Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2017.21276

88 (2017) 122–127
September

Sonocatalytic degradation of methylene blue using biochars derived from sugarcane bagasse

Guoting Li[a,*], Xi Chen[a], Luyang Xu[a], Pengcheng Lei[a], Shan Zhang[a], Cun Yang[a], Qianying Xiao[a], Weigao Zhao[b]

[a]*Department of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450011, China, Tel. +86-371-69127436, Fax +86-371-65790239, email: lipsonny@163.com (G. Li), 252680963@qq.com (X. Chen), 18738147061@163.com (L. Xu), 13027510953@163.com (P. Lei), 13027510309@163.com (S. Zhang), 15638140797@163.com (C. Yang), 13027511625@163.com (Q. Xiao)*
[b]*School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China, email: 7649222@qq.com (W. Zhao)*

Received 9 March 2017; Accepted 2 August 2017

ABSTRACT

Biochars derived from abundant natural biomasses have a very close and practical application for environmental pollution remediation. In this research, one innovative application of biochar derived from sugarcane bagasse was conducted for sonocatalytic degradation of methylene blue. Surface morphologies of the biochar pyrolized at 600°C (BC600) demonstrate that the biochar mainly consists of thin flakes with a size ranged from 10 μm to 50 μm. Although the surface area of BC600 is very limited, its sonocatalytic performance outperformed those bagasse biochars pyrolized at other temperatures. The degradation process was well fitted by pseudo-first-order kinetic model. The pseudo-first-order rate constant (K_{app}) of the sonocatalytic process was 1.77 times that of the sum of K_{app} values of both ultrasonication and catalyst adsorption, indicating a significant synergetic effect. Increasing catalyst dosage and ultrasonic power enhanced the degradation efficiency apparently. The highest sonocatalytic degradation efficiency was observed at pH 5.0. Oxidation mechanism was explored through quenching tests by iso-propanol and KBr. It indicates that, during the sonocatalytic degradation of methylene blue using bagasse biochar, a free radical chain reaction was proved to occur predominately in the interfacial region while to a lesser extent in bulk solution.

Keywords: Bagasse biochar; Advanced oxidation processes; Sonocatalytic degradation; Methylene blue; Synergetic effect

1. Introduction

Concerning removal and separation of organic pollutants from aqueous solution, many technologies have been studied and applied during water purification and recovery. These traditional technologies including coagulation, adsorption, reverse osmosis and ion exchange are generally efficient [1–4]. Nevertheless, these technologies just transfer organic pollutants from water to another phase, which could definitely cause secondary pollution. For treatment of some antibiotics such as tetracyclines, these conventional technologies including biotreatment are not as efficient as expected [5]. In contrast, due to generation of a number of strong oxidizing species such as hydroxyl radicals and hydrogen peroxide, advanced oxidation processes (AOPs) are capable of degrading and even mineralizing these organic pollutants into carbon dioxide, inorganics and water [6]. Almost all types of organic contaminants can be degraded into harmless products by AOPs [7]. Thus, many AOPs have demonstrated an excellent future for the degradation and removal of a series of organic pollutants.

Among these AOPs, sonochemical degradation processes including sonolysis and sonocatalysis have drawn

---

*Corresponding author.

increasing attention in recent years. During sonochemical process, acoustic cavitation generates hot spots with localized temperatures and pressures on the order of 5000 K and hundreds of atmospheres, respectively. Thermal dissociation of water vapor generates highly reactive hydroxyl radicals and other oxidizing species [8–10]. These oxidizing species are continuously produced by ultrasonication and contribute to the decomposition of organic contaminants. However, the degradation efficiency of ultrasonication alone is too low to be applied in practical water treatment. Hence, sonocatalytic process is developed to enhance degradation efficiency in which sonocatalyst is introduced into the ultrasonication system. Various sonocatalysts including MnO_2/CeO_2, Tb_7O_{12}/TiO_2, TiO_2 and ZnO were used for sonocatalytic process [11–14]. As such, sonocatalytic process attracted wider attention because it was capable of degrading a large variety of organic pollutants more efficiently. Further, the design of sonocatalyst plays a key role as the catalytic activity determines the degradation efficiency directly. Usually, most of the sonocatalysts being explored are inorganic matrix such as expensive metal oxides. Actually, low-cost sonocatalysts are expected as they are the most probably applied into practical water purification.

