

A Fast and Efficient Absorbant BYW-01 and its Applications in Coking Plant Wastewater Treatment

Walzli Yousaf¹, Yueli Wen², Bin Wang³, Faraz Ahmad⁴, Wei Huang⁵, Tauseef Khaliq⁶, Mudassir Habib⁷

^{1,2,3,4,5,6,7} College of Environmental Science and Engineering, Taiyuan University of Technology, Taiyuan, Shanxi, 030024, P/R China.

wenyueli@tyut.edu.cn², walzliyousaf@yahoo.com¹, tauseefkhaliq87@gmail.com⁶, uetian92@yahoo.com⁴, madsir55@gmail.com⁷

Received: 21 May, Revised: 03 June, Accepted: 09 June

Abstract— Coking plant wastewater is well-known for its excessive NH₃-N and COD content, for which it is difficult to meet emission standards even by using the biological treatment process. In this paper, a fast and efficient BYW-01 was prepared and used to remove NH₃-N and COD in coking plant wastewater from different biological treatment processes. Combined with the characterization of XRD, BET, FTIR, SEM etc, it was found that the abundant –OH and C=O functional groups on the surface of the mesoporous structure absorbent was beneficial to NH₃-N and COD capture. The NH₃-N and COD removal rate could reach about 50 %, 66 % respectively in 5 minutes. The possible adsorption mechanism was proposed.

Keywords— BYW-01 absorbent, Ammonia nitrogen, Chemical oxygen demand, Coking wastewater, Fast and efficient.

I. INTRODUCTION

Water resources are quickly polluted by human actions over the latest years. About 80% of the world population is exposed by water scarcity [1]. It is estimated that about 1.5 billion world population will face water scarcity by 2025 [2,3]. China becomes the second-largest industrial power in the world [4]. Rapid urbanization, economic development, and industrialization in China have been accompanied by significant water pollution. In 2015 China Ministry of environmental protection, 2017 classified water into quality classes I-III, VI-V and <V accounted for 64.5 %, 26.7 % and 8.8 % of the surface water, and the distribution of wastewater, COD and NH₃-N emissions among this categories was 73,530, 22.2 and 2.3 million ton of the industrial pollution accounted for 27.1 %, 13.2 % and 9.4 % [5,6].

Ammonia nitrogen (NH₃-N) and chemical oxygen demand (COD) are two core industrial water pollutants [7]. In the nitrogen cycle, ammonia nitrogen in the form of NH₄⁺ and NH₃ is present, mainly in natural water [8,9]. Nitrogen is an essential nutrimental element for all life forms. One of the major causes of eutrophication is a high amount of nitrogen, especially total

ammonia nitrogen (NH₃, NH₄⁺, and TAN), in receiving waters [10]. COD representing organic load in the water body, which leads to oxygen depletion and threatens to aquatic life. Generally, Industrial wastewaters such as coke-plant, textile, coal gas purification, refining, tannery, and fertilizer wastewater contain a high concentration of ammonia nitrogen [11]. Wastewater contains phenol, ammonia (NH₃), carbon dioxide (CO₂), hydrogen sulfide (H₂S), tar, etc. [12]. Determination of Nitrogen from industrial wastewater is vital for pollution control because ammonia, nitrites, nitrates, and many other nitrogenous compounds act as nutrients for algae and other aquatic plants [13]. One of the major sources of ammonia nitrogen is the discharge of these industrial wastewaters [14]. Ammonium is predominant when the pH is below 8.75, and ammonia is predominant when the pH is above 9.75 [15,16].

In the past years, various analytical techniques have been proposed for the treatment of NH₃-N and COD. Traditional methods for the determination of high concentration of ammonia nitrogen contain biological system [17], Chemical precipitation [18], supercritical water oxidation [19,20], steam-stripping [21], microwave (MW), Ion exchange, reverse osmosis, Electrochemical, Folding point chlorination, Solvent extraction [22] and so on.

After biological treatment, the ammonia concentration is still high because of the high ammonia concentration leads to a low ratio of C/N [23]. Further purified wastewater is using the microbial growth process to make sure a degree of purification meets the discharge standards. It is very effective and economical, but it is time taking. Chemical precipitation requires extra reagents, which may produce new pollutants. Supercritical water oxidation needs high temperature and high pressure in Steam-stripping high energy required for stripping tower. Microwave is still having no clear idea for the full-scale application. Ion exchange and reverse osmosis incur large operation costs due to resin preparation and pressure driving [24,25]. Electrochemical and folding point chlorination is used only for low concentration ammonia nitrogen [26]. Solvent

extraction is costly, requires high input, and may not substantially decrease pollutant concentration [27].

