Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.781724

51 (2013) 3794–3799
May

Taylor & Francis
Taylor & Francis Group

Household-based combined process for the emergent treatment of groundwater micropollutants

Zhi-sheng Liu[a,b,*], Jun Yin[c], Xiao-yu Zhang[c], Yi-hui Pu[a]

[a]*School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, P.R. China*
Email: Lzs008@sohu.com
[b]*China Northeast Municipal Engineering Design and Research Institute, 618 Gongnong Road, Changchun 130021, P.R. China*
[c]*Jilin Province Key Laboratory of Water Pollution Control and Resources Reuse, Jilin Architectural and Civil Engineering Institute, Changchun 130021, P.R. China*

Received 8 August 2012; Accepted 25 February 2013

ABSTRACT

Groundwater micropollutant has been a steady threat to the rural residents with household-based water supply. In this work, a multi-barrier technology is designed, that is, rice husk ash (RHA) adsorption and enhanced coagulation, followed by heating and boiling (azotropic). The removal efficiency of nitrobenzene from groundwater was investigated using this household-based combined process. The experimental results indicate that the nitrobenzene concentration can be under the limit determination in the finished water, treated by the combined process. Ames test indicates that the combined process, especially RHA, is safe and reliable. The combined process is a cost-effective technology for emergent nitrobenzene removal in decentralized water supply.

Keywords: Emergent treatment; Combined process; Decentralized water supply; Nitrobenzene

1. Introduction

Water pollution is one of the most important environmental problems in the world. The rural drinking problem has proved to be a bottleneck to the development of the rural economy and the living standard therein. Traditionally, water supply is mainly self-served by peasants themselves from groundwater, leading to serious health concerns [1]. The decentralized water supply is not provided with the advantage of centralized water supply in urban areas. So, how to conceive a multibarrier technology to rural area with reasonable price is of urgency.

In this article, nitrobenzene is selected as target pollutant, one of the nitroaromatic compounds having considerable industrial importance. It has been estimated that about 19 million lb of nitrobenzene is released into the environment annually [2,3]. It causes vomiting, skin and eye irritation, and headache. Its continuous exposure leads to liver damage and anemia. Affect of nitrobenzene on human health has been well known, and nitrobenzene toxicology has been widely reported in many aspects [4,5]. Because of its toxicity, nitrobenzene has been placed as one of the

---

*Corresponding author.

Presented at the 2012 Qingdao International Desalination Conference June 26–29, 2012, Qingdao, China

Table 1
Typical water quality of groundwater utilized

Parameters	Value
Turbidity (NTU)	0.35–0.56
COD_{Mn} (mg/L)	1.85–2.47
Fe (mg/L)	0.80–1.32
Mn (mg/L)	1.37–2.28
Alkalinity (mg/L)	235–288
Hardness (mg/L)	293–341

129 priority pollutants by United States Environmental Protection Agency. It was also one of the 68 priority control pollutants in China. The removal of nitrobenzene from aqueous solutions was the focus in biodegradation of wastewater and theoretical investigation [6,7]. Physical adsorption is also widely used because of relatively high stability of nitrobenzene [8].

In this work, a novel combined process was invented for household-based emergent treatment of groundwater polluted by nitrobenzene, that is, rice husk ash (RHA) adsorption and enhanced coagulation, followed by azotropic. The operation feasibility and efficiency of the combined process and its units were investigated, in order to offer a technical sustenance for the practical applications (Table 1).

2. Materials and methods

2.1. Raw waters

Water samples containing nitrobenzene were prepared from groundwater and nitrobenzene (A.R. grade). Groundwater samples were collected from rural well along the Songhua River, Jilin Province, P.R. China. Typical water quality of groundwater utilized is shown in Table 2, in which alkalinity and hardness are expressed as $CaCO_3$.

2.2. Adsorption on RHA

Adsorption rate experiments were carried out by stirring a known amount of RHA adsorbent with 5 L of the solution containing nitrobenzene on a magnetic stirrer equipped with temperature controller. At predetermined time intervals, portions of the mixture were drawn by a syringe and filtrated. Bath studies were performed to determine the theoretical saturation capacities of RHA. A series of accurately weighted RHA doses were added to 500 mL aqueous solutions containing certain initial concentrations of nitrobenzene. All adsorption experiments were kept at 15 ± 0.2℃. Rice husk was taken from a rural area along the Songhua River and converted into RHA by burning.

