Enhanced removal of antimony in dyeing wastewater by mixing Fe3O4 with manganese sand filter material

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• Abstract

Wastewaters from the printing and dyeing industries contain many contaminants in particular antimony (Sb) that end up in the environment. Both manganese sand filter and Fe_3O_4 have good removal effect on Sb, and are cheap and easy to obtain. We made a filter material by mechanically mixing the manganese sand filter material and ferro-ferric oxide (Fe_3O_4). The Fe–Mn oxide filter material was analyzed by X-ray diffraction. We studied the filtration of real wastewater from a dyeing wastewater resource recovery facility in Suzhou, China, containing Sb at high concentration of 410 μg/L, using dynamic tests in adsorption columns during 7 days. We tested the effects of filter material volume filling ratio, the empty bed contact time (EBCT), pH, and back washing on the removal of Sb. Results show that the addition of Fe_3O_4 enhanced the removal of Sb, reaching 85% of initial Sb. When the initial influent pH of the raw water is 3.0, the volume filling ratio of filter material is 60%, the EBCT is 20 min, and the developed dynamic Fe–Mn oxide filter has the best removal effect on Sb. Daily back washing of the filter keeps a Sb removal rate of about 80%.

• Practitioner points

- A novel and cheap Fe–Mn oxide was developed for Sb removal from dyeing wastewater.
- A self-designed filter device was designed to verify performance of the low-cost material.
- Optimal design and operational parameters of the filtration process were determined.

• Key words

antimony removal; dyeing wastewater; dynamic filter; heavy metal; iron and manganese mixture

Introduction

Large amounts of printing and dyeing wastewaters have been produced by the printing and dyeing industries in recent years (Xi, He, & Kong, 2016). On August 4, 2018, the discharge of industrial waste has forced the closure of wastewater resource recovery facilities due to excessive Sb levels found in a river of Suzhou, China. Sb pollution has thus become a major problem. In the dyeing industry, it is necessary to use Sb compounds such as antimony acetate and ethylene glycol antimony as catalysts to produce the polyester fiber by poly-condensation reactions (Jiang, Su, & Song, 2016; Wang, Chen, et al., 2018; Wang, Ye, Yu, & Jing, 2018). Previous studies have shown that the toxicity of Sb varies with Sb valence, for example, the toxicity of Sb(III) is ten times higher than that of Sb(V) (Ungureanu, Santos, Boaventura, & Botelho, 2015).

Strict regulations on Sb contents in drinking water have been implemented worldwide (Herath, Vithanage, & Bundschuh, 2017). For example, the U.S. Environmental Protection Agency sets a maximum limit of 6 μg/L for Sb in drinking water (Herath et al., 2017), whereas it is 10 μg/L in the European Union (Davies & Mazurek, 2014). Because of the largest antimony reserves and rapid development, China is suffering from environmental pollution caused by the exploitation of antimony ores (Wen, Zhou, Zhou, Liu, & Xie, 2016). Chinese authorities have decreased the limit of Sb emission in water from 100 μg/L in 2012 to 50 μg/L in 2015 and 5 μg/L in 2019 (Gao et al., 2019).

Sb can be removed from the waters by precipitation, coagulation/flocculation, adsorption and electrochemical methods. Experiments show that combining different methods to remove antimony at the same time can achieve better results, such as dual-functional electroactive filter system (Liu, Liu, et al., 2019; Liu, Wu, et al., 2019). Coagulation and sedimentation are simple and easy to operate, but require a large amount of precipitant; these processes produce a large amount of Sb containing sludge and thus cause secondary pollution. Electrochemical methods have the advantages of a short reaction time and less secondary pollution, but it is more suitable for treating high-strength wastewater (Li et al., 2018; Ungureanu et al., 2015).

Adsorption is also widely used to remove Sb due to high adsorption efficiency and easy to operate (Mubarak et al., 2015; Saleh, Sarı, & Tuzen, 2017). For instance, the manganese sand filter is cheap and stable for long-term operations. The real wastewater used in this study was based on the adsorption of manganese sand filter material as the main method to remove Sb. The main component of the manganese sand filter material is manganese dioxide, a common adsorbent in water treatments (Liu & Ackermann 2016, Xu et al., 2013; Zhang, Liu, Dai, Zhou, & Liu, 2014).