This study introduced a new BYW-01 absorbent, which is very fast and efficient to remove NH₃-N and COD from the coking wastewater plant in 5 minutes.

II. EXPERIMENTAL

A. Absorbent preparation

All the chemicals used in this study were of analytical grade and purchased from chinese chemical reagent company.

The absorbent were made from coal ash, and some chemicals were used for modification. First, 1 mol crylic acid and 0.5 mol diethanol amine mixed well with 0.5 mol ethylene glycol, then 2 mol concentrated sulfate acid was added in the mixed solution. After relaxating the obtained mixed solution for 4 hours, 3.5 mol NaOH was used to neutralize it, and solution B was obtained. Second, 1 mol acrylic amide was added in B, after mixing well, N₂ was bubbled in at 25 °C. After reacting with 0.007 mol sodium bisulfite and 0.006 mol ammonium persulfate at 40 °C for 8 hours, 70 g coal ash was added in and kept reacting for another 6 hours at 50 °C with continous stirring. Washed the obtained solid with distilled water for several times and dried at room temperature. The obtained solid was named as BYW-01.

B. Characterization

UV752N UV- Visible Spectrophotometer (Shanghai YOKE instrument CO., Ltd.) was used do the absorption spectral scanning, and it was quantified by absorbance of 425 nm. HCA-100 COD auto-digestion reflux instrument (Taizhoumeixu instrument equipment Co.,Ltd.) was used to digest wastewater samples.

X-ray diffraction (XRD) patterns were performed on a DX-2700 X-ray diffractometer for continuous scanning, using Cu K α as the radiation source. The scanning range was 5°-85°, and the scanning rate was 8°/min.

Nitrogen adsorption-desorption characterization was performed on a Quantachrome SI gas adsorption analyzer (product from Conta, USA). The samples were degassed at 200°C under vacuum for 6 h prior to characterization. The specific surface area of the catalyst was calculated by using the BET method, and the pore volume and pore size were calculated by the BJH formula.

Fourier transform infrared (FT-IR) spectra were collected by using a Thermo Nicolet 6700 instrument with a measurement range of 400-4000 cm⁻¹.

Surface morphology of the absorbents was observed by scanning electron microscopy (SEM) using Quanta 400 FEG type instrument of American FEI Company , and the acceleration voltage was 20 kV.

C. Sample collection

The wastewater used in the experiments was taken from different biological treatment processes of a coking plant located at Taiyuan, Shanxi, China. The wastewater treatment plant process for coking plant was shown in Fig. 1.

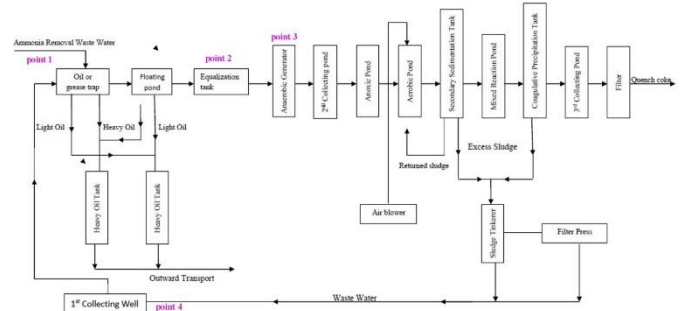


Figure 1. Wastewater treatment process flow chart of a coking plant

The sample collection plan was designed to cover almost all essential processes points of the coking plant. Four samples were taken from different sampling points (Point 01- Steamed Ammonia wastewater, point 02- Equalization tank wastewater, point 03- Anoxic tank wastewater, and point 04- collecting well wastewater.) and named as point 1-4. These samples contained a significant amount of ammonia nitrogen (NH₃-N) concentrations, and chemical oxygen demand (COD) as shown in Table I.