2.3. Jar tests

Coagulation and sedimentation experiments were performed by the jar tests. The coagulant was added to the beaker containing synthetic water. Each sample was rapidly mixed at 250 rpm for 1 min, slowly mixed at 100 rpm for 5 min, and slowly mixed at 50 rpm for 10 min, and then quiescent settled for 30 min. Next, the supernatant samples were passed through a 0.45 μm filter and again analyzed by gas chromatograph.

2.4. Heating and boiling (azotropic)

About 3.5 L of synthetic water was added to the family ferric water jug, and then 1,000 W of electric cooker was used for heating and boiling. After cooled at room temperature, boiled water samples was analyzed.

2.5. Analytical methods

The amounts of nitrobenzene were measured by the liquid–liquid microextraction method, using a

Table 2
Removal efficiency of nitrobenzene by RHA and coagulation

Sample no.	Raw water (μg/L)	RHA dose (g/L)	After adsorp./sedim. (μg/L)	After coag./sedim. (μg/L)
1	85	0.75	26.46	15.71
2	85	1.0	7.86	6.15
3	170	1.5	41.21	26.65
4	170	2.5	16.10	8.46
5	340	3.5	23.70	11.63
6	340	4.5	14.60	7.02

Shimadzu 2,100 gas chromatograph (Shimadzu Co., Japan) equipped with an electron capture detector (ECD). The carrier gas was highly pure nitrogen and the temperature program was the initial 110℃ for 4 min, which was ramped from 35℃/min to 280℃ and held for 1 min to clean the column in the preparation for the next sample. The total operation time was 9.86 min. The temperature of injector and 63Ni-ECD was kept as 240 and 290℃, respectively. Liquid–liquid microextraction with *n*-hexane was used for the separation of nitrobenzene in the samples filtrated through 0.45-μm membrane according to the following procedure: 50 mL of each sample was added into a 50-mL volumetric flask, which contained 5 g NaCl. After the dissolution of the salt, 1 mL of *n*-hexane (HPLC grade, Fisher Chemalert®, USA) was added and the samples were extracted for 5 min. After the phase separation, 1 μL of the extracted sample was injected in a capillary column (RTX-5), 30 m × 0.25 mm × 0.25 μm. Under these conditions, the detection limit of nitrobenzene was found to be 0.2 μg/L. The recovery with standard addition was 98.12–104.85% with a relative standard deviation of 6.2%. This determination precision was not taken into account for the results evaluation. With reference to the Sujbert et al. 2006, Ames test was carried out.

3. Results and discussion

3.1. Adsorption by RHA

The use of activated carbon for removal of poisonous matter has been widely studied. In spite of the usefulness of activated carbon as an efficient adsorbent for water treatment, the high capital and regeneration costs of the activated carbon inhibit its large-scale use as an adsorbent. Hence, an economical and easily available adsorbent would certainly make an adsorption-based process a viable alternative for the treatment of groundwater containing nitrobenzene pollutant. Rice husk, an agricultural waste, was chosen to be applied as a precursor adsorbent due to its granular structure, insolubility in water, chemical stability, high mechanical strength, and its local availability at almost no cost [9,10].

In order to establish equilibration time for maximum uptake and to know the kinetics of the adsorption process, the adsorption of nitrobenzene on RHA as a function of contact time and the results are shown in Fig. 1. The initial concentration of nitrobenzene and dose of RHA is 85 μg/L and 0.5 g/L, respectively. It is seen that the rate of uptake of nitrobenzene is rapid in the beginning and about 80% adsorption is completed within 10 min. This rapid adsorption reflects the fact that adsorption is a surface phenomenon and the surfaces are readily accessible to the molecule in solution. Fig. 1 also indicates that the time required for equilibrium adsorption is 60 min, but adsorption capacity of 30 min is 96.8% of that of 60 min. So, the contact time of 30 min is considered as a sufficient equilibrium time in practical applications.

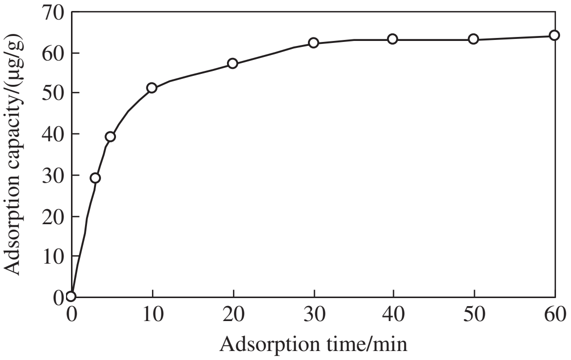

Fig. 1. Adsorption rate of nitrobenzene on RHA.