Manganese dioxide has rich and varied crystal morphology, a strong oxidation ability, and specific adsorption for heavy metals (Chon, Cho, Nam, Kim, & Song, 2018; Islam, Morton, Johnson, Mainali, & Angove, 2018). Iron oxide composite adsorption materials are also widely used to treat wastewater with heavy metals and organic pollutants for their advantages of low-cost, high adsorption capacity and uniform particle dispersion (Nizamuddin et al., 2019; Yang et al., 2017). Fe_3O_4 magnetic particles are widely used because of their simple preparation, low-cost, nontoxic, and high specific surface area (Kumari, Pittman, & Mohan, 2015).

When manganese and iron oxides are combined as ferromanganese oxides, Sb can be removed by both oxidation and adsorption (Bai, Jefferson, Liang, Yang, & Qu, 2017). The removal of Sb ions from water using Fe and Mn bimetallic oxides as adsorbents has been shown (Shi et al., 2018); however, few investigations have tested these oxides during dynamic processes (Ochirkhuyag et al., 2008). Moreover, previous studies have often produced adsorbents by costly and complex chemical synthesis, which is often costly. The use characteristics of materials can only be determined through dynamic experiments, and the actual operating conditions can be simulated through dynamic experimental data to determine the amount of materials added and the composition ratio. Therefore, this study combines the advantages of both materials to explore the feasibility of this low-cost and easy-to-use synthesis method. Our objective was therefore to design a filter which filled with a mixture of Fe_3O_4 and manganese sand filter material to remove Sb in real wastewater and to explore the effect of filter material volume filling ratio, EBCT, pH, and back washing on its removal efficiency.

Materials and Methods

Dyeing wastewater

Real wastewater was taken from the secondary effluent of a dyeing wastewater resource recovery facility that uses a contact oxidation process in Suzhou, China. It is detected that pH in the wastewater was 9.0–9.5, and COD was 1,090.0 mg/L; the main valence of Sb is +5, and the concentration was 410 μg/L. From the effluent water quality index, it was found that the contact oxidation method has a good removal effect on chemical oxygen demand (COD) and NH_3–N, but does not remove Sb efficiently. Wastewater plant originally used manganese sand filter material as the main method to remove Sb. On this basis, we modified the filter material to improve the removal rate of antimony.

Characterization of the manganese sand filter material

The study subject in this paper is the mixture of Fe_3O_4 and manganese sand filter material. The main component of the manganese sand filter material is MnO_2. Because manganese sand filter and iron oxide are often used as water treatment materials, neither material will introduce secondary pollution (Liu, Liu, et al., 2015). The particle size of the study manganese sand filter is 0.5 mm, containing MnO_2 as the main composition and a small amount of SiO_2. It has a strong adsorption capacity to heavy metals. The picture and XRD of the manganese sand filter material can be referred to Supporting Information Figure S1.

Synthesis of the Fe–Mn oxide filter material

We used a physical, gentle blending, stratified dosing method to prepare the materials, which does not require complicated chemical synthesis. Firstly, the manganese sand filter material and Fe_3O_4 were mixed at a mass ratio of 3:1, and ultrasonically dispersed with pure water for 2 hr; then, the composite filter was taken out and dried; subsequently, the dried composite filter was put into adsorption columns for dynamic investigations.

Preparation of filters

Treatment of real Sb-containing wastewater was studied in a filter column packed with the Fe–Mn oxide filter material (Figure 1). The diameter of the filter column is 3.16 cm, and the total volume is 39.19 cm^3. The volume filling ratio refers to the percentage of the filter volume to the total volume of the filter column. A continuous flow filtration process was used to study dynamic performance of the Fe_3O_4 enhanced manganese sand filter.

Optimization of operational parameters

The volume filling ratio of filters, EBCT, pH, and effects of back washing was investigated at room temperature with dynamic tests. The test results are based on the change in antimony content in the influent and effluent water, and

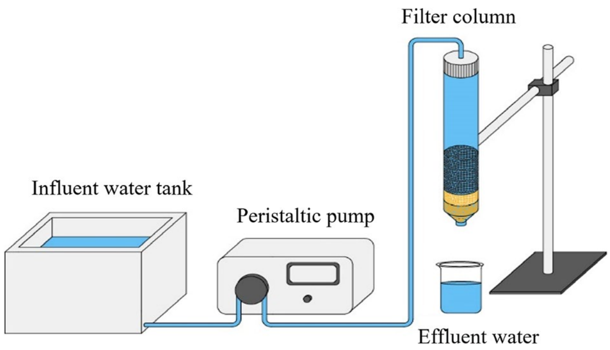

Figure 1. Diagram illustration of the dynamic filtration tests.