Carbonaceous materials such as waste biomass are abundant in natural environment. Carbonaceous sonocatalysts could be cost-effective for application. Biomass-based sonocatalysts might be good candidates as some carbonaceous materials have unique particle size, surface structures and functional groups. Raw biomasses are usually not suitable for sonocatalytic degradation process due to the apparent organic leaching. Differently, biochars, which is derived from the biomass via incomplete combustion operations such as pyrolysis and carbonization, are carbon-rich and stable enough to avoid organic leaching and secondary pollution [15–17]. Most of the biochars are simply prepared from waste material and they are widely explored for practical application. One example is the utilization of low-temperature pyrolyzed biochar as adsorbents for the removal of environmental pollutants has emerged as a promising technology [18–20]. The environmental friendly biochars are playing more and more important roles in water purification.

In this study, for the first time, sonocatalytic performance of biochar for the degradation of methylene blue is innovatively and systematically investigated. The biochar pyrolized from sugarcane bagasse was utilized as it had a better sonocatalytic activity than other biochars involved. Effect of pyrolytic temperature of biochar, sonocatalyt dosage and synergetic effect were investigated. Additionally, the oxidation mechanism was indirectly evaluated by adding scavengers such as iso-propanol and KBr.

2. Materials and methods

2.1. Materials and apparatus

Methylene blue (mass fraction > 98.5%, chemical pure) was purchased from Tianjin Chemical Reagent Research Institute. The other chemicals used were of analytical grade. Sonication was performed in a 40 kHz ultrasonic cleaning bath (AS3120A, Jiangsu Kunshan Ultrasonic Instrument Co., China). Deionized (DI) water was used to prepare all solutions.

2.2. Preparation of sugarcane bagasse biochar

The detailed procedures for the preparation of the sugarcane bagasse biochars can be referred to our previous study [21]. Briefly, the bagasse biomass was washed, dried, crushed and sieved using a 100 mesh sieve. The bagasse biochars were prepared via pyrolyzing the bagasse biomass at various temperatures under oxygen-limited conditions for 2 h. Subsequently, the prepared biochars were subjected to demineralization in a 4 mol/L HCl solution for 12 h. The separated residues were rinsed with DI water to neutral solution pH and then dried in an oven at 80°C overnight. The treated biochars were finally preserved in a desiccator for further use. The prepared bagasse biochars pyrolyzed at 200°C, 300°C, 400°C, 500°C and 600°C were designated as BC200, BC300, BC400, BC500 and BC600.

2.3. Characterization

The morphologies of the bagasse biochar were recorded on a Philips Quanta-2000 scanning microscope coupled with an energy dispersive X-ray (EDX) spectrometer. The BET surface area, pore volume, and pore size of the bagasse biochars were determined using a Nova 4000e surface area and pore size analyzer.

2. 4. Sonocatalytic degradation of methylene blue by bagasse biochar

Sonocatalytic degradation of methylene blue (MB) was carried out in a beaker for 60 min. The available volume of the beaker was 250 mL and 200 mL of MB solution (5 mg/L) was added. The power of the ultrasonic cleaning bath was 50 W unless otherwise stated. The water-circulating unit was used to control water bath temperature.

2.5. Analyses

Samples were collected and filtered through a 0.45 µm membrane before analyzing. The concentration of MB was determined by measuring the maximum absorbance at a fixed wavelength 664 nm, using an UVmini-1240 spectrophotometer (Shimadzu, Japan).

The removal efficiency of MB was calculated as:

$$\text{Removal efficiency} = (1 - C_t/C_0) \times 100\% \quad (1)$$

The pseudo first-order kinetics for MB degradation was simulated as:

$$\ln(C_0 / C_t) = K_{app}t \quad (2)$$

where C_t is the MB concentration at time t, C_0 is the initial MB concentration, and K_{app} is the apparent first-order rate constant.