TABLE I. THE NH₃-N AND COD CONCENTRATIONS OF THE WASTEWATER SAMPLES

Samples	Point 1	Point 2	Point 3	Point 4
NH ₃ -N (mg/L)	56.14	98.25	10.08	215.59
COD (mg/L)	4400.00	1080.00	600.00	1440.00

D. Wastewater treatment procedure and analytical methods

i. Wastewater treatment procedure

25 g absorbent was added in 25, 50,100,150, and 200 mL volume of wastewater for which the ratio of wastewater volume to absorbent mass was 1, 2, 4, 6, 8 mL/g respectively. The mixture was stirred continuously for 5 minutes. After that, the absorbent was separated by filtration, and then was ready for NH₃-N and COD determination.



Figure 2. The flow chart for NH₃-N treatment and determination

ii. Analytical methods

For determination of ammonia nitrogen: 2 mL sample before and after treatment was taken in a colorimetric tube, and shaken well after diluted with distilled water to the mark. Then 1 mL potassium sodium tartrate and 1.5 mL Nessler's reagent was

added in. After shaking well and waiting for 30 minutes, the samples were taken in 1 cm cuvette and the absorbance was tested by the spectrophotometer at wavelength of 425 nm by using ammonia free distilled water as reference. The detailed procedure was shown in Fig.2.

For determination of COD: 1 mL sample before and after treatment was taken in 250 mL conical flask and diluted with 20 mL distilled water and followed by adding 3 mL potassium dichromate. Auto-digestion reflux was used to digest the organic substances. 5 mL of mercury sulfate-sulfuric acid was added to mask the chlorine ion. The mixture was heated and refluxed for 150 minutes. After standing for 3 hours at room temperature (22° to 27°), the solution was diluted in 150 mL distilled water, 3 drops of ferroin indicator were added in. And then the solution was titrated with 0.05 mol/L ammonium ferrous sulfate until the color changed. The detailed steps was shown in Fig.3



Figure 3. The flow chart for COD treatment and determination.

III. RESULTS AND DISCUSSION

A. Characterization of absorbent BYW-01

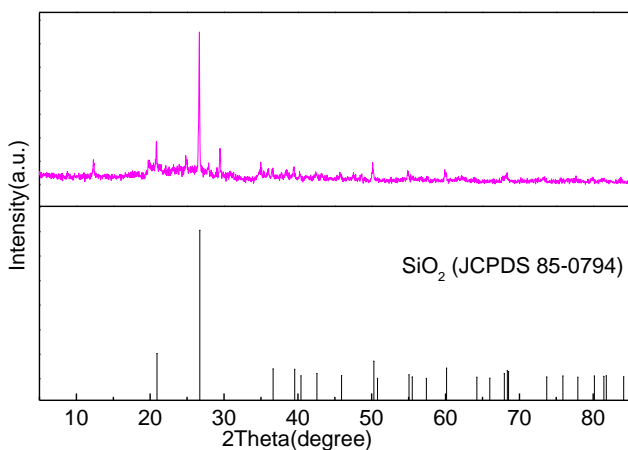


Figure 4. XRD pattern of absorbent BYW-01

Fig. 4 shows the XRD pattern of BYW-01, the peaks at 20.9°, 26.7°, 50.3° could be attributed to the (100), (011), (11-2) crystal face of SiO₂(JCPDS 85-0794). No other substances were detected.

Fig.5 displays the N₂ adsorption-desorption isotherms and corresponding pore size distribution of BYW-01 (the inset

image). According to the IUPAC classification, the isotherms exhibited IV with H3-type hysteresis loop. It had a relative large adsorbance of N₂ with a broad hysteresis loop at a relative pressure p/p₀ of 0.10-0.95 and a bimodal pore diameter distribution concentrating on 3.8 nm and 7.7 nm. The N₂ adsorption-desorption isotherms and pore size distribution revealed that the absorbent BWY-01 were of mesopore structure. It was noting that the broad hysteresis loop was due to the strong capillarity phenomena existing within the compact structure. As shown in the table in Fig.5, the multipoint BET specific surface of area was 11.78 m²/g and the pore volume was 0.02 cm³/g.