converted to the percentage of antimony removal. Firstly, the effect of the filter volume filling ratio on the removal of Sb was studied by testing the different volume filling ratios of the synthesized Fe_3O_4–MnO_2 sand material in the filter column. The running filling ratios are 30%, 40%, 50%, 60%, and 70%, respectively. After the optimal filling ratio of 60% was found, this filling ratio was used to carry on the follow-up tests. Then, three EBCTs of 10, 20, and 30 min were tested and optimized. EBCT refers to the amount of water treated per unit volume of particulate filler in unit time and is generally expressed in min. The effect of influent pH on the removal rate was studied by adjusting the initial pH of real wastewater to 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 with 0.1 mol/L HCl or NaOH solution, respectively. Finally, the effect of back washing on the removal efficiency was investigated. Two identical filter columns were operated in parallel; one of the filter columns was operated without back washing, and the other was back washed every day.

Samples were taken every day, passed through a 0.45 μm filter, and then, the Sb concentration was measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, PE Optima 8000, PerkinElmer, Waltham, Massachusetts,) with forward power of 1.15 kW and auxiliary gas of 0.5 L/min.

Results and Discussion

We studied the effect of adding Fe_3O_4 in a manganese sand filter on Sb adsorption in real Sb-contaminated wastewaters using dynamic adsorption experiments during 1–7 days. We tested the effects of filter column filling ratio, empty bed contact time, influent pH, and back washing.

Kinetics of the study filter

The kinetics of single manganese sand filter and Fe_3O_4-mixed manganese sand filter were studied by static test with preconfigured Sb pure solution. The results are shown in Figure 2. The adsorption equilibrium capacity of the Fe_3O_4-mixed manganese sand filter for Sb is 0.66 mg/g, which is slightly higher than the adsorption equilibrium capacity of Sb by single manganese sand filter (0.63 mg/g). At the same time, the R^2 values of both materials reached 0.99. Therefore, the pseudo-second-order adsorption kinetic equation can be used to describe the adsorption kinetics of Sb.

Performance of the manganese sand filter material mixed with or without Fe_3O_4

Dynamic Sb removal of the study filters is shown in Figure 3. The manganese sand filter material has the lowest Sb removal rate. When the manganese sand filter material and Fe_3O_4 are mixed, the removal rate has been improved obviously. It can be indicated from the figure that compared with the simple manganese sand filter, mechanical mixing of the manganese sand filter and Fe_3O_4 has a significant increase in Sb removal rate. This is because Fe_3O_4 has a higher specific surface area for better removal of Sb, but it is easy to agglomerate and affect the removal effect, so mixing it with manganese sand filter material can exert the better removal effect of Fe_3O_4 on Sb. However, single Fe_3O_4 is prone to corrosion and agglomeration, resulting in a significant decrease in its adsorption capacity (Yang et al., 2017). Therefore, this study considers manganese sand filter material as the main adsorption carrier. By grafting a small amount of Fe_3O_4 to the manganese sand filter, the adsorption site of the material can be increased, improving Sb adsorption on the surface of the manganese sand filter (Islam et al., 2018). Compared with other synthetic filters, the composite manganese-Fe_3O_4 sand filter can be prepared without complicated synthesis process.

Dynamic Sb removal by filters is shown in Figure 3. Results show that the Fe_3O_4 manganese sand filter induces a higher Sb removal of 75% versus 83% for the manganese sand filter at day 1. This finding is explained by the magnetic properties and high specific surface area of Fe_3O_4. Our results are supported by a previous report showing that grafting a small amount of Fe_3O_4 to a manganese sand filter improves Sb adsorption (Islam et al., 2018). Grafting Fe_3O_4 to a manganese sand filter is better than that using Fe_3O_4 alone because Fe_3O_4 is prone to corrosion and agglomeration, resulting in a significant decrease in its adsorption capacity (Yang et al., 2017). Moreover, compared with other synthetic filters, the composite manganese-Fe_3O_4 sand filter can be prepared without complicated synthetic steps.

