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Advanced treatment of piggery tail water by dual coagulation with Na^+ zeolite and Mg/Fe chloride and resource utilization of the coagulation sludge for efficient decontamination of Cd^{2+}

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ABSTRACT

With the stricter sewage discharge standards and higher environmental quality requirements, the development of advanced treatment technology of piggery tail water (the effluent of biochemical unit) is particularly urgently needed. We used dual coagulation with Na^+ modified zeolite (NMZ) and Mg^{2+}/Fe^{3+} chloride to remove COD, TP, $NH_3{-}N$ and turbidity from piggery tail water. Thereafter, the on-site coagulation sludge was oxygen-limited pyrolyzed, and the pyrolyzed sludge (PS) showed a great capacity to adsorb and remove Cd^{2+} from water. Fourier transform infrared (FTIR) and X-ray photoelectron spectra (XPS) analysis showed that abundant new binding sites were generated after pyrolysis, and the surface morphology of PS composites were examined by scanning electron microscopy (SEM). The results confirmed the presence of NMZ, Mg/Fe metal oxides, biochar and phosphates in PS composites, leading to a synergistic effect for high efficient Cd^{2+} removal. The Cd^{2+} adsorption on the composite PS500 (sludge pyrolyzed at 500 °C) can be well expressed by Langmuir isotherm model with theoretical maximum adsorption capacity of 139.28 mg g^{-1}. The adsorption behaviors of PS500 were affected by solution pH, coexisting ions and humic acids. Hence, dual coagulation with NMZ-Mg/Fe chloride is one of the effective methods for the advanced treatment of piggery wastewater, and the coagulation product can be utilized to remove Cd^{2+}, which is beneficial to reduction of environmental pollution and resource recovery.

1. Introduction

Direct discharge or irrigation of piggery biochemical tail water can easily cause the eutrophication of surface water. According to the discharge standard of pollutants for livestock and poultry breeding (Second Consultative Paper, Circular Office Letter [2014] 335) in China, the allowed emission concentration of COD_{Cr} and $NH_3{-}N$ decreased from 400 to 150 and 80 to 40 mg L^{-1}, respectively, compared with the previous standard (GB, 18596-2001). However, it is difficult to meet the above requirements through conventional treatment methods (biochemical or ecological) (Borin et al., 2013). An efficient and economically feasible method based on the existing processes of advanced treatment of piggery tail water was required.

Coagulation technology can remove contaminants with a short hydraulic retention time. Based on the original wastewater treatment units, a coagulation sedimentation tank can be built after the biochemical tank, which does not affect the operation of the original processes, and further improve the quality of the effluent. Due to their high cation-exchange capacity, zeolite has been widely used as an adsorbent to treat pollutants, for instance, ammonium and heavy metal ions from aqueous solutions (Wang and Peng, 2010). NaCl modified zeolite (NMZ), which has a greater cation exchange capacity, can effectively remove ammonia nitrogen and metal cations in water (Reeve and Fallowfield, 2018). Our previous study found that the addition of coagulants Mg^{2+}/Fe^{3+} chloride can achieve a desired effect on COD, TN and TP removal. In this paper, suitable coagulation conditions were further explored, which can

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effectively remove COD, TP and NH_3–N, and improve the transparency of water.

Cadmium is widely distributed in wastewater such as electroplating, mining, smelting, dyestuff and breeding industry. Cadmium is frequently detected in piggery tail water and is harmful to human beings and nature due to its bioaccumulation and strong toxicity (Li et al., 2018; Tinkov et al., 2017). Compared to other metal cations in piggery tail wastewater such as Zn^{2+} and Cu^{2+}, Cd^{2+} is more hazardous and not easy to remove by chemical precipitation. Biochars derived from excess sludge (Huang et al., 2017), straws (Li et al., 2017a, b), peanut husks (Cheng et al., 2016), tobacco stem (Zhou et al., 2018) and other plants were used to remove heavy metal such as Cd^{2+}, Pb^{2+} and Cu^{2+} from water. However, the risk of exposure of excess exogenous carbonaceous materials to ecology cannot be ignored (Ren et al., 2018). Treatment of piggery wastewater by biochemical methods results in huge amounts of sludge which contains large amounts of organic matter, and can be turned to biochars to stabilize soil (Tang et al., 2018; Yoo et al., 2018), adsorb phosphate (Yang et al., 2018) and remove heavy metals (e.g. Pb, Hg) (Ho et al., 2017; Ifthikar et al., 2018). However, the biochar derived by recovering sludge during biochemical treatment usually contains large quantities of toxic substances, such as heavy metals, which would pose serious risks to the environment. Tail water of piggery after biochemical treatment contains nutrients and suspended solid, with few toxic and harmful substances (Fridrich et al., 2014). It is a feasible method to use environment-friendly coagulant for advanced treatment of piggery tailing water and then recover and use coagulant sediment. Utilizing the pyrolysis composite as an adsorbent for heavy metal removal, which could meet the requirements of cleaner production.