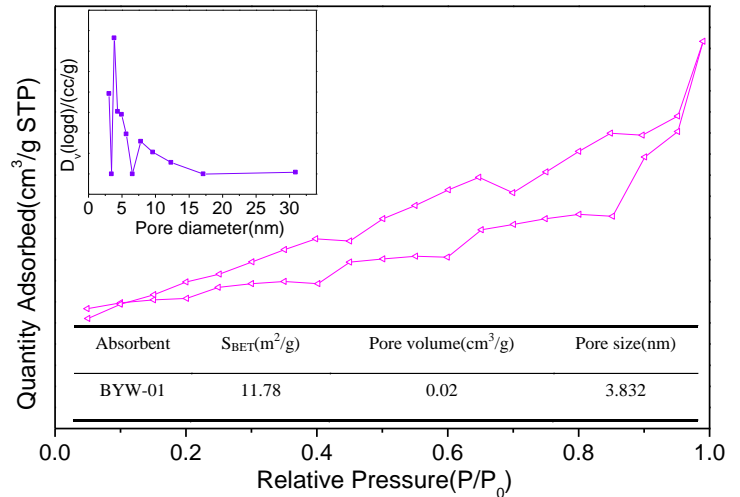


Figure 5. N₂ adsorption-desorption isotherms and corresponding pore size distribution of BYW-01.

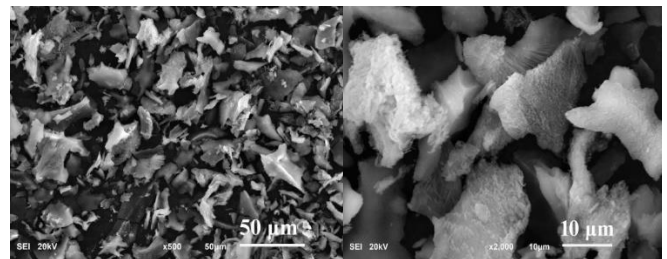


Figure 6. SEM spectra of BYW-01

Fig. 6 shows the SEM spectra of BYW-01. As shown in the inset graph of Fig. 6 b, the absorbent was composed of small spherical particles, which were self-organized as leaf-like microstructure as shown in Fig.6a. And there were many pores on every leaf as shown in Fig.6b, which was agree with BET characterization and contributed to the good performance for NH₃-N and COD removal.

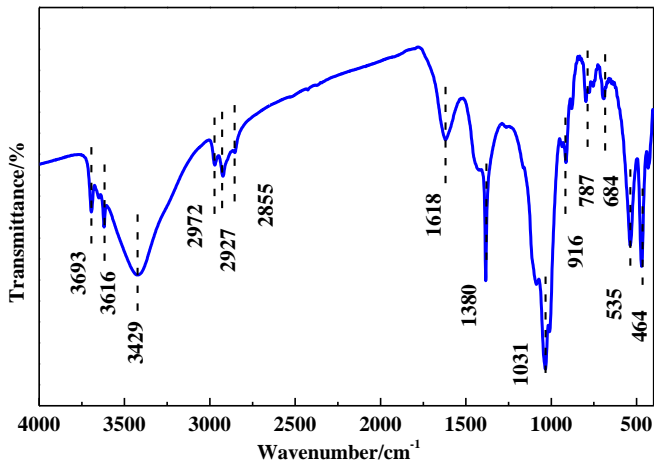


Figure 7. FTIR spectrum of BYW-01

Fig.7 gives the information about functional groups on the surface of BYW-01 by FTIR spectrum. The bands at 2927cm-1 and 2855 cm-1 could be attributed to C-H asymmetric and symmetric stretching vibration absorption of CH₂ and the shoulder at 2972 cm-1 prepresented the asymmetric C-H stretching of vibration absorption CH₃[28]. The band at 464 cm-1 was caused by Si-O bending vibrations[29]; and the bands at 916 cm-1 and 1380 cm-1 were ascribed to bending vibration absorption of OH in carboxylic acid. The bands at 1031 cm-1 could be assigned to C-O-C asymmetric stretching vibration absorption of aromatic compounds. In addition, the band at 535 cm-1 could be ascribed to in-plane bending vibration of C-C=O in aliphatic ketone. The intensity and shape of the band at 3429 cm-1 and 3616 cm-1 were assigned to dissociated and intramolecular associated OH groups, which derived from water absorbed from air. In summary, the absorbent BYW-01 exhibited good adsorptive property for NH₃-N and COD partly because of the abundant of -OH and C=O functional groups on the surface of the absorbent.