Effect of volume filling ratios

The filter material volume filling ratio is an important parameter affecting performance of the filter. Excessive filling is likely to cause clogging of the filter material. If the volume filling ratio is too small, the adsorption site is insufficient and the effluent is not satisfactory. Therefore, this investigation conducted dynamic tests under five different filling ratios. When the volume filling ratio is 60%, saturated adsorption can be achieved with a Sb removal rate above 80% (Figure 4). Found through subsequent tests the removal rate of the composite adsorbent has a significant upward trend when rising the volume filling ratio from 30% to 60%, implying that the adsorption position of the study filter was still at an insufficient state. When the filling ratio is increased from 60% to 70%, the removal rate did not increase significantly, indicating that the filter medium has reached a saturated

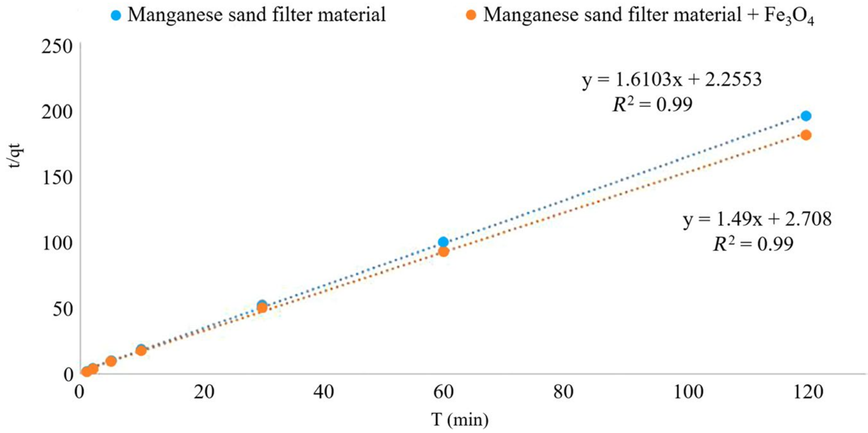

Figure 2. Pseudo-second-order kinetic curves of the study filters.

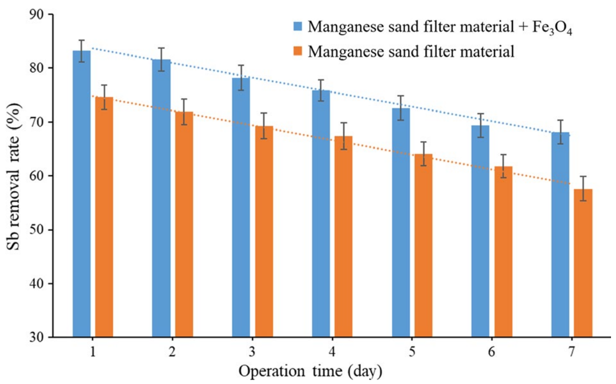

Figure 3. Comparison of adsorption performance of Sb in real wastewater by different filters.

state. Although the removal rate did not increase significantly when the filling ratio reached 70%, the filter column is more likely to occur plugging and blockage problems during operation. This is because that the increase of filling ratio is also controlled by the size of filter medium. If the size is too small, the larger filling ratio will reduce the water permeability of the filter column and lead to poor performance (Liu, Liu, et al., 2015). Considering the economic benefits, the optimal filling ratio is determined as 60% for the study dynamic composite filter. At this time, the optimal removal rate of the filter column is 90%. When the filter column is continuously operated for 7 days without back washing, the removal rate of the filter column can still be maintained at about 77%.

Effect of empty bed contact time

Subsequently at room temperature, real Sb wastewater was put into the adsorption column with the optimized filter filling ratio of 60%. Performances of the Fe_3O_4–MnO_2 sand material dynamic filter under the empty bed contact time of 10, 20, and 30 min were investigated, respectively. The results are shown in Figure 5.

Results show that reducing EBCT increases the filtration rate, resulting in poor Sb removal when the contact time is less than 20 min. Performance of the Fe_3O_4–MnO_2 sand material dynamic filter was only slightly enhanced when the EBCT was increased from 20 to 30 min, indicating that the maximum utilization rate of adsorbed particles was almost achieved when the EBCT reached 20 min. A previous study has also shown that the best adsorption capacity is achieved for EBCT of 20 min (Shakya & Ghosh, 2018).