The decrease of apparent rate constant (pseudo first-order) K_{app} resulted from iso-propanol and KBr quenching can be used to indicate the contribution and contribution percentages of hydroxyl radicals and free radicals, which was calculated as the following equation [22, 23]:

$$\text{Contribution } K_{app} = K_{app} - K_{app}\text{ (quenching)} \tag{3}$$

$$\text{Contribution percentage} = (1 - K_{app}\text{ (quenching)}/K_{app}) \times 100\% \tag{4}$$

3. Results and discussion

3.1. Characterization of bagasse biochar (BC600)

As the surface morphologies of the biochars derived from sugarcane bagasse were adequately presented in our previous study [21], only the morphologies of the biochar pyrolyzed under 600°C (BC600) were demonstrated herein. Typically, as presented in Fig. 1, BC600 mainly consists of thin flakes with the sizes ranged from 10 µm to 50 µm. Usually, particles in this range benefit the sonocatalytic degradation under the experimental conditions. The carbon content increased from 57.7% of the raw bagasse to 75.3% of BC600. Considering the chemical inertness and stability of BC600, the bagasse biochar is expected to be suitable for sonocatalytic process.

Additionally, BET surface area and pore volumes of raw bagasse and biochars including BC300, BC400 and BC500 are listed in Table 1. Compared to the surface area 63.53 m^2/g of raw bagasse, the surface area of BC300, BC400 and BC500 significantly increased. This is consistent with the fact that the surface area of the biochars usually increases with an increase in pyrolytic temperature at up to ≤ 700°C [15]. The increased surface area of biochars is deduced to increase their sonocatalytic degradation performance to some extent.

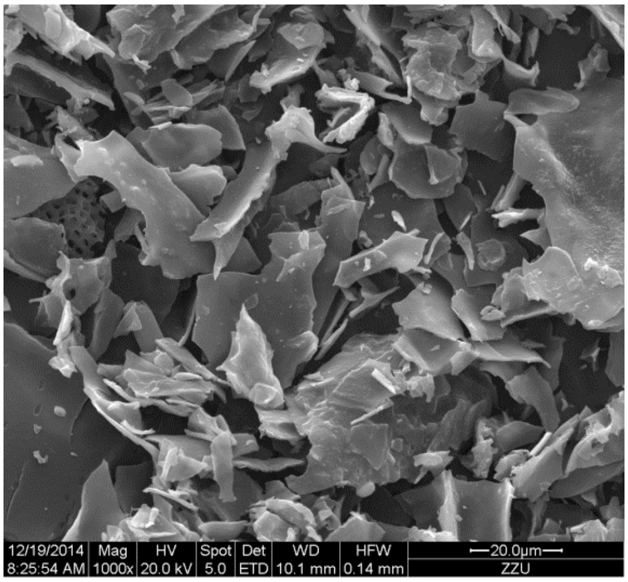

Fig. 1. SEM micrograph of the bagasse biochar pyrolyzed at 600°C.

Table 1
The BET surface areas and pore volumes of the raw bagasse and the biochars including BC300, BC400 and BC500

	raw BC	BC300	BC 400	BC 500
BET surface area (m^2/g)	63.53	177. 3	115.6	138.4
Total pore volume (cm^2/g)	0.05480	0.1532	0.1253	0.1402
Pore size (nm)	3.450	3.457	4.336	4.053

3.2. Effect of pyrolytic temperature of biochar on the sonocatalytic degradation of MB

As we know, the application of biochar avoids organic leaching and secondary pollution from the raw biomass, which could facilitate the application of biochars. The carbon content, stability, structure and surface properties of the biochars could be regulated by the varied pyrolytic temperature [16,24]. It is expected that the pyrolytic temperature for biochars production might be one of the most significant parameters influencing the sonocatalytic performance. Accordingly, the effect of pyrolytic temperature of biochars on the sonocatalytic degradation of MB was investigated and the results are plotted in Fig. 2. By pseudo-first-order kinetic simulation, the K_{app} values for the BC200, BC300 BC400, BC500 and BC600 are of 0.0204, 0.0165, 0.0229, 0.0178 and 0.0242 min^{-1} (R^2 = 0.919, 0.916, 0.992, 0.884 and 0.989), respectively. Evidently, the increased pyrolytic temperature is beneficial for the sonocatalytic degradation of MB. Though BC400, BC500 and BC600 have a better sonocatalytic degradation performance as well, the highest K_{app} value was observed for BC600. However, as list in Table 1, the surface area of BC600 is notably lower than those of other biochars, which was deduced to be unfavorable for the adsorption and subsequent degradation of MB before test. Considering the effect of surface area and stability of biochars, the bagasse biochar BC600 is more eligible for sonocatalytic degradation and it was therefore selected in the following tests.

