

Feasibility of Pd-catalytic onto nontronite mineral and H₂O₂ produced from H₂ and O₂ to degrade organic contaminants

Yasir AlAni¹

(Received 25/11/2016; accepted 1 /1/ 2017)

Abstract

A novel electro-Fenton process based on Pd-catalytic production of H₂O₂ from H₂ and O₂ has been studied and examined recently for altering and degrading organic contaminants in different types of wastewaters. The study endeavors to synthesize an integrated catalyst by loading Pd onto the clay mineral, nontronite, (Pd/NTm) so that H₂O₂ and Fe(II) can be produced simultaneously in the electrolytic system. In an undivided electrolytic cell, rhodamine B, a probe organic contaminant, is degraded by 93% within 60 min under conditions of 50 mA, 1 g/L Pd/NTm, pH 3 and 20 mg/L initial concentration. A distinct mechanism, reductive dissolution of solid Fe(III) in nontronite by atomic H chemisorbed on Pd surface, is responsible for Fe(II) production from Pd/NTm.

Key Words: Pd-catalytic, electro-Fenton, nontronite, organic contaminants, degradation

دراسة امكانية ازالة المواد العضوية باستخدام المعدن الطيني (النوترونايت) مع عامل مساعد (Pd) والفتون (H₂O₂) المنتج مختبريا

ياسر العاني

الخلاصة

تم دراسة استحداث طريقة جديدة لازالة المواد العضوية بالاعتماد على طريقة الالكتر-فتون المخضر مختبريا وباستخدام العامل المساعد عنصر البلاديوم وكذلك الحديد الموجود في المعدن الطيني النوترونايت. سعت الدراسة الى تحميل العامل المساعد على المعدن. وبذلك تم ازالة المركبات العضوية باستخدام الفتون والحديد من المعدن الطيني (Pd/NTm) الطيني وتحضير المركب. وتم استخدام المركب العضوي (رودمين - ب) كملوث ويتم معالجته و قد حصلت على كفاءة ازالة تصل الى 93% خلال 60 دقيقة وقد كان معدل التيار الكهربائي المستخدم بمعدل 50 ملي امبير وباستخدام 1غم/لتر وكان الرقم الهيدروجيني 3 لازالة الملوث بتركيز 20 ملغم/لتر. تم توضيح ميكانيكية عملية الازالة و بيان عملية اختزال الحديد في المعدن الطيني من ثلاثي الى ثنائي التكافؤ.

1. Introduction

The electro-Fenton (EF) process has been widely used to treat wastewater-containing dyes, herbicides, antibiotics, and landfill leachate because of its convenience and strong oxidation ability [1-4]. In the EF process, Fe²⁺ is commonly obtained by the addition of ferrous salts, the reduction of Fe³⁺, or the oxidation of a sacrificial iron anode[5-9], while H₂O₂ is in situ generated via the electrochemical reduction of O₂ on the cathode, which can avoid the long distance transportation of H₂O₂. The commonly used cathodes include graphite, activated carbon fiber (ACF), carbon sponge, and so on [1,7,10]. However, these cathodes could only produce H₂O₂ by the two-electron reduction of molecular oxygen[11]. This single H₂O₂ generation way would restrict the efficiency of the EF process.

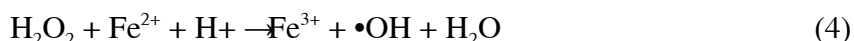
Recently, a novel E-Fenton process, termed Pd-based E-Fenton, was developed based on Pd-catalytic production of H₂O₂ from electro-generated H₂ and O₂. For instance, Yuan et al. developed

¹ Lecturer at Civil Engineering Department , University of Anbar.

a new Pd-based EF process to produce H_2O_2 via the reaction of electro-generated H_2 and O_2 on the Pd catalyst [12-14]. Water electrolysis produces O_2 and H^+ on the anode (Reaction 1), while produces H_2 and OH^- on the cathode (Reaction 2). Under acidic conditions, H_2O_2 is produced from the combination of H_2 and O_2 on the surface of Pd catalyst (Reaction 3) [15, 16]. In the presence of Fe^{2+} , $\bullet\text{OH}$ is produced by (Reaction 4). This process has shown high performance on degrading many organic contaminants including trichloroethylene [15], phenol [12] and toluene [17] in wastewater and groundwater.