The adsorption process is controlled by the time of the surface contact, the diffusion of the adsorbate in the filter space, and adsorption by electrostatic attraction or chemical bonds (Gheju, 2018). If EBCT is larger than 20 min, and the contact time between the solid phase and the liquid phase in the adsorption zone is sufficient, inducing high adsorption efficiency. Therefore, for our composite adsorbent of Fe_3O_4 mixed with manganese sand filter material, we found that 20 min is the optimal EBCT. Under this condition, the optimal Sb removal is 91%.

Significantly, the use of Fe_3O_4-reinforced manganese sand filter material can significantly reduce the material synthesis cost while obtaining a good adsorption effect, which is very suitable for practical engineering.

Effects of the initial pH value

We tested the effect of pH by changing the real wastewater pH with NaOH or HCl. Initial influent pH is a major factor affecting the adsorption of pollutants. Figure 6 shows an increase of Sb removal by the Fe_3O_4-manganese sand filter from 88.5% at pH 3 to 70.0% at pH 10. This finding is explained by the fact that Sb mainly is in the form of the $[Sb(OH)_6]^-$ anion in water. Indeed, at acidic pH, surfaces are more protonated, thus inducing electrostatic attraction of anions. Lower pH might weaken the protonation of the adsorbent surface, thereby reducing the amount of adsorbed contaminants (Liu, Xu, et al., 2015; Yang et al., 2018).Therefore, for the composite Fe_3O_4-manganese sand filter, the pH of the influent should be acidic. When the pH is 3.0, the optimal removal rate of the filter column can reach 89%. After 7 days of continuous operation, the removal rate of the filter column can still be maintained above 80% (Figure 6).

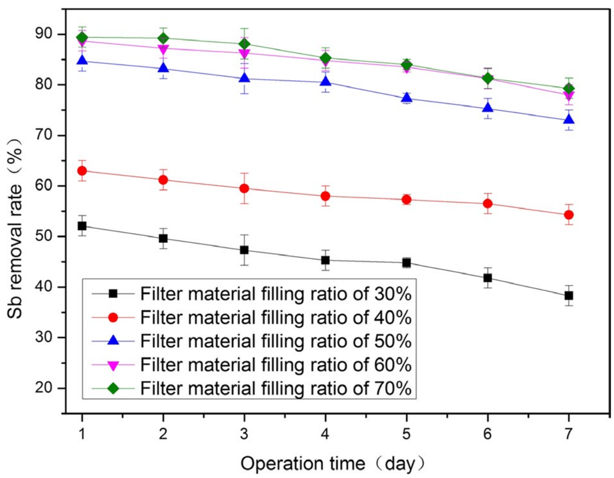

Figure 4. Comparison of adsorption performance of Sb in real wastewater under different filter material filling ratios.

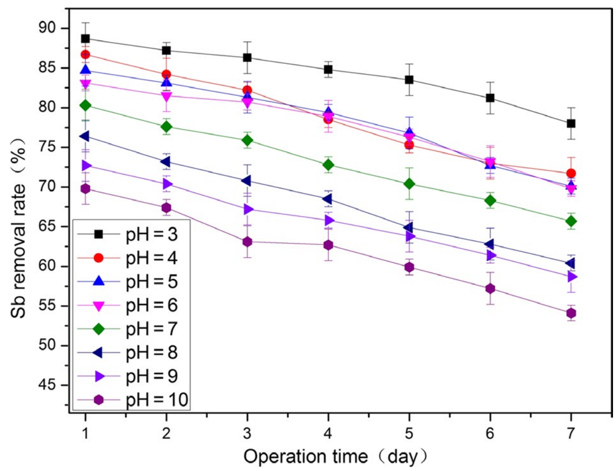

Figure 6. Comparison of adsorption performance of Sb on real wastewater under different pH conditions.

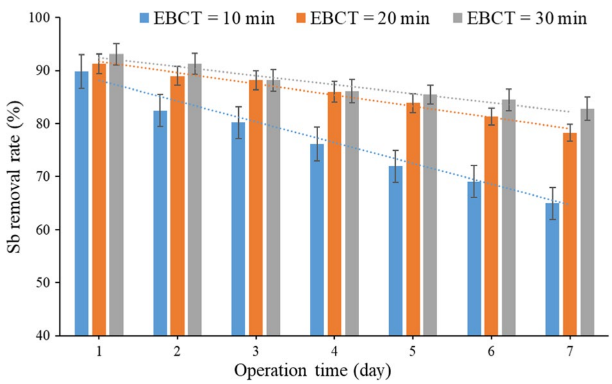

Figure 5. Comparison of adsorption performance of Sb in real wastewater under different empty bed contact times.