3.3. Synergetic effect for the sonocatalytic degradation process

Synergetic effect of an excellent sonocatalyst is usually investigated during sonocatalytic degradation. As pre-

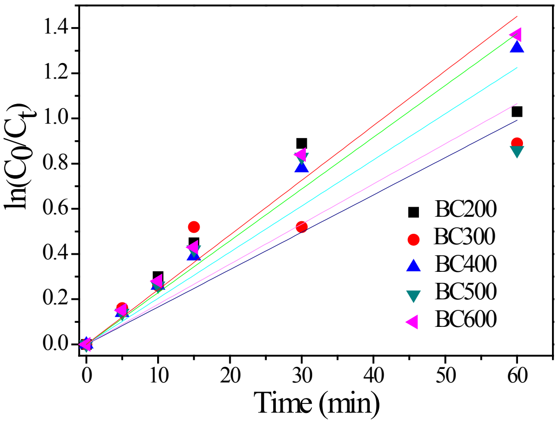

Fig. 2. Effect of pyrolytic temperature of biochars on the sonocatalytic degradation of MB. Catalyst dosage 150 mg in 200 mL MB solution, at neutral solution pH.

sented in Fig. 3, three processes including ultrasonication alone, catalyst adsorption alone and the combined sonocatalytic degradation process were compared within 60 min. The K_{app} values for ultrasonication, catalyst adsorption and sonocatalytic degradation process were of 3.84×10^{-4}, 0.0133 and 0.0242 min^{-1} (R^2 = 0.966, 0.989 and 0.998), respectively. The K_{app} for the combined process is 1.77 times that of the sum of K_{app} values of the other two processes, indicating a significant synergetic effect. Meanwhile, the adsorption of MB almost achieved equilibrium within several hours while the degradation of MB could be maintained continuously. From this point of view, the synergetic effect of the sonocatalytic degradation process could be more significant with a prolonged reaction time.

3.4. Effect of biochar dosage on MB degradation

The effect of catalyst dosage on the sonocatalytic degradation of MB was also investigated, as illustrated in Fig. 4. The dosages of 50, 100, 150 and 200 mg in 200 mL of solution with MB concentration of 5 mg/L were selected. It can be observed that the K_{app} values for the dosages at 50, 100, 150 and 200 mg were of 0.00838, 0.0143, 0.0242 and 0.0280 min^{-1} (R^2 = 0.992, 0.999, 0.989 and 0.988), respectively. The increased catalyst dosage enhanced the degradation efficiency apparently as a result of the increased catalyst sites on the bagasse biochar. Compared to the dosage of 150 mg, the K_{app} value at the dosage of 200 mg was not increased notably and the biochar dosage was fixed at 150 mg in the following tests.