In addition, because of wide spread occurrence of iron-bearing clays and clay minerals in soils and sediments, several studies have examined the reactivity of structural Fe^{2+} in chemically reduced montmorillonite, nontronite, illite, vermiculite, and kaolinite towards heavy metals reduction and immobilization [18-20].

Many types of clay minerals are ubiquitous in the environment and often contain iron in their structure, and they are the most plentiful and chemically active parts of the surface mineral world of earth [21]. Structural Fe(II) produced from chemical and microbial reduction of iron-bearing clay minerals has been shown to reduce a variety of contaminants through taking part in the redox reactions [22-24], and the Fe(II)/Fe(III) valence state is thought to be an important redox buffer across an extensive domain of redox conditions [25-27]. It has been shown in previous studies that reduced clay (containing structural Fe(II)) can reduce and mutate the contaminants fate and mobility such as chlorinated solvents [27-29], nitroaromatic compounds [30], and organic compounds [26]



In this study, a new integrated catalyst of Pd/Nontronite mineral (Pd/NTm) containing both Pd and Fe is synthesized and characterized. The performance of this new catalyst on simultaneously producing H_2O_2 and Fe^{2+} is evaluated for the Pd-based E-Fenton degradation of organic contaminants. Using Rhodamine B (RhB) as a probe organic contaminant and studying the effect of solution pH. The mechanisms of production of Fe^{2+} and reactive oxidizing species (ROS) will be elucidated. It is mainly aimed to provide an integrated catalyst for the simultaneous production of H_2O_2 and Fe^{2+} in the Pd-based E-Fenton process.

2. Research Method and Materials

2.1 Chemicals

Nontronite (purchased from the Source Clays Repository of the Clay Minerals Society (Purdue University, West Lafayette, Indiana, USA) was used for redox experiments. Rhodamine B (RhB) was purchased from Sinopharm Chemical Reagent Co. Ltd.. Palladium acetate was purchased from Shanxi Kaida Chemical Reagent Co. Ltd., China. $\text{Pd/Al}_2\text{O}_3$ powder (5% wt. Pd, Shanxi Kaida Chemical Ltd, China), with particle size of 1.5-5 μm , was used for comparison. Deionized water (18.0 $\text{m}\Omega\text{ cm}$) was obtained from a Millipore Milli-Q system and used in all the experiments. All other chemicals used in this study were higher than analytical grade.

2.2 Synthesis of Pd/NTm catalyst

Nontronite was reduced chemically using the sodium citrate, bicarbonate, and dithionite (CBD) method as explained by Stucki [30].

0.5g of nontronite in a flask, then adding 0.2g of sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_4$), 20mL of deionized water, and 10mL of CB buffer salts (1 M sodium bicarbonate and 0.9 M sodium citrate in 24:1 mixing rate), and later put in water bath at 70 °C for 4 hrs. After one hour cooling, the reductive nontronite was centrifuged and washed by 1MNaCl and finally washed five times by D.I. water.

2.3 Pd/NTm catalyst Characterization by XRD

The finely grinded particles were characterized by X-ray diffraction (XRD) on a D8-FOCUS X-ray diffractometer with Cu K radiation (Bruker AXS., Germany). The analysis was carried out at 40 KV and 40 mA at the scanning step size of 0.01° and step time of 0.05 s.

To detect any mineralogical changes as a result of chemical reduction and reaction with (RhB), XRD was performed for unreduced and reduced clay minerals. Clay mineral were prepared on petrographic slides and air-dried overnight at 30 °C inside a glove box incubator.

2.4 Degradation Experiments

The degradation was carried out in a conventional undivided electrolytic cell. An MMO mesh was used as the anode and cathode spaced in parallel position to sustain water electrolysis. For each test, 200 mL of 20 mg/L (RhB) solution was transferred into a glass beaker (250 mL), and 1 g/L Pd/NTm was added. The solution was mechanically stirred using a Teflon-coated magnetic stirring bar. The reaction temperature was 25 ± 1 °C. A constant electric current of 50 mA was applied with a cell potential of about 12 V. Solution pH was adjusted to neutral by addition of dilute 1 M H_2SO_4 and 1 M NaOH before electrolysis and was not adjusted during the process.