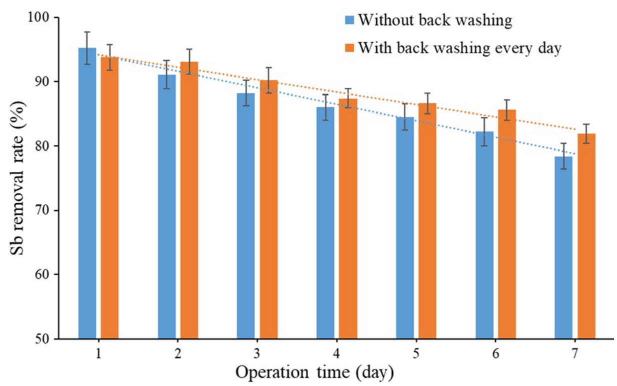

Figure 7. Effect of back washing on Sb adsorption performance of the filter column.

Effects of back washing

As an important operational parameter for filter columns, back washing has a great influence on Sb removal. Back washing is the process of washing the filter material with reverse water flow to restore the normal operation of the filter column. Water flows through the bottom of the filter column in the reverse direction to flush out the blocking material in the filter. In this study, two filter columns with identical operating conditions were used for 7 days of operation. One of the filter columns was back washed every 24 hr while the other column was operated without back washing. Back washing at the initial stage of the reaction does not have a significant effect on performance of the filter column, but the positive influence is gradually amplified when the filter column is operated to the third day (Figure 7). When the filter is operated for a period of time, the surface and gap of the filter material are gradually saturated by the contaminants, resulting in a decrease in the removal rate of the Sb and an increase in the head loss. The removal rate of Sb in the wastewater will be significantly reduced when the head loss decreased rapidly, resulting in a continuous decline in quality of the filtered wastewater. However, when back washing is implemented every day, the removal rates of the Fe–Mn oxide filters remain constant and there is no obvious agglomeration observed in the filter media. This is because after back washing, the solid material covered on surface of the filter can be removed, and the performance of the filter can be restored (Gheju, 2018).

Wastewater generated by back washing is not suitable for reuse due to heavy load of suspended solids. The use of polyaluminium chloride (PAC) as a coagulant treating discharged wastewater from back washing is recommended. Figure 7 indicated that the Fe_3O_4-mixed manganese sand filter was a promising technology removing Sb from wastewater, with an optimal removal rate of 92%. The filter can be stably operated for at least 7 days without back washing. The filter column should be back washed every 24 hr to remove pollutants on surface and gap of the filter material so that it can be regenerated, thereby maintaining a stable and excellent filtration performance.

Conclusions

This study has developed and explored the Fe–Mn oxide filter material which is low-cost, easy-to-synthesize, and easy-to-operate. Manganese sand filter material and Fe_3O_4 both have a good removal effect on Sb, but Fe_3O_4 is not suitable for practical wastewater treatment due to its shortcomings such as agglomeration. Fe_3O_4 is attached to the surface of the manganese sand filter by mechanical mixing, which enhances the adsorption effect of the manganese sand filter and avoids the agglomeration of Fe_3O_4. The investigation shows that manganese sand filter mixed with Fe_3O_4 is suitable for improving the antimony removal efficiency of the manganese sand filter. Optimized parameters for the developed dynamic Fe–Mn oxide filter are as follows: The initial influent pH of the raw water is 3.0, the volume filling ratio of filter material is 60%, and the EBCT is 20 min. The adsorption column should be back washed every day. Optimal removal rate of the filter column against Sb is 92%. This paper provides a method for upgrading the antimony removal of manganese sand filter media for printing and dyeing wastewater resource recovery facilities.

Acknowledgments

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Conflict of interest

The authors have declared no conflict of interest.

References

Bai, Y., Jefferson, W. A., Liang, J., Yang, T., & Qu, J. (2017). Antimony oxidation and adsorption by in-situ formed biogenic Mn oxide and Fe–Mn oxides. *Journal of Environmental Sciences*, *54*, 126–134. https://doi.org/10.1016/j.jes.2016.05.026

Chon, C.-M., Cho, D.-W., Nam, I.-H., Kim, J.-G., & Song, H. (2018). Fabrication of Fe/Mn oxide composite adsorbents for adsorptive removal of zinc and phosphate. *Journal of Soils and Sediments*, *18*, 946–956. https://doi.org/10.1007/s11368-017-1784-3

Davies, J. C., & Mazurek, J. (2014). *Pollution control in United States: Evaluating the system*. Abingdon, UK: Routledge.