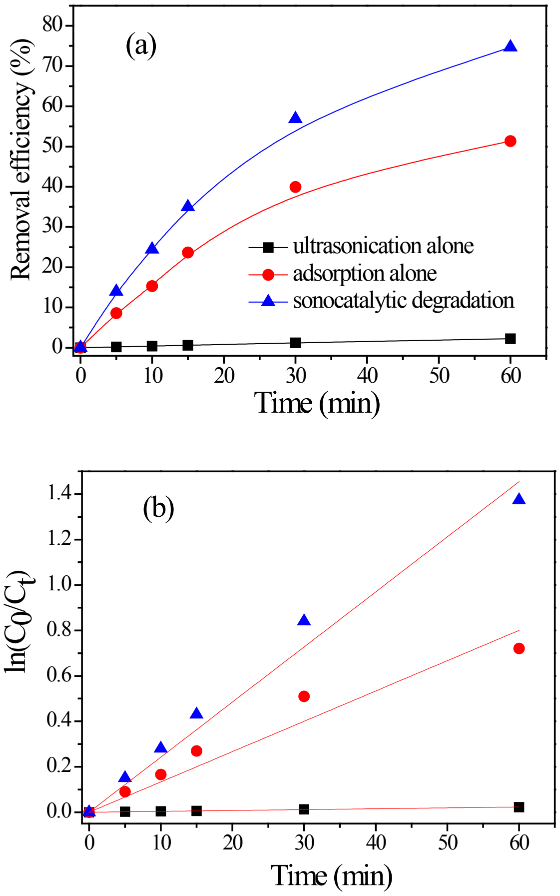

Fig. 3. Removal efficiency as a function of time (a) and pseudo-first-order degradation (b) of MB by sonocatalytic process. BC600 dosage 150 mg in 200 mL MB solution. MB concentration 50 mg/L, at neutral solution pH.

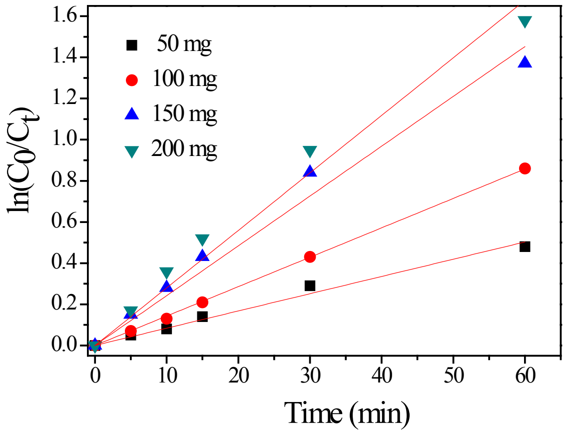

Fig. 4. Effect of biochar BC600 dosage on the sonocatalytic degradation of MB.

3.5. Effect of solution pH on MB degradation

Solution pH is always an important factor influencing the degradation efficiency as the interaction between MB molecules and the biochar is usually dependent on pH conditions. Effect of solution pH on the sonocatalytic degradation of MB was investigated and the results are illustrated in Fig. 5. The K_{app} values at pH 3.0, 5.0, 7.0, 9.0 and 11.0 are 0.0173, 0.0301, 0.0242, 0.0234 and 0.0231 min^{-1} (R^2 = 0.993, 0.993, 0.989, 0.990 and 0.984), respectively. The highest degradation efficiency was observed at pH 5.0, which is consistent with the results of our previous study using fly ash as sonocatalyst [25]. Meanwhile, this result roughly suggests that the increasing solution pH values benefits

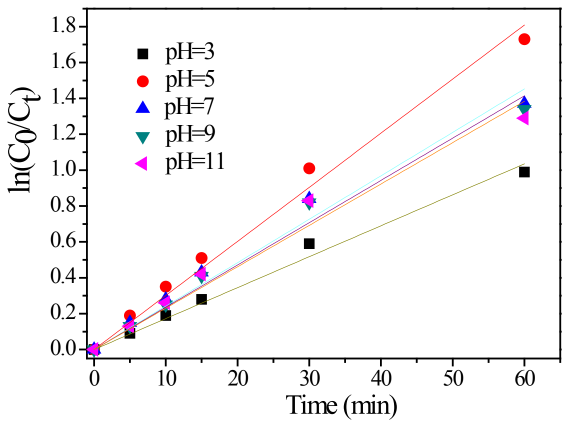

Fig. 5. Effect of solution pH on the sonocatalytic degradation of MB.

the sonocatalytic degradation of MB. MB is a cationic dye throughout the pH range examined while the normally negatively-charged bagasse biochar BC600 is expected to be more negatively-charged with the increasing solution pH [15]. As a result, the electrostatic attraction force could be enhanced and more dye molecules can be adsorbed onto the biochar. This is beneficial for the degradation of MB as the adsorption of MB is the first step for the total degradation process. On the other hand, the oxidizing species generated in sonocatalytic process are dependent on solution pH conditions. With increasing concentration of OH^-, the generation of hydroxyl radicals is considered to increase as well. The oxidation mechanism by hydroxyl radicals is usually prevailing under alkaline condition [25,26]. As such, alkaline conditions are roughly beneficial for the sonocatalytic degradation of MB in this case.