In this study, we explored the appropriate conditions for the NMZ-Mg/Fe chloride dual coagulation method and conducted on-site coagulation test. The sludge from the on-site coagulation test was recovered and pyrolyzed at different temperatures. The as-synthesized product was used to remove Cd^{2+} and its adsorption behaviors were studied. More specifically, our goals in this study were to (a) determine the optimum conditions for coagulation, (b) develop a composite adsorbent by recycling coagulation sediment and pyrolyzing it under O_2-limited environment, (c) investigate the adsorption behaviors of Cd^{2+} on the PS composite and factors that influence the adsorption process, including pH, coexisting ions and humic acid and (d) explore the mechanism of PS composite adsorbing Cd^{2+}.

2. Methods and materials

2.1. Materials

Analytically pure NaCl, $MgCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, NH_4Cl, KH_2PO_4, KCl and $CaCl_2$ got from Guangzhou Chemical Regent Factory (Guangzhou, PRC) were used in this study. Zeolite and $Cd(NO_3)_2 \cdot 4H_2O$ were obtained from the factory of Tianjin Fuchen and Chemical Reagent Co., Ltd of Tianjin Kermel, respectively. Starch (TAIGANG, refer to COD) was purchased from Shenzhen Taigang Food Co., Ltd. Deionized-water was utilized in all experiment.

2.2. Preparation of simulated wastewater and Na^+ modified zeolite

To stably and systematically study the influences of pH and other conditions on the coagulation effect, simulated wastewater used in coagulation experiments were referenced from a biochemical unit tail water of a piggery which long-term cooperated with our group (Huizhou, Guangdong, China). 1.0 g dry pig manure was added to 1.0 L H_2O to simulate the chromaticity of piggery wastewater, after magnetic stirring for 24 h and suction filtration, filtrate left. There was 2.0 L filtrate which consisted of: 0.1225 g L^{-1} NH_4Cl, 0.0440 g L^{-1} KH_2PO_4 and 0.1885 g L^{-1} starch. The resulting solution was simulated wastewater of coagulation experiments. Characteristics of experimental water samples were presented in Table 1.

Preparation of NaCl-modified-zeolite (NMZ): put 10.0 g zeolite (<0.150 mm) into 1.0 L NaCl (0.3 mol L^{-1}), then heated in water bath (99 °C). After naturally cooling to room temperature, removed residual NaCl with deionized-water, centrifuged, dried, milled and sieved (<0.150 mm). Experiments showed that NMZ had better ammonia nitrogen adsorption capacity than natural zeolite (Fig. S1).

2.3. Coagulation experiments and on-site small-scale test

All coagulation experiments were carried out in a coagulation test mixer (ZR4-6). 250 mL simulated wastewater to six beakers, respectively. Next, after adding NMZ (0–8 g L^{-1}), began agitation at the speed of 200 $r \cdot min^{-1}$ for 60 min. The next stirring (150 $r \cdot min^{-1}$ for 5min, then 50 $r \cdot min^{-1}$ for 20 min) was carried out after adding coagulant (Mg^{2+}, Fe^{3+}). After the stirring, stood for 30 min, then measured the supernatant. The pH of solutions were adjusted with small amount of Na_2CO_3/HCl solution. The influence factors include NMZ dosage, initial solution pH (from 4.55 ± 0.1 to 9.55 ± 0.1) and Mg^{2+}/Fe^{3+} coagulants were discussed.

The solely adsorption ability and coagulation ability of NMZ dosage in the range of 1.0–6.0 g L^{-1} were explored. In other coagulation experiments in this study, the addition of zeolite was set at 4.0 g L^{-1}. The influence of Mg^{2+} and Fe^{3+} were examined independently and the effect of ratio of Mg^{2+}/Fe^{3+} was discussed. The pH value of the simulated wastewater was around 5.6 ± 0.1, and this value did not change in other mixed coagulation experiments.

On-site small-scale test was carried out in a piggery (Huizhou, Guangdong, China). The coagulation test was consisted of three parts: (1) took the biochemical pool effluent (200 L) as the coagulation influent, added NMZ (2 g L^{-1}) and stirred it quickly; (2) added the coagulants with $Mg^{2+}/Fe^{3+} = 2{:}1$, stirred rapidly and then stirred slowly; (3) after 30 min standing, took the supernatant and measured it, then retrieved the sediment.

The removal efficiency of reaction in this study was counted by: Removal rate (%) $= \frac{(C_0 - C_e)}{C_0} \times 100$, where C_0 and C_e ($mg \cdot L^{-1}$) were the concentration before and after the reaction.

2.4. Preparation of adsorbent

The method to synthesize PS composites was based on our previous study about sludge biochar (Huang et al., 2017). In order to recycling the sediment from on-site coagulation, the sediment was centrifugated, oven-dried and grinded. The pretreated sludge was called unpyrolyzed sludge (Un-PS). Put Un-PS in a nickel crucible, pyrolyzed them under O_2-limited environment at different temperatures (200, 300, 400, 500, 600 °C) with the rate of 20 $°C \cdot min^{-1}$ in a close roaster for 4 h. After cooling naturally to room temperature, milled and sieved the materials (<0.075 mm). The resulting sludge samples were referred to as PS, for instance, sludge pyrolyzed in 200 °C was named PS200, and so on.

2.5. Characterization

The external surface of Un-PS and PS were observed by SEM (Hitachi, S-4700) and the surface of the samples were sputter-coated with gold before observation. The surface area of samples were detected by analyzer- TriStar II 3020. FTIR spectra of Un-PS and PS composites were recorded by a PerkinElmer 1725× FTIR