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Cation resin fixed-bed column for the recovery of valuable THAM reagent from the wastewater

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ABSTRACT

Two commercial available cation resins, i.e. Amberlite IR-120 and Dowex HCR-W2, were tested as ion exchange adsorbents to investigate their isotherms, kinetics, breakthrough characteristics and regeneration on removal and recovery of tetra-methyl ammonium hydroxide (TMAH) from wastewater. Batch and column experiments were investigated to obtain experimental data for theoretical modelling and verify the column performance of the ion exchange process. The Langmuir isotherm represents better equilibrium behavior of both resins on TMAH uptake. The ion exchange kinetics follows the pseudo second order rate law also for both resins. Furthermore, breakthrough characteristics study shows the breakthrough curves follow the Thomas model and Yoon–Nelson model very well. The recovery efficiencies of TMAH were obtained as 99.6 and 98.0% from wastewater by ion exchange resin column by using 9 N HCl regeneration for Amberlite IR-120 and Dowex HCR-W2 resins, respectively. The comparative study on TMAH ion exchange removal by Amberlite IR-120 and Dowex HCR-W2 resins in fixed bed column suggested that Dowex HCR-W2 demonstrates higher ion exchange capacity than that of Amberlite IR-120 resin.

1. Introduction

Tetra-methyl ammonium hydroxide (TMAH) is broadly used in various industrial processes for manufacturing integrated circuits, liquid crystal displays, printed circuit boards, etc., especially in thin-film transistor liquid crystal display (TFT-LCD) industries as an important reagent for the photolithography process (Chang et al., 2015; Wu et al., 2012). TMAH is foremost utilized as a developer in photolithography, anisotropic etchant of silicon, and cleaning solution of wafer in above mentioned industries. In Taiwan, there were more than two thousand tons of TMAH used each month in year 2008 (Wu et al., 2008). The applications of TMAH in industries generate huge amount of wastewater containing spent TMAH. Therefore, wastewaters with high TMAH concentration are discharged to the industrial wastewater treatment plants (WWTPs) from TFT-LCD and semiconductor manufacturing. Originally, TMAH is used in research and thermochemlysis purposes in small scale and is investigated to have relatively low level of toxicity (Wu et al., 2008). However, industrial application of TMAH is in a form of concentrated strong alkaline and may cause severer hazardous effects. A case study reported that a young engineer died 8 days later, after he was accidentally exposed with high concentration of TMAH solution (25%, pH 13.5). This report presented that TMAH is a potential fatal hazard to workers in TFT-LCD industry (Wu et al., 2008). Furthermore, three fatality cases have been reported to be accidentally 25% TMAH exposed and 7–29% of total body surface area chemical burns, in recent years. Thus, TMAH wastewater issue also catches awareness from industries and public at the mean time.

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Due to the aquatic ecotoxicity (Mori et al., 2015), hazardous properties and human exposure risk (Wu et al., 2012) of TMAH, the treatment of TMAH wastewater brings much attention also from government enforcement. TMAH in industrial wastewater is recognized as slow biodegradable organic compound and lack of its biological treatability information (Hu et al., 2012). In general, low concentration TMAH in wastewater is transformed into ammonium nitrogen (NH_4^+–N) and nitrate by activated sludge process in wastewater treatment plant. The effluent with excess NH_4^+–N discharge performs harmful effect to the aquatic organisms and expresses the ecotoxicity to the waterbody. Therefore, specific and more restrict discharge requirements for TFT-LCD and semiconductor industrial effluents on NH_4^+–N and TMAH are enforced to reduce the impacts on aqueous environment in Taiwan. The discharge limit of TMAH from TFT-LCD and semiconductor industries to the industrial wastewater treatment plant (WWTP) has been regulated to be below 30 mg l^{-1} from 2015 in Central Taiwan Science Park (CTSP) (Central Taiwan Science Park, 2015/11/13). However, traditional biological treatment like activated sludge process hardly treat wastewater contaminated with spent TMAH reagent. It was reported that aerobic biological treatment of TMAH was start inhibited and completely inhibited when concentrations excess 150 and 450 mg l^{-1}, respectively (Hu et al., 2012). On the other hand, under methanogenic conditions, the up-flow anaerobic sludge blanket (UASB) sludge can treat TMAH initial concentration up to 1500 mg l^{-1} (Hu et al., 2012). Furthermore, research integrating Fenton oxidation with activated sludge process was presented to reduce toxicity of bioluminescent bacteria and shorten the adaptation period of activated sludge from 47 to 30 days (Kim et al., 2002). Therefore, it is urgent to reveal alternative technologies other than biological treatment for removal of TMAH from industrial discharge effluents and meeting regulations.