3.6. Oxidation mechanism

As one of the typical advanced oxidation processes, sonocatalytic degradation of MB is based on the generation of a number of reactive oxygen species (ROSs) such as OH radicals, H_2O_2 and $HO_2\cdot^-$ [27]. Hydroxyl radicals are considered to be the key ROSs responsible for ultrasonic degradation. The generation of Hydroxyl radicals consists of complicated processes. Basically, hydroxyl radicals, H_2O_2 and other ROSs can be generated by sonolysis alone. Meanwhile, the formation of cavitation bubbles can be increased by the heterogeneous nucleation of bubbles, generating hot spots in the solution. These hot spots can cause H_2O molecules to pyrolyze to form more OH radicals as well. Actually, the generation of cavitation bubbles can be accelerated by the presence of heterogeneous catalyst which acts as nucleus. Once the size of catalyst particle is in the same order of magnitude as the resonance size of cavitation bubbles, these catalysts could act as cavitation nucleus. As estimated in our previous study [28], in which the sonocatalytic degradation was conducted under the same experimental conditions, the resonance size of cavitation bubbles in water is calculated to be 43.1 µm. As the size of bagasse biochar BC600 particles ranges from 10 µm to 50 µm, they could act as nucleus to enhance the generation of more cavitation bubbles and concurrently improve the ultrasonic degradation performance.

Alcohols such as iso-propanol (ISP) can scavenge hydroxyl radicals and they are often used as the quenchers of hydroxyl radicals to evaluate the production and contribution of hydroxyl radicals [22,23,29]. Alcohol is a known scavenger for the gaseous region and/or interfacial region of the collapsing bubble. Differently, potassium bromide (KBr) is known as a non-volatile scavenger which can be readily oxidized by free radicals from the bulk liquid region and possibly from the interfacial region of the cavitation bubble [30].

The inhibitive effect of ISP and KBr on the oxidation process can be quantatively indicated by the decline in reaction rate constants (K_{app}) [22,23,28,31]. As plotted in Fig. 6, the quenching effect of ISP (0.05 mol/L) and KBr (0.05 mol/L) on the sonocatalytic degradation of MB was investigated. The K_{app} values for the ISP and KBr quenching reaches 0.0105 and 0.0172 min^{-1} (R^2 = 0.879 and 0.978), respectively. Compared to the K_{app} value without quenching (0.0242 min^{-1}, R^2 = 0.989), the decline of K_{app} value (Contribution K_{app}) for ISP and KBr quenching amounts to 0.0137 and 0.00701 min^{-1}, respectively. Accordingly, the contribution percentage of hydroxyl radicals and free radicals from the bulk liquid region and possibly from the interfacial region reaches 56.5% and 29.0% to the total degradative capability, respectively. The role of hydroxyl radicals is much more predominant than that of other free radicals or oxidizing species. As a result, it indicates that during the sonocatalytic degradation of MB a free radical chain reaction occurs predominately in the interfacial region and to a lesser extent in bulk solutions.

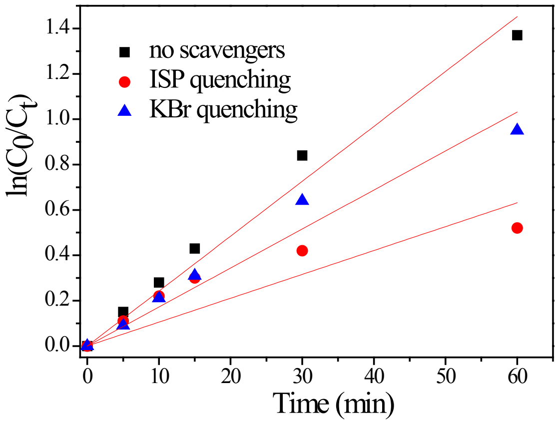

Fig. 6. Effect of iso-propanol (ISP, 0.05 mol/L) and KBr (0.05 mol/L) quenching on the sonocatalytic degradation of MB.