Gao, B., Gao, L., Gao, J., Xu, D., Wang, Q., & Sun, K. (2019). Simultaneous evaluations of occurrence and probabilistic human health risk associated with trace elements in typical drinking water sources from major river basins in China. *Science of the Total Environment*, *666*, 139–146. https://doi.org/10.1016/j.scitotenv.2019.02.148

Gheju, M. (2018). Progress in understanding the mechanism of CrVI removal in Fe0-based filtration systems. *Water*, *10*, 651. https://doi.org/10.3390/w10050651

Herath, I., Vithanage, M., & Bundschuh, J. (2017). Antimony as a global dilemma: Geochemistry, mobility, fate and transport. *Environmental Pollution*, *223*, 545–559. https://doi.org/10.1016/j.envpol.2017.01.057

Islam, M. A., Morton, D. W., Johnson, B. B., Mainali, B., & Angove, M. J. (2018). Manganese oxides and their application to metal ion and contaminant removal from wastewater. *Journal of Water Process Engineering*, *26*, 264–280. https://doi.org/10.1016/j.jwpe.2018.10.018

Jiang, X., Su, S., & Song, J. (2016). Metal pollution and metal sustainability in China. In R. M. Izatt (Ed.) *Metal sustainability: Global challenges, consequences, and prospects* (pp. 169–199). Hoboken, NJ: Wiley.

Kumari, M., Pittman, C. U. Jr, & Mohan, D. (2015). Heavy metals [chromium (VI) and lead (II)] removal from water using mesoporous magnetite (Fe_3O_4) nanospheres. *Journal of Colloid and Interface Science*, *442*, 120–132. https://doi.org/10.1016/j.jcis.2014.09.012

Li, J., Zheng, B., He, Y., Zhou, Y., Chen, X., Ruan, S., … Tang, L. (2018). Antimony contamination, consequences and removal techniques: A review. *Ecotoxicology and Environmental Safety*, *156*, 125–134. https://doi.org/10.1016/j.ecoenv.2018.03.024

Liu, R., Liu, F., Hu, C., He, Z., Liu, H., & Qu, J. (2015a). Simultaneous removal of Cd (II) and Sb (V) by Fe–Mn binary oxide: Positive effects of Cd (II) on Sb (V) adsorption. *Journal of Hazardous Materials*, *300*, 847–854. https://doi.org/10.1016/j.jhazmat.2015.08.020

Liu, R., Xu, W., He, Z., Lan, H., Liu, H., Qu, J., & Prasai, T. (2015b). Adsorption of antimony (V) onto Mn (II)-enriched surfaces of manganese-oxide and Fe Mn binary oxide. *Chemosphere*, *138*, 616–624. https://doi.org/10.1016/j.chemosphere.2015.07.039

Liu, W., & Ackermann, L. (2016). Manganese-catalyzed C–H activation. *ACS Catalysis*, *6*, 3743–3752. https://doi.org/10.1021/acscatal.6b00993

Liu, Y., Liu, F., Qi, Z., Shen, C., Li, F., Ma, C., … Li, J. (2019a). Simultaneous oxidation and sorption of highly toxic Sb(III) using a dual-functional electroactive filter. *Environmental Pollution*, *251*, 72–80. https://doi.org/10.1016/j.envpol.2019.04.116

Liu, Y., Wu, P., Liu, F., Li, F., An, X., Liu, J., … Wolfgang, S. (2019b). Electroactive modified carbon nanotube filter for simultaneous detoxification and sequestration of Sb(III). *Environmental Science & Technology*, *53*(3), 1527–1535. https://doi.org/10.1021/acs.est.8b05936

Mubarak, H., Chai, L.-Y., Mirza, N., Yang, Z.-H., Pervez, A., Tariq, M., … Mahmood, Q. (2015). Antimony (Sb)–pollution and removal techniques–critical assessment of technologies. *Toxicological and Environmental Chemistry*, *97*, 1296–1318.

