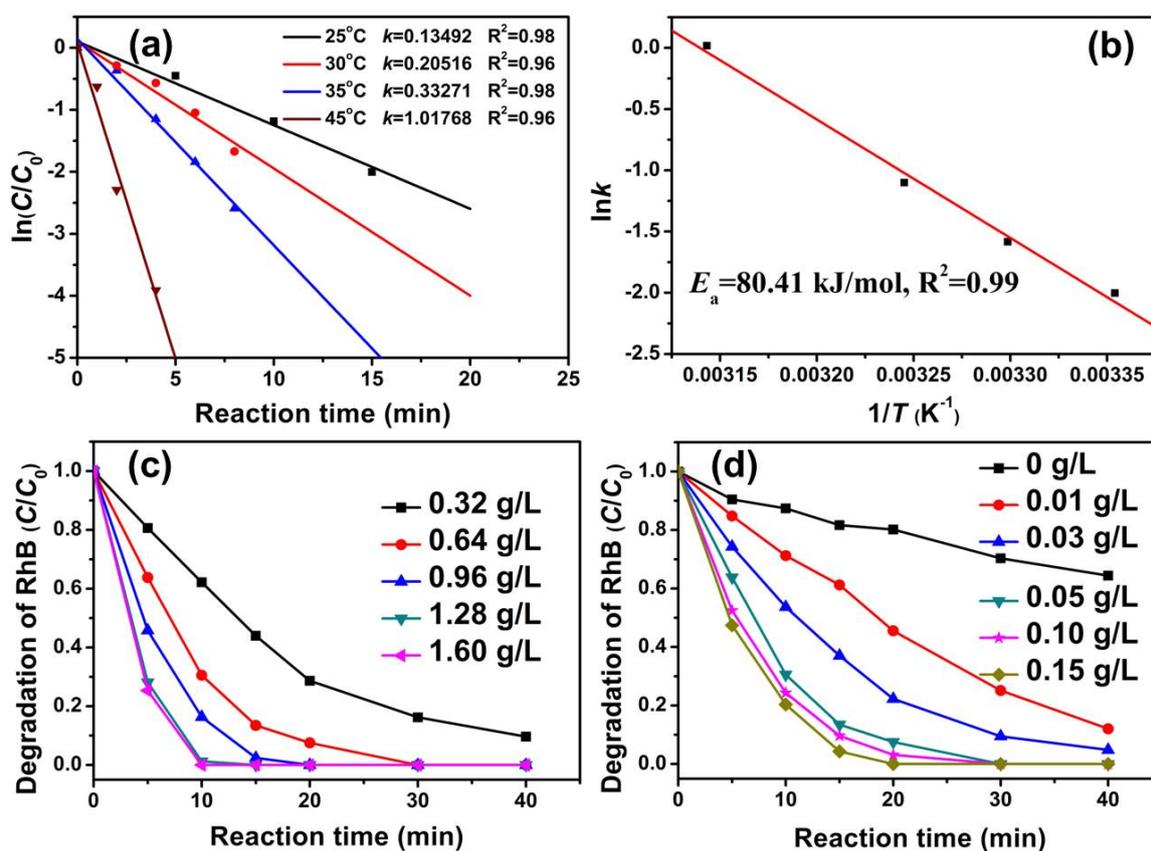


Figure 4 Kinetic curves (a) and the Arrhenius curve (b) of RhB removal at different temperature in Co-TNTs/PMS system. Effects of PMS concentration (c) and Co-TNTs dosage (d) on RhB degradation.

It is well known that sulfate-radical based advanced oxidation process can work in a wider pH range as compared with conventional Fenton reaction [3]. Figure 5a reveals that the degradation efficiency of RhB increases considerably when the initial pH value rises from 3.4 to 10.0, and decreases significantly at 11.0. The relatively weak RhB removal under acidic condition is due to the strong hydrogen bond between H^+ and O-O bond in PMS that will obviously inhibit the interaction