The removal efficiency of nitrobenzene on the contact time of 60 min was also investigated as a function of RHA dose and initial concentration of 881 μg/g nitrobenzene, and the results are shown in Fig. 2. It was found that when residual concentration is 3.5 μg/L, maximum adsorption amount is 44 μg/g. This favorable adsorption performance is due to greater specific surface area of RHA and adsorption site of exposed SiO_2 [11,12].

3.2. Enhanced coagulation

Polyferric chloride, polyaluminum chloride, ferric chloride, and aluminum sulfate were chosen as coagulates, respectively. The coagulation/sedimentation results illustrate that the removal rate is no more than 10% and an increase in coagulant has no an distinct

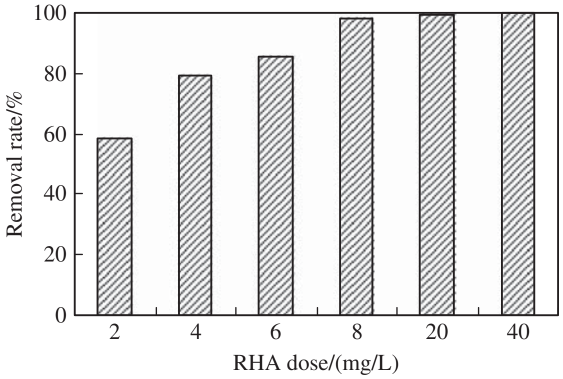

Fig. 2. Effects of RHA dosage on nitrobenzene removal.

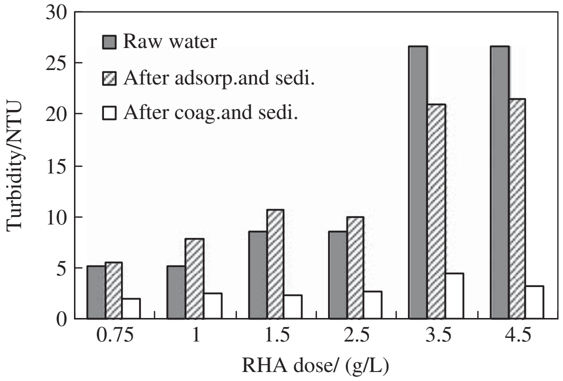

Fig. 3. Effect of RHA and coagulation on turbidity.

benefit. But the removal efficiency of ferric coagulants is little better than that of alum.

In order to remove residual turbidity and fine granule from RHA adsorption, after 30 min of RHA adsorption and 30 min of quiescent settling, coagulation with 40 mg/L polyaluminum chloride was tested and the results are shown in Fig. 3 and Table 2. It has been seen from Fig. 3 that turbidity can be increased by RHA in the range of low turbidity of raw water and coagulation can decrease the residual turbidity of water samples from RHA adsorption.

It is seen from Table 2 that total removal of nitrobenzene is 81–98%, but removal efficiency is increased to 35–52% only, by coagulation after RHA adsorption. It is as a result of continuous adsorption of unsaturated RHA, coagulant hydrolysate, and RHA congeries with hydrolysate.

3.3. Heating and boiling (azotropic)

Drinking boiled water is healthful to human body [13]. It is a fact that volatile organic matter, Fe/Mn, and hardness is less in boiled water, and at the same time, disinfection is accomplished [14]. Figs. 4 and 5 illustrate the removal efficiency of nitrobenzene by heating and boiling. From Fig. 4, before boiling, 45–67% nitrobenzene is removed from water by heating. As shown in Fig. 5, as boiling time is prolonged, residual nitrobenzene is decreased. When the time of boiling is 10 min, removal rate is more than 90%.

In order to further investigate the removal efficiency of nitrobenzene by heating and boiling, after and before boiled water samples was scanned by visible/UV rays, and the results are presented in Fig. 6. The clear receding of the absorbed peak (267 nm) indicates that nitrobenzene has been removed. At the same time, new adsorbed peaks unfound prove that new organic matters are not created. Obviously, heating and boiling is very effective in eliminating nitrobenzene from groundwater. This is because nitrobenzene has been volatilized with vapor by coboiling.