The effects of initial solution pH (3 and 7) was studied to investigate the acidity and neutral conditions. About 1 mL of aqueous solution was taken out at predetermined time intervals for analysis of (RhB). (RhB) samples were analyzed by a spectrometer (UV-1800 PC, Shanghai Mapada Spectrum Instrument Co., Ltd.) at detection wavelengths of 550 nm.

3. Results

3.1 XRD Characterization

XRD spectra of the novel Pd/NTm catalyst is exhibited in Fig. 1. It is evident that a series of characteristic diffractive peaks of crystal materials can be observed at certain (2θ).

As shown in Figure, XRD patterns showed that the Hanford sediments were dominated by quartz, albite, muscovite, mica, illite, nontronite, and goethite.

The Pd/NTm catalyst XRD pattern results show that diffraction peaks of unreduced nontronite appear at (2θ) of 8° peaks that attributed to the crystal of Fe(III), meanwhile the XRD profiles for chemical reduced nontronite showed peaks around 28 ° which denoted by (*) are indicative of crystalline of Fe(III).

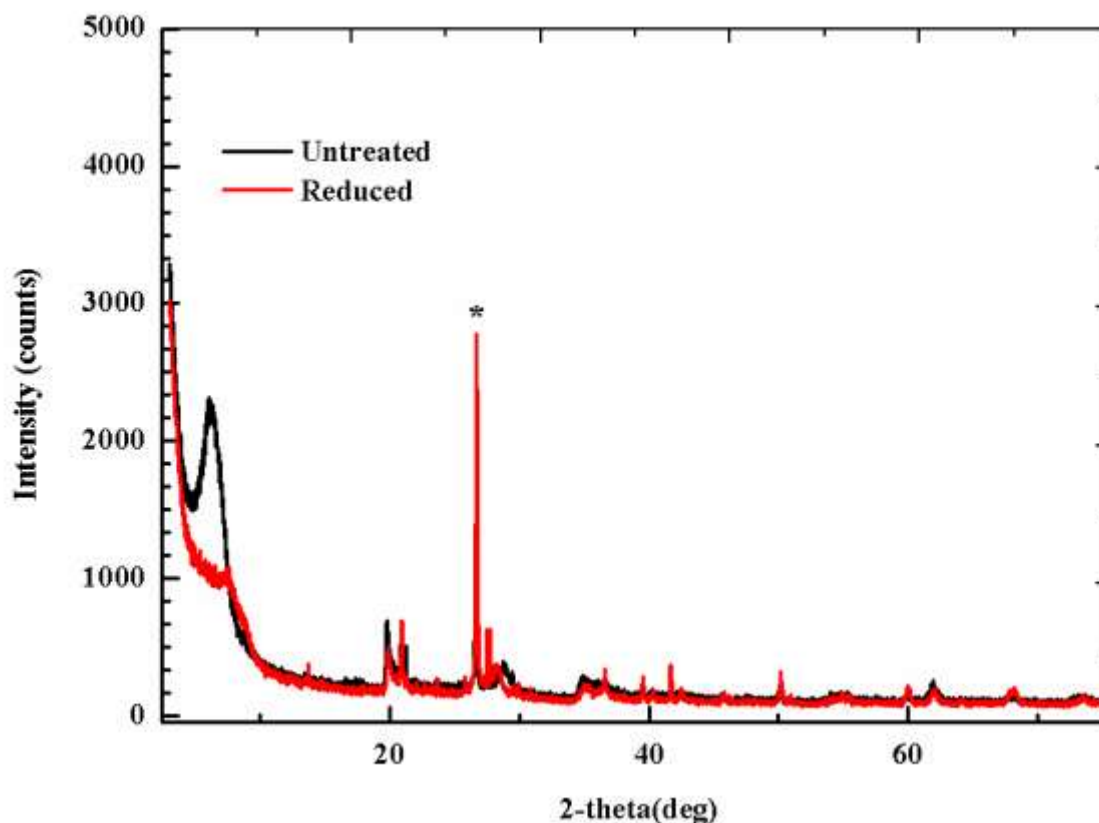


Figure 1, XRD spectra of the novel Pd/NTm catalyst

3.2 Neutral Conditions

Figure (2) reveals the results of (RhB) degradation in neutral conditions where pH of the solution is 7. Each curve in this figure represented an experiment of removal along 60 minutes under different cases to show the effect of Pd-catalytic onto nontronite mineral on the efficiency on the degradation. Firstly, a preliminary experiment was implemented by using a raw and reductant clay mineral (nontronite) to study its ability to reduce the (RhB) concentrations in wastewaters as well as the E-Fenton application. The results elucidated that the removal efficiency of (RhB) was higher in case we use reductant nontronite than using raw nontronite in E-Fenton process that because of the ferric produced from the reduction process on the clay mineral. From the figure we can conclude that under neutral conditions of pH 7 the removal efficacy could be more by uploading the mineral by Pd-catalytic which enhance