between PMS and Co-TNTs. The hydrogen bond will be continuously weakened with increasing the pH value, thus the degradation efficiency of RhB can be remarkably improved under near neutral condition. Meanwhile, hydroxyl radicals will be inevitably introduced into the catalytic system, particularly under alkaline condition, they can also contribute to the oxidation process greatly. However, the pK_a of PMS, namely the second pK_a of H_2SO_5 , is about 9.4, and thus strong alkaline condition can induce PMS to deprotonate and transform into less oxidative SO_5^{2-} , which should be responsible for the sharp decrease in degradation efficiency [11]. The recycling tests are carried out to investigate the catalytic stability of Co-TNTs (Fig. 5b). It is found that the degradation efficiency of RhB in 30 min decreases from 100% to 56.1% after three times cycling, and the analysis indicates that the leaching of active sites (Co^{2+}) is the primary reason. Interestingly, the reloading Co^{2+} on the repetitiously used Co-TNTs can recover its catalytic activity, demonstrating the easy regeneration of this novel catalyst.

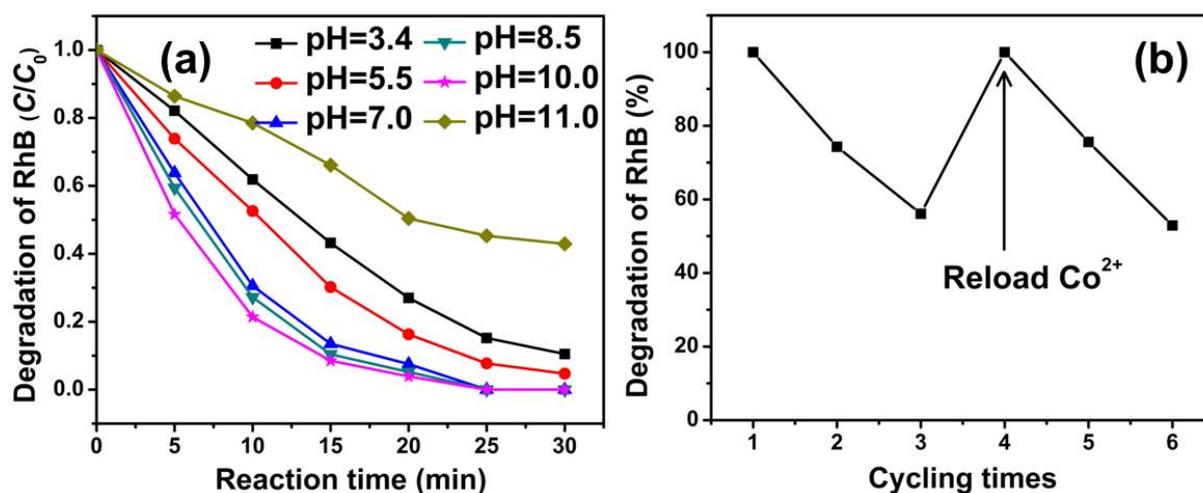


Figure 5 Effect of initial pH value on RhB degradation (a) and reusability tests of Co-TNTs for RhB degradation.

Conclusions

1. A novel heterogeneous catalyst, Co-TNTs, could be easily prepared by simple ions exchange between Co^{2+} and titanate nanotubes. The process of ion exchange did not destroy the basic structure of TNTs, but produced highly isolated Co^{2+} sites on the surface of TNTs.
2. Co-TNTs exhibited better catalytic activity than conventional $CoFe_2O_4$ and Co_3O_4 in PMS activation for RhB degradation, where Co-TNTs could promise a complete removal of RhB in 30 min, while $CoFe_2O_4$ and Co_3O_4 only presented RhB degradation at 78.0% and 64.4% after 40 min, respectively.
3. When the reaction temperature was manipulated from 25 °C to 45 °C, the kinetic rate constants would be sharply increased from 0.135 min^{-1} to 1.018 min^{-1} , and the corresponding E_a for RhB degradation was 80.41 kJ/mol.
4. Highly isolated Co^{2+} sites resulted in the low optimum dosages for PMS (1.28 g/L) and catalyst (0.15 g/L), suggesting an attractive prospect of Co-TNTs in potential applications. Co-TNTs/PMS catalytic system could work in a wide pH range from 5.5 to 10.0.
5. Co-TNTs were catalytically active in repeated batch experiments, and its activity could be easily recovered by reloading Co^{2+} .

Acknowledgement

This research was financially supported by Open Project of State Key Laboratory of Urban Water Resource and Environment, HIT (QA201414), China Postdoctoral Science Foundation (2014T70341

and 2013M541394).

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