3.7. Effect of ultrasonic power

Effect of ultrasonic power on the sonocatalytic degradation of MB was investigated. The K_{app} values at an ultrasonic power of 50, 80 and 100 W were 0.0242, 0.0294 and 0.0422 min^{-1} (R^2 = 0.989, 0.988 and 0.970), respectively. Apparently, almost a linear relationship between the ultrasonic power and the K_{app} values was observed within this ultrasonic power range. This is because increasing ultrasonic power could increase the energy of cavitation while lower the threshold of cavitation. Consequently, the quantity of cavitation bubbles is enhanced [32]. As afore-mentioned results, the free radical chain reaction occurs predominately in the interfacial region of the bubbles. It can be deduced that more oxidizing species are generated in the interfacial region, which mainly contributes to the sonocatalytic degradation of MB.

4. Conclusion

The bagasse biochars were innovatively utilized as sonocatalytsts for the sonocatalytic degradation of methylene blue. The biochar pyrolized at 600°C (BC600) mainly consists of thin flakes with the size ranged from 10 µm to 50 µm. The surface area of BC600 is the lowest, while its sonocatalytic performance outperformed those biochars pyrolized at other temperatures. A significant synergetic effect was observed during the sonocatalytic process. Increased catalyst dosage and ultrasonic power enhanced the degradation efficiency apparently. The highest sonocatalytic degradation efficiency was observed at pH 5.0. A free radical chain reaction was proved to occur predominately in the interfacial region.

Acknowledgement

The Authors thank for the financial support from the National Natural Science Foundation of China (Grant No. 51378205), and the foundation for university key youth teacher by Henan Province of China (2013GGJS-088).

References

[1] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation /flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manage., 93(1) (2012) 154–168.

[2] V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, Adsorption of basic dyes on granular acivated carbon and natural zeolite, Wat. Res., 35 (2001) 3357–3366.

[3] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—development to date and future potential, J. Membr. Sci., 370 (2011) 1–22.

[4] H.A. Abdulgader, V. Kochkodan, N. Hilal, Hybrid ion exchange–Pressure driven membrane processes in water treatment: A review, Sep. Purif. Technol., 116 (2013) 253–264.

[5] D. Belkheiri, F. Fourcade, F. Geneste, D. Floner, H. Ait-Amar, A. Amrane, Combined process for removal of tetracycline antibiotic-Coupling pre-treatment with a nickel-modified graphite felt electrode and a biological treatment, Int. Biodeter. Biodegr., 103 (2015) 147–153.

[6] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today, 53 (1999) 51–59.

[7] S. Esplugas, P.L. Yue, M.I. Pervez, Degradation of 4-chlorophenol by photolytic oxidation, Water Res., 28 (1994) 1323–1328.

[8] Y.G. Adewuyi, Sonochemistry in environmental remediation. 1. Combinative and hybrid sonophotochemical oxidation processes for the treatment of pollutants in water, Environ. Sci. Technol., 39 (2005) 3409–3420.

[9] A. Henglein, Sonochemistry: historical developments and modern aspects, Ultrasonics, 25(1) (1987) 6–16.

[10] Y. Asakura, M. Maebayashi, S. Koda, Study on efficiency and characterization in a cylindrical sonochemical reactor, J. Chem. Eng. Jpn., 38 (2005) 1008–1014.

[11] H. Harada, Sonophotocatalytic decomposition of water using TiO_2 photocatalyst, Ultrason. Sonochem., 8 (2001) 55–58.

[12] H. Zhao, G.M. Zhang, Q.L. Zhang, MnO_2/CeO_2 for catalytic ultrasonic degradation of methyl orange, Ultrason. Sonochem., 21 (2014) 991–996.

[13] L.M. Song, C. Chen, S.J. Zhang, Sonocatalytic performance of Tb_7O_{12}/TiO_2 composite under ultrasonic irradiation, Ultrason. Sonochem., 18 (2011) 713–717.

[14] J. Wang, Z. Jiang, Z.H. Zhang, Y.P. Xie, X.F. Wang, Z.Q. Xing, R. Xu, X.D. Zhang, Sonocatalytic degradation of Acid Red B and Rhodamine B catalyzed by nano-sized ZnO powder under ultrasonic irradiation, Ultrason. Sonochem., 15(5) (2008) 768–774.