the removal process by its activity on E-fenton and ferrous iron produced by the reluctant nontronite that finally transferred to ferric which is easily removed by precipitation process. The figure revealed that the E-Fenton process is inefficient to degrading such types of organic contaminants used in this study represented by (RhB). Figure (1) show that Pd-catalytic onto nontronite mineral and H_2O_2 produced from H_2 and O_2 to degrade (RhB) at an efficiency of 71% within 60 minutes at pH 7.

3.3 Acidic Conditions

The experiments were implemented in another conditions which different to that used in first part of the results to explain the effect of acidity on the overall removal of (RhB) which explained in Figure (2).

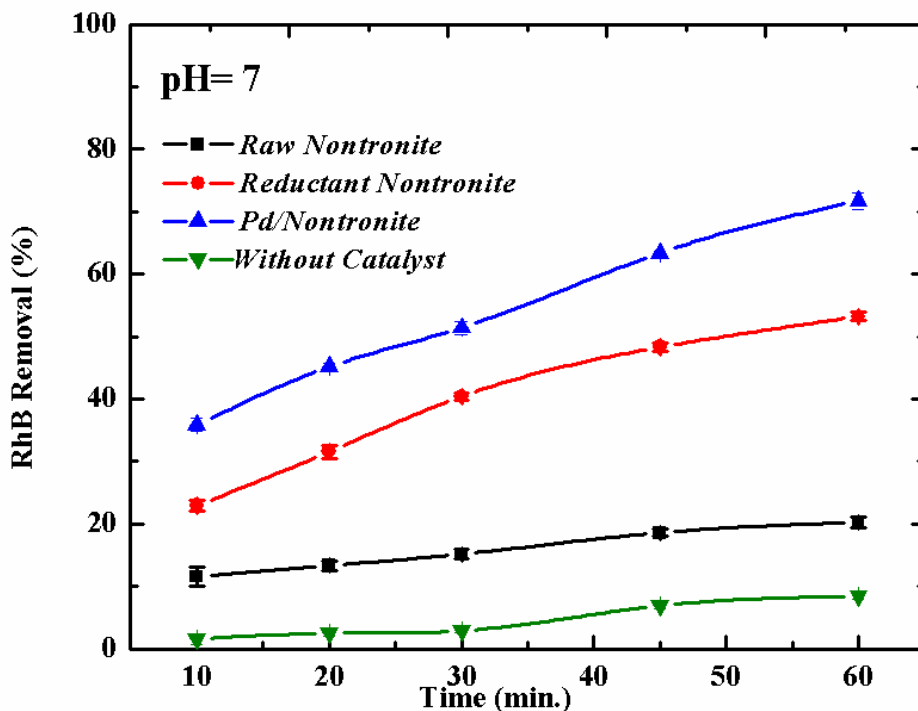


Figure 2, (RhB) degradation in neutral conditions.

Figure (3) illustrated that when the (RhB) solution has an acidic nature then this will lead to enhance the removal efficiency of (RhB) to more than 93% within one hour. The enhancement was got from the increment of ferric production in the nontronite reduction process that generated.

After reduction process a blue green color was observed for reductive nontronite that can give an index that reduction was successful chemically, hereafter in synthesizing process it was changed to a greenish yellow color after supporting Pd as a result of oxidation. The figure accentuates that 93% of (RhB) was degraded by the improved Pd-based E-Fenton process using the Pd/ NTm catalyst within 60 min under conditions of 50 mA, 1 g/L Pd/ NTm, pH 3 and (20mg/L) (RhB) initial concentration. H_2 and O_2 produced from water electrolysis on the Pt electrodes dissolve into the solution, and then are chemisorbed on the Pd surface. Chemisorption of H_2 on the Pd surface produces atomic H, while chemisorption of O_2 on the Pd surface prolongs the O=O double bond. H_2O_2 was produced by the combination of two atomic H and one activated O_2 . Fe(II) in nontronite could heterogeneously catalyze the decomposition of H_2O_2 into $\bullet OH$ radicals.