At this stage of technology development, few technologies such as biodegradation (Hu et al., 2012; Kim et al., 2002), advanced oxidation (Wang and Liang, 2014; Chiou et al., 2013), adsorption (Chang et al., 2015; Nishihama et al., 2012) and ion exchange (Shibata et al., 2006) were investigated to deal with TMAH wastewater. UV/persulfate advanced oxidation process was demonstrated to feasibly treat TMAH in bench scale with an observed first order rate constant of 0.0331 min^{-1} (Wang and Liang, 2014). Chiou et al. investigated the mineralization of low concentration TMAH, i.e., 20 mg l^{-1}, in aqueous solution by ozone related processes and found that the UV/O_3 process was the most powerful process with 95% mineralization among all ozone related processes including $UV/H_2O_2/O_3$, H_2O_2/O_3 and O_3 alone processes (Chiou et al., 2013). An investigation of low concentration TMAH (10 mg l^{-1}) adsorption by zeolite adsorbents was conducted following cation exchange mechanism with the highest adsorption amount of 0.0113 mmol g^{-1} by Templated-X adsorbent (Nishihama et al., 2010). The adsorption study of TMAH on graphene oxide showed higher capacity of adsorption than zeolite and activated carbon as well as better recovery of TMAH (Chang et al., 2015). Shibata et al. proposed a process combining cation and anion resins for treatment and recovery of TMAH from industrial wastewater. The tested column was able to treat 67 times of bed volume of TMAH wastewater and the total recovery after elution was 71.4% (Shibata et al., 2006).

Among these technologies, ion exchange technology is a mature, well established technology with ease to regenerate beneficial effect which can treat TMAH effluent and recovery TMAH reagent. Ion exchange technology is highly effective, low-cost material, efficient, and is ease to operate among physicochemical treatment processes (Dizge et al., 2009). It is similar to the adsorption process which has been demonstrated by researchers using cubic mesoporous silica (Kelleher et al., 2001) and graphene oxide (Chang et al., 2015). Recently, ion exchange technology has been applied to treat various pollutants from wastewater. It is one of the most popular technologies for the removal of heavy metal ions from wastewaters. Those metal ions include nickel (Dizge et al., 2009; Juang et al., 2006), uranium (Tavakoli et al., 2013), chromium (Alguacil et al., 2004), Palladium (II) (Hubicki et al., 2008), and tungsten (Di Natale and Lancia, 2007). Chromium (III) in wastewater had been proved to be effectively removed by Amberlite IR-120 cation resin column and the Langmuir isotherm was found to be adequate to describe the equilibrium behavior (Alguacil et al., 2004). Nickel (II) in wastewater was effectively treated by Lewatit MonoPlus SP112 cation exchange resin and Langmuir isotherm fitted well with experimental data. The pseudo second order kinetic model and pore-surface mass transfer diffusion model were confirmed. At the same time, the maximum nickel (II) adsorption capacity of resin was revealed to be 170.94 mg g^{-1} at 298 K (Dizge et al., 2009). Amberlite CG-400 was proved to be an efficient adsorbent for uranium recovery and 90% recovery was obtained by applying 0.5 M HNO_3 desorption (Tavakoli et al., 2013). In aqueous phase, TMAH resulting tetra-methyl ammonium ion (TMA) is a simple quaternary ammonium compound cation form. Therefore, cation exchange technology is expected as a promising process to remove TMAH from industrial wastewater. Furthermore, two commercial available strong acid cation exchange resins, i.e., Amberlite IR-120 and Dowex HCR-W2, are proposed to treat TMAH wastewater and recover TMA ions in industrial wastewater. Nevertheless, to the best of our knowledge, there are few studies of using ion exchange resin to remove TMAH, and the kinetics and breakthrough study of this technology has not been investigated thoroughly.

The aims of this work are to develop a fixed-bed column ion exchange process for removing TMAH from wastewater and recovering the valuable TMAH regent by regeneration of ion exchange resin. The resin ion exchange isotherm, kinetics and column breakthrough characteristics were studied for two commercial available cation exchange resins, i.e. Amberlite IR-1200 and Dowex HCR-W2 in fixed bed columns. To ensure cation resins can be applied to the real industrial TMAH wastewater, a fixed-bed cation resin filled column was demonstrated to study the effects of resin type, flow rate, TMAH initial concentration, and pH and also the regeneration approaches. The breakthrough curves were obtained for various operating parameters and used for breakthrough kinetics study.

2. Materials and methods

2.1. *Materials and apparatus*

TMAH ($(CH_3)_4NOH$, molecule weight 91.15 g mol^{-1}, pH 11–13) was purchased from Alfa Aesar, UK, as 25% electronic grade TMAH solution. The experimental TMAH solution was prepared by diluting 25% TMAH with D.I. water to obtain various initial TMAH concentrations of 300, 500 and 1000 mg l^{-1}. Methanesulfonic acid (CH_3SO_3H, molecule weight 96.11 g mol^{-1}) was purchased from Merck and used as mobile phase of ion chromatograph. Amberlite IR-120 resin and

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