B. Adsorption performance

i. Effect of V/m ratio on NH₃-N removal rate

The effect of the ratio of wastewater volume to absorbent mass (V/m) on the NH₃-N removal rate was investigated, as shown in Table II and Fig. 8. It was observed that for different wastewater taken from various points of a coking plant wastewater treatment process, the removal rate has the same trend, in which the NH₃-N removal decreased with V/m increasing from 1 to 8 mL/g. The results showed that for different types of wastewater like steamed ammonia wastewater, equalization tank wastewater, anoxic pond wastewater, and collecting well wastewater, BYW-01 showed excellent performance for NH₃-N removal in very short contact time (5 minutes). The best removal rate could reach to 48.67 % for collecting well wastewater in point 4. Combined with the original concentration of NH₃-N listed in Table I, it was also observed that the removal rate increased with the concentration increasing (point 3-1-2-4) even for different V/m.

TABLE II. THE NH₃-N REMOVAL RATE FOR WASTEWATER FROM DIFFERENT SAMPLING POINTS

Sample volume (mL)	Absorbent mass (g)	V/m (mL/g)	Removal rate %			
			Point 1	Point 2	Point 3	Point 4
25	25	1	29.85	30.37	24.32	48.67
50	25	2	28.64	29.95	18.92	48.35
100	25	4	18.64	29.40	17.57	40.51
150	25	6	13.10	19.69	14.86	40.13
200	25	8	10.19	18.30	12.16	36.40

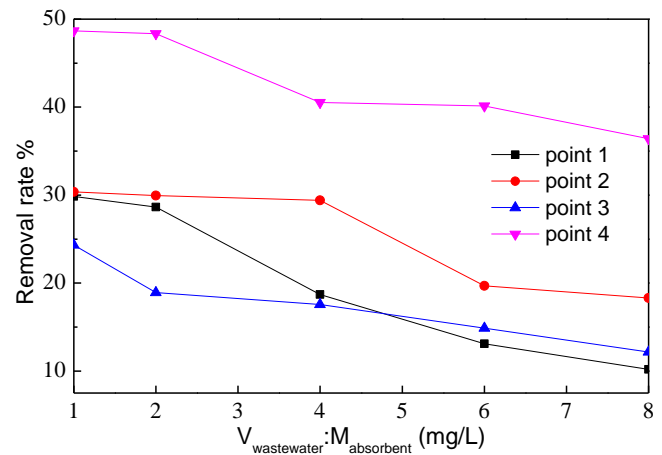


Figure 8. Effect of V/m on NH₃-N removal rate at different sampling points

ii. Effect of V/m ratio on COD removal rate

The effect of the ratio of wastewater volume to absorbent mass (V/m) on the COD removal rate was also investigated, as shown in Table III and Fig. 9. Samples before treatment with different volumes (25, 50, 100, 150, 200) were treated with 25 g absorbent, so the V/m ratio was 1, 2, 4, 6, 8 mL/g respectively. The results showed that with the V/m ratio increasing, the COD removal rate was generally decreasing for wastewater from different coking plant processes. The best removal rate could reach near to 70 % for anoxic pond wastewater at point 3 with the COD concentration of 600 mg/L. But when the V/m ratio was more than 6 mL/g, the removal rate reduced slightly or kept constant. This might be because the COD concentration was too high, and the absorbent could not absorb them in such a short time (5 minutes) for a lower COD concentration ratio below 1080 mg/L (anoxic pond wastewater and equalization tank wastewater). This might be because the amount of absorbent was not sufficient to capture the COD anymore.

TABLE III. THE COD REMOVAL RATE FOR WASTEWATER FROM DIFFERENT SAMPLING POINTS.

Sample volume (mL)	Absorbent mass (g)	V/m (mL/g)	Removal rate %			
			Point 1	Point 2	Point 3	Point 4
25	25	1	50.45	59.00	66.66	55.55
50	25	2	19.81	25.00	46.66	30.55
100	25	4	14.41	7.40	33.33	22.22
150	25	6	10.81	3.70	20.00	8.32
200	25	8	8.10	3.70	20.00	2.77