3.4. Efficiency of the combined process

The 20 L groundwater samples with 85 μg/L of nitrobenzene were studied by 1 g/L RHA adsorption and enhanced coagulation, followed by heating and 5 min of boiling. No more than 1 μg/L nitrobenzene of finished water samples was achieved. The potential mutagenic effect of various water samples were inspected with Ames test [15]. According to the data shown in Figs. 7 and 8, the untreated groundwater may exert mutagenic effect on TA-98 and TA-100. For the treated water samples, the number of revertant colonies of TA-98 and TA-100 did achieve and exceed the double of spontaneous. It is proved that the combined process can remove nitrobenzene from groundwater and guarantee safety to household-based

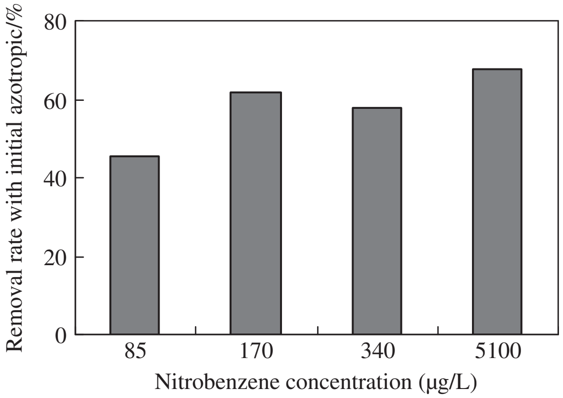

Fig. 4. Removal rate of nitrobenzene in different concentration by initial azotropic.

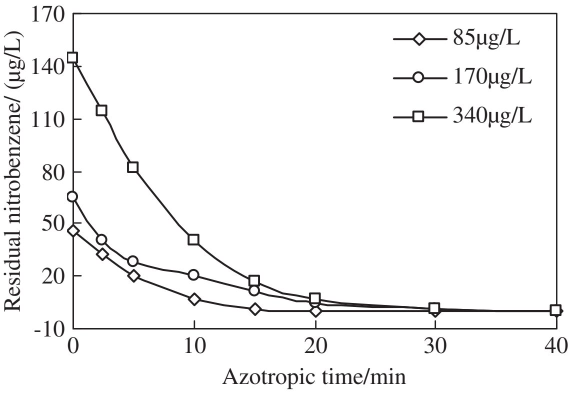

Fig. 5. Removal rate of nitrobenzene by azotropic at different time.

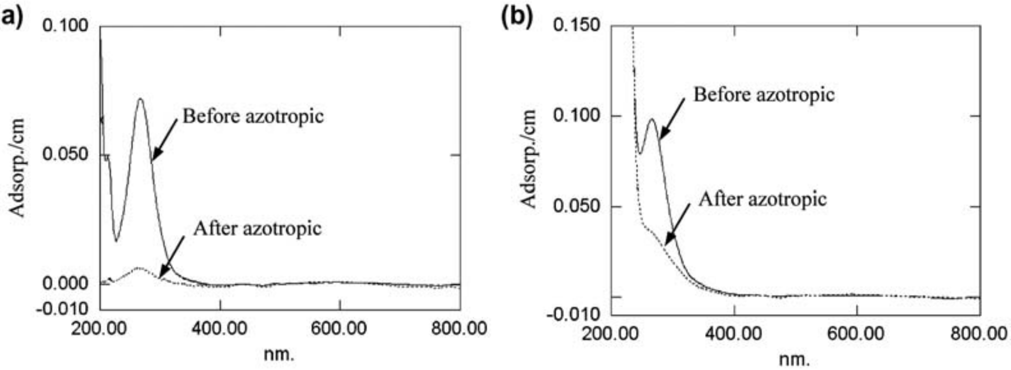

Fig. 6. UV–visible scanning of water samples with 351 μg/L of nitrobenzene concentration in raw waters, and (a) is background of pure water and (b) is background of groundwater.

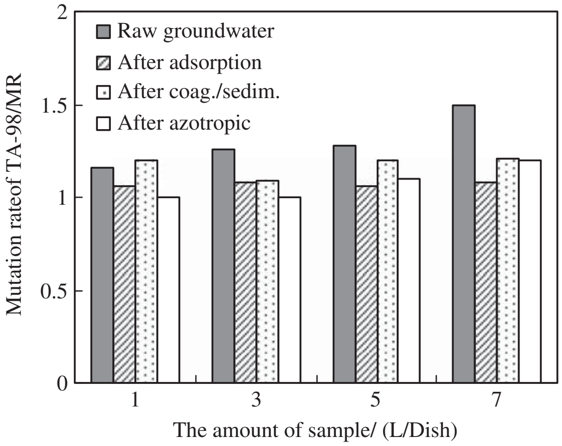

Fig. 7. Genotoxic activities expressed as induction factors of TA-98.