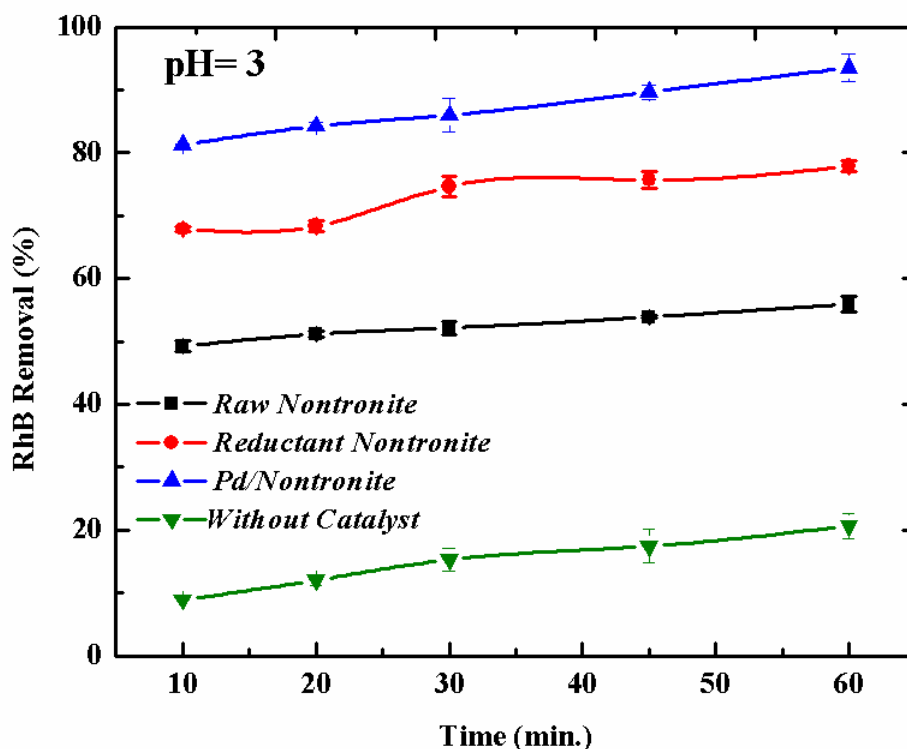


Figure 3, (RhB) degradation in acidic conditions.

Atomic H chemisorbed by Pd loaded on nontronite is a strongly reducing agent, which may reduce the solid Fe(III) in nontronite to Fe(II). Pd is the active component for the production of atomic H and H_2O_2 so that (RhB) degradation significantly more with Pd loadings on nontronite than raw nontronite. This is ascribed to the production of more H_2O_2 by supporting Pd on nontronite, which significantly contributed to the generation of $\bullet OH$ radicals. Therefore, $\bullet OH$ radicals can be supposed to be the predominant reactive oxidizing species for (RhB) degradation in this process.

5. Conclusion

This study demonstrates the generation of H_2O_2 in the presence of O_2 using Pd-based catalyst and H_2 . The production of low concentrations of $\bullet OH$ slightly contributes to (RhB) oxidation under neutral and acidic conditions. In particular, when Fe(II) is present, H_2O_2 efficiently decomposes to $\bullet OH$ resulting in a shift in dominant pathway from heterogeneous hydrodechlorination to homogeneous oxidation. This shift is most pronounced at high Fe(II) concentrations and low pH values. These findings may contribute to understanding the nature for organic contaminants degradation by Pd-catalytic hydrodechlorination in the presence of O_2 , especially when Fe(II) at a level of ppm is present. In the Pd-containing electrolytic system, oxidation of organic contaminants in general and especially (RhB) in the presence Fe(II) is proved to be significantly more effecting than hydrodechlorination in the absence Fe(II) under weak acidic conditions. The conclusions derived were set as, the organic contaminants represented by rhodamine B in this research were efficiently degraded by the addition of Pd/NTm into an undivided electrolytic cell under conditions of 50 mA, 1 g/L Pd/NTm, pH 3 and 20 mg/L initial concentration. As obvious, Pd/NTm catalyzed the production of H_2O_2 from anodic O_2 and cathodic H_2 . However, a distinct mechanism of Fe(II) production, the reductive dissolution of solid Fe(III) in nontronite by atomic H chemisorbed on Pd surface, was revealed.