[15] M. Ahmad, A.U. Rajapaksha, J.E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S.S. Lee, Y.S. Ok, Biochar as a sorbent for contaminant management in soil and water: A review, Chemosphere, 99 (2014) 19–33.

[16] B.L. Chen, Z.M. Chen, Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures, Chemosphere, 76 (2009) 127–133.

[17] D. Mohan, A. Sarswat, Y.S. Ok, C.U. Pittman Jr., Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent—A critical review, Biores. Technol., 160 (2014) 191–202.

[18] J.W. Lee, B. Hawkins, D.M. Day, D.C. Reicosky, Sustainability: the capacity of smokeless biomass pyrolysis for energy production, global carbon capture and sequestration, Energ. Environ. Sci., 3 (2010) 1695–1705.

[19] M.X. Xie, W. Chen, Z.Y. Xu, S.R. Zheng, D.Q. Zhu, Adsorption of sulfonamides to demineralized pine wood biochars prepared under different thermochemical conditions, Environ. Pollut., 186 (2014) 187–194.

[20] Ma. Inyang, B. Gao, Y. Yao, Y.W. Xue, A.R. Zimmerman, P. Pullammanappallil, X.D. Cao, Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass, Biores. Technol., 110 (2012) 50–56.

[21] G.T. Li, W.Y. Zhu, L.F. Zhu, X.Q. Chai, Effect of pyrolytic temperature on the adsorptive removal of benzoquinone, tetracycline and PVA, Korean J. Chem. Eng., 33(7) (2016) 2215–2221.

[22] G.T. Li, K.H. Wong, X.W. Zhang, C. Hu, J.C. Yu, R.C.Y. Chan, P.K. Wong, Degradation of AO7 using magnetic AgBr under visible light: the roles of oxidizing species, Chemosphere, 76 (2009) 1185–1191.

[23] G.T. Li, M.Y. Zhu, J. Chen, Y.X. Li, X.W. Zhang, Production and contribution of hydroxyl radicals between the DSA anode and water interface, J. Environ. Sci., 23 (2011) 744 –748.

[24] Y.N. Sun, B. Gao, Y. Yao, J. Fang, M. Zhang, Y.M. Zhou, Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties, Chem. Eng., 240 (2014) 574–578.

[25] G.T. Li, Y.M. Feng, B.B. Wang, M.D. Wang, Contribution of hydroxyl radicals to the degradation of Acid Orange 7 by fly ash under ultrasonic irradiation. Desal. Water Treat., 57 (2016) 18168–18174.

[26] R. Kidak, N.H. Ince, Ultrasonic destruction of phenol and substituted phenols: A review of current research. Ultrason. Sonochem., 13 (2006) 195–199.

[27] J. Peller, O. Wiest, P.V. Ka, Synergy of combining sonolysis and photocatalysis in the degradation and mineralization of chlorinated aromatic compounds, Environ. Sci. Technol., 37 (2003) 1926–1932.

[28] G.T. Li, W.G. Zhao, B.B. Wang, Q.Y. Gu, X.W. Zhang, Synergetic degradation of Acid Orange 7 by fly ash under ultrasonic irradiation, Desal. Water Treat., 57 (2016) 2167–2174.

[29] Y. Sun, J.J. Pignatello, Evidence for a surface dual hole-radical mechanism in the titanium dioxide photocatalytic oxidation of 2,4-D, Environ. Sci. Technol., 29 (1995) 2065–2072.

[30] D.G. Wayment, D.J. Casadonte, Frequency effect on the sonochemical remediation of alachlor, Ultrason. Sonochem., 9 (2002) 251–257.

[31] M. Stylidi, D.I. Kondarides, X.E. Verykios, Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO_2 suspensions, Appl. Cata. B: Environ., 40 (2003) 271–286.

[32] Y. Jiang, C. Petrier, T.D. Waite, Kinetics and mechanisms of ultrasonic degradation of volatile chlorinated aromatics in aqueous solutions, Ultrason. Sonochem., 9 (2002) 317–323.