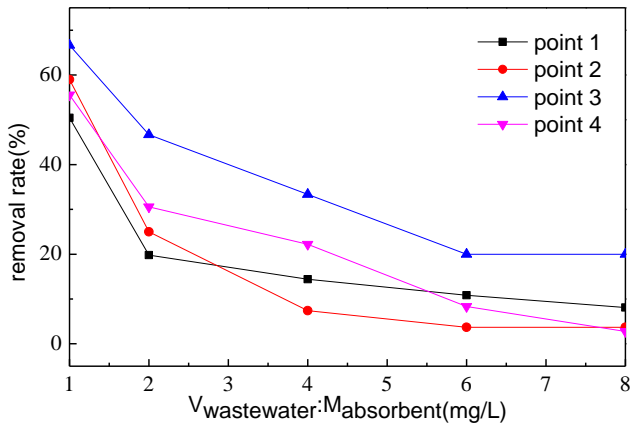


Figure 9. Effect of V/m on COD removal rate at different sampling points

TABLE IV. THE NH₃-N AND COD CONCENTRATION BEFORE AND AFTER TREATMENT AND THEIR REMOVAL RATES AT V/M=1 ML/G

Concentration (mg/L)	Point 1	Point 2	Point 3	Point 4
NH ₃ -N before treatment	56.14	98.25	10.08	215.59
NH ₃ -N after treatment	39.38	68.41	7.63	110.65
Removal rate (%)	29.85	30.37	24.32	48.67
COD before treatment	4400.00	1080.00	600.00	1440.00
COD after treatment	2200.00	440.00	200.00	640.00
Removal rate (%)	50.45	59.00	66.66	55.55

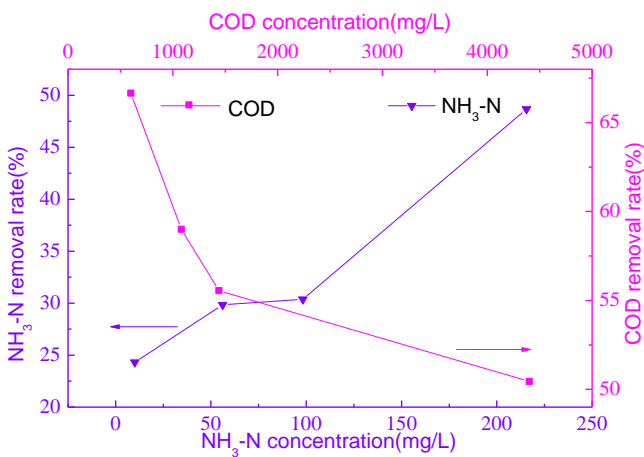


Figure 10. The effect of NH₃-N and COD concentration on the removal rate

Table IV and Fig.10 shows NH₃-N and COD concentration before and after treatment and the corresponding removal rates at V/m=1 mL/g. The removal rate variation trends with the concentration before treatment for COD and NH₃-N at V/m=1 mL/g were completely different as shown in Fig. 7. For NH₃-N, the removal rate increased with its concentration before treatment decreasing in the sequence of point 4-2-1-3, while the COD removal rate decreased with its concentration before treatment decreasing in the sequence of point 3-2-4-1. That mainly because that NH₃-N concentration was relatively lower than COD and the absorbent was sufficient to capture them so

the higher NH₃-N concentration was, the more NH₃-N molecules were captured. But for COD, the concentration was too high to be absorbed, and only a small percentage of COD around the absorbent could be captured, which lead to a lower removal rate.

Fig. 11 displays the proposed adsorption mechanism of BYW-01. The coal ash had plentiful pores, which would do good to absorb the NH₃-N and COD and let them get close to the absorbent. Furthermore, the coal ash after modification had abundant -OH and C=O functional groups on the surface, which would interact with NH₃-N and COD, and capture them tightly.