References

- [1] Liu H., Wang C., Li X. Z., Xuan X. L., Jiang C. C., Cui H. N. A Novel Electro-Fenton Process for Water Treatment: Reaction- Controlled pH Adjustment and Performance Assessment Environ. Sci. Technol. 2007, 41, 2937–2942.
- [2] Moreira F. C., Garcia-Segura S., Boaventura R. A.R., Brillas E., Vilar V. J. P. Degradation of the Antibiotic Trimethoprim by Electrochemical Advanced Oxidation Processes Using a Carbon-PTFE Air-Diffusion Cathode and a Boron-Doped Diamond or Platinum Anode. Appl. Catal. B: Environ. 2014, 160, 492–505.
- [3] Zhang H., Ran X. N., Wu X. G. Electro-Fenton Treatment of Mature Landfill Leachate in a Continuous Flow Reactor. J. Hazard. Mater. 2012, 241, 259–266.
- [4] Borràs N., Oliver R., Arias C., Brillas E. Degradation of Atrazine by Electrochemical Advanced Oxidation Processes Using a Boron-Doped Diamond Anode. J. Phys. Chem. A 2010, 114, 6613–6621.
- [5] Yu F. K., Zhou M. H., Zhou L., Peng R. D. A Novel Electro- Fenton Process with H₂O₂ Generation in a Rotating Disk Reactor for Organic Pollutant Degradation. Environ. Sci. Technol. Lett. 2014, 1, 320–324.
- [6] Oturan M. A., Peirotten J., Chartrin P., Acher A. J. Complete Destruction of p-Nitrophenol in Aqueous Medium by Electro-Fenton Method. Environ. Sci. Technol. 2000, 34, 3474–3479.
- [7] Li J. P., Ai Z. H., Zhang L. Z. Design of a Neutral Electro- Fenton System with Fe@Fe₂O₃/ACF Composite Cathode for Wastewater Treatment. J. Hazard. Mater. 2009, 164, 18–25.
- [8] Zhao H. Y., Wang Y. J., Wang Y. B., Cao T. C., Zhao G. H. Electro-Fenton Oxidation of Pesticides with a Novel Fe₃O₄@Fe₂O₃/Activated Carbon Aerogel Cathode: High Activity, Wide pH Range and Catalytic Mechanism. Appl. Catal. B: Environ. 2012, 125, 120– 127.
- [9] Boye B., Farnia G., Sandona G., Buso A., Giomo M. Removal of Vegetal Tannins from Wastewater by Electroprecipitation Combined with Electrogenenerated Fenton Oxidation. J. Appl. Electrochem. 2005, 35, 369–374.
- [10] Özcan A., Sahin Y., Koparal A. S., Oturan M. A. Carbon Sponge as a New Cathode Material for the Electro-Fenton Process: Comparison with Carbon Felt Cathode and Application to Degradation of Synthetic Dye Basic Blue 3 in Aqueous Medium. J. Electroanal. Chem. 2008, 616, 71–78.
- [11] Brillas E., Sirés I., Oturan M. A. Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. Chem. Rev. 2009, 109, 6570–6631.
- [12] Luo M. S., Yuan S. H., Tong M., Liao P., Xie W. J., Xu X. F. An Integrated Catalyst of Pd Supported on Magnetic Fe₃O₄ Nanoparticles: Simultaneous Production of H₂O₂ and Fe²⁺ for Efficient Electro-Fenton Degradation of Organic Contaminants. Water Res. 2014, 48, 190–9.
- [13] Liao P., Yuan S. H., Chen M. J., Tong M., Xie W. J., Zhang P. Regulation of Electrochemically Generated Ferrous Ions from an Iron Cathode for Pd-Catalytic Transformation of MTBE in Groundwater. Environ. Sci. Technol. 2013, 47, 7918–26.
- [14] Yuan S. H., Fan Y., Zhang Y. C., Tong M., Liao P. Pd- Catalytic in situ Generation of H₂O₂ from H₂ and O₂ Produced by Water Electrolisis for the Efficient Electro-Fenton Degradation of Rhodamine B. Environ. Sci. Technol. 2011, 45, 8514–20.
- [15] Yuan S. H., Mao X. H. & Alshawabkeh A. N. Efficient degradation of TCE in groundwater using Pd and electro-generated H₂ and O₂: A shift in pathway from hydrodechlorination to oxidation in the presence of ferrous ions. Environ. Sci. Technol. 46, 3398–3405 (2012).