Nizamuddin, S., Siddiqui, M., Mubarak, N., Baloch, H. A., Abdullah, E., Mazari, S. A., … Tanksale, A. (2019). Iron oxide nanomaterials for the removal of heavy metals and dyes from wastewater, nanoscale materials in water purification. In S. Thomas, D. Pasquini, S.-Y. Leu, & D. A. Gopakumar (Eds.) *Nanoscale materials in water purification* (pp. 447–472). Amsterdam, the Netherlands: Elsevier.

Ochirkhuyag, B., Mori, T., Katsuoka, T., Satone, H., Tsubaki, J., Choi, H., & Sugimoto, T. (2008). Development of a high-performance cake-less continuous filtration system. *Chemical Engineering Science*, *63*(21), 5274–5282.

Saleh, T. A., Sarı, A., & Tuzen, M. (2017). Effective adsorption of antimony (III) from aqueous solutions by polyamide-graphene composite as a novel adsorbent. *Chemical Engineering Journal*, *307*, 230–238.

Shakya, A. K., & Ghosh, P. K. (2018). Simultaneous removal of arsenic, iron and nitrate in an attached growth bioreactor to meet drinking water standards: Importance of sulphate and empty bed contact time. *Journal of Cleaner Production*, *186*, 1011–1020. https://doi.org/10.1016/j.jclepro.2018.03.176

Shi, Z., Peng, S., Wang, P., Sun, Q., Wang, Y., Lu, G., & Dang, Z. (2018). Modeling coupled kinetics of antimony adsorption/desorption and oxidation on manganese oxides. *Environmental Science: Processes & Impacts*, *20*, 1691–1696. https://doi.org/10.1039/C8EM00323H

Ungureanu, G., Santos, S., Boaventura, R., & Botelho, C. (2015). Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption. *Journal of Environmental Management*, *151*, 326–342. https://doi.org/10.1016/j.jenvman.2014.12.051

Wang, J., Chen, Y., Zhang, Z., Ai, Y., Liu, L., Qi, L. I., … Liang, Q. (2018a). Microwell confined iron oxide nanoparticles in honeycomblike carbon spheres for the adsorption of Sb (III) and sequential utilization as a catalyst. *ACS Sustainable Chemistry & Engineering*, *6*, 12925–12934. https://doi.org/10.1021/acssuschemeng.8b02300

Wang, L., Ye, L., Yu, Y., & Jing, C. (2018b). Antimony redox biotransformation in the subsurface: Effect of indigenous Sb (V) respiring microbiota. *Environmental Science and Technology*, *52*, 1200–1207. https://doi.org/10.1021/acs.est.7b04624

Wen, B., Zhou, J., Zhou, A., Liu, C., & Xie, L. (2016). Sources, migration and transformation of antimony contamination in the water environment of Xikuangshan, China: Evidence from geochemical and stable isotope (S, Sr) signatures. *Science of the Total Environment*, *569*, 114–122. https://doi.org/10.1016/j.scitotenv.2016.05.124

Xi, J., He, M., & Kong, L. (2016). Adsorption of antimony on kaolinite as a function of time, pH, HA and competitive anions. *Environmental Earth Sciences*, *75*, 136. https://doi.org/10.1007/s12665-015-4916-3

Xu, M., Wang, H., Lei, D., Qu, D., Zhai, Y., & Wang, Y. (2013). Removal of Pb(II) from aqueous solution by hydrous manganese dioxide: Adsorption behavior and mechanism. *Journal of Environmental Sciences*, *25*, 479–486. https://doi.org/10.1016/S1001-0742(12)60100-4

Yang, K., Zhou, J., Lou, Z., Zhou, X., Liu, Y., Li, Y., … Xu, X. (2018). Removal of Sb (V) from aqueous solutions using Fe–Mn binary oxides: The influence of iron oxides forms and the role of manganese oxides. *Chemical Engineering Journal*, *354*, 577–588. https://doi.org/10.1016/j.cej.2018.08.069

Yang, K., Zhou, J., Lv, D., Sun, Y., Lou, Z., & Xu, X. (2017). Preparation and application of iron-based composite materials for the removal of antimony from aqueous solution. *Progress in Chemistry*, *29*(11), 1407–21.

Zhang, Y.-L., Liu, Y.-J., Dai, C.-M., Zhou, X.-F., & Liu, S.-G. (2014). Adsorption of clofibric acid from aqueous solution by graphene oxide and the effect of environmental factors. *Water, Air, and Soil Pollution*, *225*, 2064. https://doi.org/10.1007/s11270-014-2064-0

Supporting Material

Figure S1