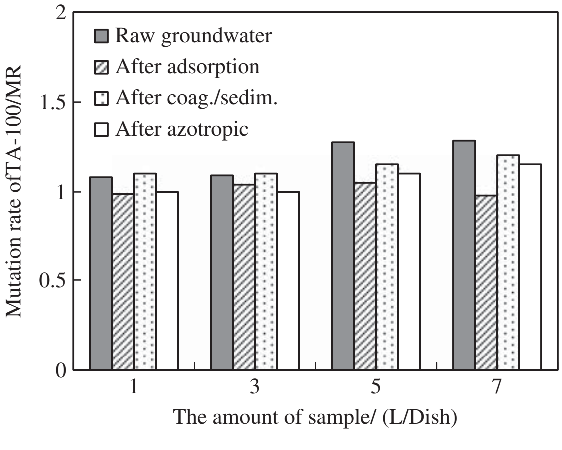

Fig. 8. Genotoxic activities expressed as induction factors of TA-100.

emergency water supply. Removal of nitrobenzene should make the most of RHA adsorption in practical applications, because "Fore-col" can ensure drinking water adequately.

4. Conclusions

The aim of this study is to find a combined process for the emergent treatment of groundwater micropollutants. The equilibrium time of nitrobenzene adsorption by RHA is 30 min. When residual concentration is 3.5 μg/L, maximum adsorption amount is 44 μg/g. The coagulation/sedimentation alone has little effect on removal of nitrobenzene, but RHA adsorption and removal efficiency is increased to 35–52%. The heating and boiling can eliminate nitrobenzene with more than 90% removal rate from groundwater. RHA adsorption and enhanced coagulation, followed by heating and boiling is a cost-effective process, especially in rural household. The process is not aimed only at nitrobenzene contamination, but applied also to other emergent water pollution and routine water quality improvement.

References

[1] B. Ou, S. Fu, Y. Wang, L. Wang, The comprehensive evaluation of rural drinking water security in Yunnan province, Procedia Earth Planet. Sci. 5 (2012) 155–158.
[2] F.N. Nnadi, M. Fulkerson, Assessment of groundwater under direct influence of surface water, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 37(7) (2002) 1209–1222.
[3] W. Min, M. Bo, Nitrobenzene pollution water survey, Chin. Public Health 21(1) (2005) 51–52 (in Chinese).
[4] M.-H. Sui, J. Ma, S. Li, MnOx/GAC catalytic ozonation for degradation of nitrobenzene, Modern Chem. Ind. 25(8) (2005) 31–37 (in Chinese).
[5] Z.-Z. Sun, L. Zhao, J. Ma, Degradation of nitrobenzene in aqueous solution by modified ceramic honeycomb-catalyzed ozonation, Environ. Sci. 26(6) (2005) 84–88 (in Chinese).
[6] P.S. Majumder, S.K. Gupta, Hybrid reactor for priority pollutant nitrobenzene removal [J], Water Res. 37 (2003) 4331–4336.

[7] J.-M. Shen, Z.-L. Chen, X.-Y. Li, F. Qi, M.-M. Ye, Effect and mechanism of degradation of nitrobenzene in aqueous solution by O_3/H_2O_2, Environ. Sci. 27(9) (2006) 1791–1797 (in Chinese).

[8] Z.-L. Chen, J. Ma, G.-B. Li, J.-M. Shen, F. Ji, Emergency treatment of songhua river raw water polluted by nitrobenzene, Chin. Water Wastewater 29(5) (2003) 27–30 (in Chinese).

[9] Q.-C. Hong, Study on adsorption performance of rice hull ash, Chin. Oils Fats 27(1) (2009) 29–30 (in Chinese).

[10] D.-F. Zhou, J. Hao, Comprehensive utilization of rice husks, Changchun Ind. Univ. J. 25(1) (2004) 59–62 (in Chinese).

[11] Y.Y. Ang, Rice hull ash structure and bleaching performance by ashing at various times and temperatures, J. Am. Oil Chem. Soc. 6 (2001) 657–660.

[12] Y.-D. Ou, K. Chen, SEM/TEM study on the microstructure of rice husk ash and nano-SiO_2, J. Electron Microsc. Soc. 22(5) (2003) 390–394 (in Chinese).

[13] J. Yin, Z.-S. Liu, Discussion on the significance of oxidation reduction potential in drinking water for health, Chin. Water Wastewater 21(9) (2005) 25–28 (in Chinese).

[14] F.-Z. Li, X.-J. Zhang, Z.-S. Wang, M.-J. Lv, Structure research of boiling and cooled water by NMR, Water Wastewater Eng. 29(5) (2003) 27–30 (in Chinese).

[15] L. Sujbert, G. Race, B. Szende, H.C. Schroder, Genotoxic potential of by-products in drinking water in relation to water disinfection: Survey of pre-ozonated and post-chlorinated drinking water by Ames-test, Toxicology 219 (2006) 106–112.