- [16] Yuan S. H., Chen M. J., Mao X. H. & Alshawabkeh A. N. A three-electrode column for Pd catalytic oxidation of TCE in groundwater with automatic pH regulation and resistance to reduced sulfur compound foiling. Water Res. 47, 269–278 (2013).
- [17] Liao P., Al-Ani Y., Ismael Z.M. & Wu X. Insights into the Role of Humic Acid on Pd-catalytic Electro-Fenton Transformation of Toluene in Groundwater. Scientific Reports. 5, 1–7(2015).
- [18] Gan H., Bailey G. W. and Yu Y. S. (1996) Morphology of lead(II) and chromium(III) reaction products on phyllosilicate surface as determined by atomic force microscopy. Clay Clay Miner. 44, 734–743.
- [19] Taylor R. W., Shen S., Bleam W. F. and Tu S. (2000) Chromate removal by dithionite-reduced clays: evidence from direct X-ray adsorption near edge spectroscopy (XANES) of chromate reduction at clay surfaces. Clays Clay Miner. 48, 648–654.
- [20] Zhuang F. F., Claire F. and White M. L. (2012) New redox-active material for permeable water remediation systems. Appl. Clay Sci. 59–60, 26–35.
- [21] Velde, B. (2013) Origin and mineralogy of clays: clays and the environment, Springer Science & Business Media.
- [22] Favre F., Stucki J.W. and Boivin P. (2006) Redox properties of structural Fe in ferruginous smectite. A discussion of the standard potential and its environmental implications. Clays and clay minerals 54(4), 466–472.
- [23] Gorski C.A., Aeschbacher M., Soltermann D., Voegelin A., Baeyens B., Marques Fernandes M., Hofstetter T.B. and Sander M. (2012) Redox properties of structural Fe in clay minerals. 1. Electrochemical quantification of electron-donating and-accepting capacities of smectites. Environmental science & technology 46(17), 9360–9368.
- [24] Neumann A., Hofstetter T.B., Lüssi M., Cirpka O.A., Petit S. and Schwarzenbach R.P. (2008) Assessing the redox reactivity of structural iron in smectites using nitroaromatic compounds as kinetic probes. Environmental science & technology 42(22), 8381–8387.
- [25] Riedel T., Zak D., Biester H. and Dittmar T. (2013) Iron traps terrestrially derived dissolved organic matter at redox interfaces. Proceedings of the National Academy of Sciences 110(25), 10101–10105.
- [26] Elsner M., Schwarzenbach R.P. and Haderlein S.B. (2004) Reactivity of Fe (II)-bearing minerals toward reductive transformation of organic contaminants. Environmental science & technology 38(3), 799–807.
- [27] Lalonde K., Mucci A., Ouellet A. and Gélinas Y. (2012) Preservation of organic matter in sediments promoted by iron. Nature 483(7388), 198–200.
- [28] Neumann A., Hofstetter T.B., Skarpeli-Liati M. and Schwarzenbach R.P. (2009) Reduction of polychlorinated ethanes and carbon tetrachloride by structural Fe (II) in smectites. Environmental science & technology 43(11), 4082–4089.
- [29] Hofstetter T.B., Neumann A. and Schwarzenbach R.P. (2006) Reduction of nitroaromatic compounds by Fe (II) species associated with iron-rich smectites. Environmental science & technology 40(1), 235–242.
- [30] Stucki J.W., Golden D. and Roth C.B. (1984) Preparation and handling of dithionite-reduced smectite suspensions. Clays Clay Miner 32(3), 191–197.