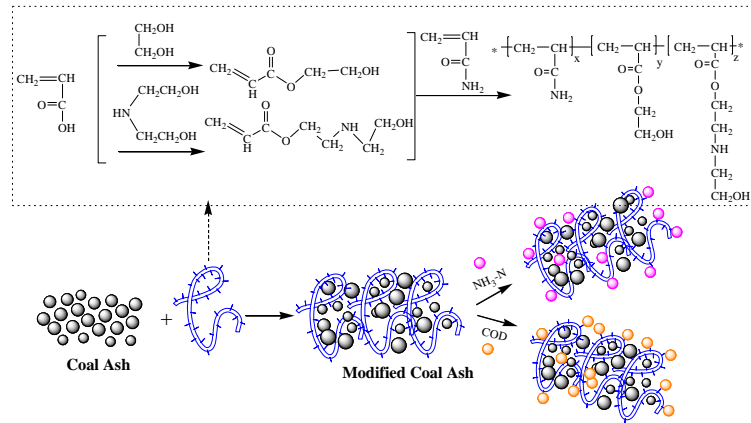


Figure 11. The proposed adsorption mechanism of BYW-01

CONCLUSION

A new, fast, and efficient absorbent was prepared by using coal ash and applied in NH₃-N and COD removal in coking plant wastewater in this work, which contained a high amount of NH₃-N and COD concentration. The NH₃-N removal rate reached about 50% for collecting well wastewater (point 04), and the COD removal rate achieved about 66% for anoxic pond wastewater (point 03) in 5 minutes by using this absorbent partly because of the abundant -OH and C=O functional groups on the surface of the absorbent and partly because of the mesoporous structure of the absorbent. The wastewater volume and concentration affected the removal rate greatly. With the volume of raw water and the concentration of NH₃-N and COD increasing before treatment, the removal rate decreased.

REFERENCES

- [1] Chen, Bo, Wang, Meng, Duan, Mingxiao, Ma, Xiaotian, Hong, Jinglan, Xie, Fei, ... Li, Xiangzhi. In search of key: Protecting human health and the ecosystem from water pollution in China. *Journal of Cleaner Production*, 228, 2019: 101-111.
- [2] Hasan, Md Khalid, Shahriar, Abrar, & Jim, Kudrat Ullah. Water pollution in Bangladesh and its impact on public health. *Heliyon*, 5(8), e02145. (2019).
- [3] WWAP, U. World Water Assessment Programme: The United Nations World Water Development Report 4: Managing Water under Uncertainty and Risk: Paris: UNESCO, 2012.
- [4] Liang, Ying, Yan, Chunmei, Guo, Qing, Xu, Jin, & Hu, Hongzhi. Spectrophotometric determination of ammonia nitrogen in water by flow injection analysis based on NH₃-o-phthalaldehyde-Na₂SO₃ reaction. *Analytical chemistry research*, 10, 2016: 1-8.

- [5] Long, Sha, Zhao, Lin, Shi, Tongtong, Li, Jingchen, Yang, Jiangye, Liu, Hongbo, . . . Yang, Yongkui. Pollution control and cost analysis of wastewater treatment at industrial parks in Taihu and Haihe water basins, China. *Journal of cleaner production*, 172, 2018: 2435-2442.
- [6] Long, S., Zhao, L., Shi, T., Li, J., Yang, J., Liu, H., & Yang, Y. Pollution control and cost analysis of wastewater treatment at industrial parks in Taihu and Haihe water basins, China. *Journal of Cleaner Production*, 172, 2018:2435-2442.
- [7] Wang, Meicheng, He, Lizhi, Wang, Min, Chen, Lin, Yao, Sicong, Jiang, Wenju, & Chen, Yao. Simultaneous removal of NH₃-N and COD from shale gas distillate via an integration of adsorption and photo-catalysis: A hybrid approach. *Journal of environmental management*, 249, 109342, 2019.
- [8] Zadorojny, C, Saxton, S, & Finger, R. Spectrophotometric determination of ammonia. *Journal (Water Pollution Control Federation)*, 1973: 905-912.
- [9] Šraj, Lenka O'Connor, Almeida, M Inês GS, Swearer, Stephen E, Kolev, Spas D, & McKelvie, Ian D. Analytical challenges and advantages of using flow-based methodologies for ammonia determination in estuarine and marine waters. *TrAC Trends in Analytical Chemistry*, 59, 2014: 83-92.
- [10] Huang, Haiming, Liu, Jiahui, Xiao, Jing, Zhang, Peng, & Gao, Faming. Highly efficient recovery of ammonium nitrogen from coking wastewater by coupling struvite precipitation and microwave radiation technology. *ACS Sustainable Chemistry & Engineering*, 4(7), 2016: 3688-3696.
- [11] Jung, Jin-Young, Chung, Yun-Chul, Shin, Hang-Sik, & Son, Dae-Hee. Enhanced ammonia nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research*, 38(2), 2004: 347-354.
- [12] Yu, Zhenjiang, Chen, Yun, Feng, Dachun, & Qian, Yu. Process development, simulation, and industrial implementation of a new coal-gasification wastewater treatment installation for phenol and ammonia removal. *Industrial & Engineering Chemistry Research*, 49(6), 2010: 2874-2881.
- [13] Albert, DK, Stoffer, RL, Oita, JJ, & Wise, RH. Rapid determination of ammonia and total nitrogen in municipal waste water by microcoulometry. *Analytical chemistry*, 41(11), 1969: 1500-1504.
- [14] Lin, Li, Yuan, Songhu, Chen, Jing, Xu, Zuqun, & Lu, Xiaohua. Removal of ammonia nitrogen in wastewater by microwave radiation. *Journal of hazardous materials*, 161(2-3), 2009: 1063-1068.
- [15] Li, Lan-Bing, Hu, Jin-Li, & Xia, Nian-Cheng. Industrial energy-pollution performance of regions in China based on a unified framework combining static and dynamic indexes. *Journal of cleaner production*, 131, 2016: 341-350.
- [16] Molins-Legua, C, Meseguer-Lloret, S, Moliner-Martinez, Y, & Campíns-Falcó, P. A guide for selecting the most appropriate method for ammonium determination in water analysis. *TrAC Trends in Analytical Chemistry*, 25(3), 2006: 282-290.
- [17] Yu, Hanqing, Gu, Guowei, & Song, Leping. Posttreatment of effluent from coke-plant wastewater treatment system in sequencing batch reactors. *Journal of Environmental Engineering*, 123(3), 1997: 305-308.
- [18] Uludag-Demirer, S, Demirer, GN, & Chen, SJPB. Ammonia removal from anaerobically digested dairy manure by struvite precipitation. *Process Biochemistry*, 40(12), 2005: 3667-3674.
- [19] Bermejo, MD, Cantero, F, & Cocero, MJ. Supercritical water oxidation of feeds with high ammonia concentrations: Pilot plant experimental results and modeling. *Chemical Engineering Journal*, 137(3), 2008: 542-549.
- [20] Segond, Nathalie, Matsumura, Yukihiko, & Yamamoto, Kazuo. Determination of ammonia oxidation rate in sub-and supercritical water. *Industrial & engineering chemistry research*, 41(24), 2002: 6020-6027.
- [21] Ghose, MK. Complete physico-chemical treatment for coke plant effluents. *Water Research*, 36(5), 2002: 1127-1134.
- [22] Chan, Alison, Salsali, Hamidreza, & McBean, Ed. Heavy metal removal (copper and zinc) in secondary effluent from wastewater treatment plants by microalgae. *ACS Sustainable Chemistry & Engineering*, 2(2), 2013: 130-137.
- [23] Melcer, Henryk, Nutt, Stephen, Marvan, Igor, & Sutton, Paul. Combined treatment of coke plant wastewater and blast furnace blowdown water in a coupled biological fluidized bed system. *Journal (Water Pollution Control Federation)*, 1984: 192-198.
- [24] Park, Man Ho, Jeong, Sangjae, & Kim, Jae Young. Adsorption of NH₃-N onto rice straw-derived biochar. *Journal of Environmental Chemical Engineering*, 7(2), 103039, 2019.
- [25] Tchobanoglous, George, Burton, Franklin L, & Stensel, H David. *Metcalf & Eddy wastewater engineering: treatment and reuse*. International Edition. McGrawHill, 4, 2003: 361-411.
- [26] Tian, Yang, Shu, Jiancheng, Chen, Mengjun, Wang, Jianyi, Wang, Yao, Luo, Zhenggang, . . . Sun, Zhi. Manganese and ammonia nitrogen recovery from electrolytic manganese residue by electric field enhanced leaching. *Journal of Cleaner Production*, 236, 117708, 2019.
- [27] Jacinto, Maria Lourdes JAJ, David, Carlos Primo C, Perez, Teresita R, & De Jesus, Benjamin R. Comparative efficiency of algal biofilters in the removal of chromium and copper from wastewater. *Ecological Engineering*, 35(5), 2009: 856-860.
- [28] Grehk, T M, Berger, R, Bexell, U. Investigation of the drying process of linseed oil using FTIR and ToF-SIMS, *Journal of Physics:Conference Series* 2008. 100, 012019-012023, 2009.
- [29] Huirong Zhang, Jin Bai, Lingxue Kong, Xiaoming Li, Zongqing Bai, and Wen Li. Behavior of Minerals in Typical Shanxi Coking Coal during Pyrolysis, *Energy & Fuels*, 29, 2015: 6912–6919