

Effect of solution parameters on the removal efficiency of humic substances by a reuse material

A.F.Y. Adou*, V.S. Muhandiki**, Y. Shimizu*** and S. Matsui****

* Suzuki Industries, 5-6 Nakayoshimicho, Yamada, Nishikyoku, Kyoto 615-8237, Japan

** International Lake Environment Committee Foundation, 1091, Oroshimo-cho, Kusatsu, Shiga 525-0001, Japan

*** Research Center for Environmental Quality Control, Kyoto University, 1-2 Yumihama, Otsu 520-811, Japan

**** Department of Environmental Engineering, Kyoto University, Yoshida-Honmachi, Sakyo-ku Kyoto 606-8501, Japan

Abstract This paper provides an overview of the ability of polypropylene (PPL), a synthetic polymeric adsorbent made from reused plastic material. The removal of humic substances (HS) in a solution pretreated with dedoxyltrimethylammoniumbromide (DDTMAB), a cationic quaternary ammonium compound (QAC), was studied under various conditions. The removal of HS was achieved in its solute complexed form but also as suspended solids. The conditions of the HS solution, which fluctuation was suspected to have an impact on the performance of the adsorbent, were tested. The parameters investigated included the pH, the initial concentration of the surfactant, and the presence of suspended solids in solution. The results of the laboratory scale experiments showed that PPL removal efficiency of HS is strongly pH dependant with higher removal achieved at pH greater than 7. However, the shift for pH above 7 induced an increase in the optimum doses of DDTMAB as more and more deprotonated HS become available to react with DDTMAB. Ionic strength did have the opposite effect: the increase of ionic strength by addition of NaCl decreased PPL removal of HS.

Keywords Adsorption; HOC; humic acid; polypropylene (PPL); surfactant

Introduction

Although activated carbon (AC) has been widely promoted as the adsorbent for the removal of a broad range of both organic and inorganic contaminants, it requires expensive initial investment and generates excessive operating cost due in part to carbon regeneration. Unlike AC, synthetic adsorbents can be manufactured with certain physical and surface properties to meet the requirements of a particular application. Therefore, synthetic adsorbents like PPL are more specific and able to achieve a higher removal of specific contaminants. In particular, they can adsorb some compounds without the interference of humic substances, a major cause for the regeneration requirement of AC (Radke and Pransnitz, 1972; Jain and Snoeyink, 1973; Murin and Snoeyink, 1979; Benz and Sontheimer, 1990; Srivastava and Tyagi, 1995). In this research, particles of polypropylene (PPL), an adsorbent named after the waste plastic material from which it was generated, were used. Previous researches have shown that PPL, effectively adsorbs hydrophobic organic compounds (HOCs) from the effluent of municipal wastewater treatment plants (Hirane, 1996; Muhandiki, 1997). Examples of HOCs of prime concern are the polycyclic aromatic hydrocarbons (PAHs) and the polychlorinated biphenyls (PCBs).

Furthermore, the adsorption capacity of PPL increased (almost two fold) when it was coated with a thin film of *n*-hexane (PPL-HEX). However, PPL and PPL-HEX did not adsorb humic substances (HS), as confirmed by similar works that outlined the weak adsorption capacity of synthetic adsorbents for HS. While PPL and PPL-HEX can achieve

the removal of “free” HOC (HOC not bound to dissolved organic matters (DOM)), the fraction of HOC bound to the DOM remains in solution. In this research, in order to remove additionally the HOC bound to the DOM using PPL, a quaternary ammonium compound (QAC) surfactant was introduced in the HS solution.

In recent years, cationic surfactants have been increasingly used in different separation technologies for their particular physicochemical properties (Boethling, 1984; Scamehorn and Harwell, 1987; Swisher, 1987). A surfactant is composed of two entities; one is hydrophobic and the other hydrophilic. Depending upon the two moieties, the surfactant is more or less soluble in water. The hydrophilic portion may or may not dissociate in the aqueous phase to give an ionic (anionic/cationic), a nonionic or an amphoteric surfactant. Unlike non-quaternary cationic surfactants which are generally sensitive to pH, QAC are unaffected by pH (Rosen, 1988). The reaction of the negatively charged DOM and different cationic surfactant was investigated. The solute complex and suspended solids (SS) formed during the reaction were adsorbed onto PPL, confirming the successful removal of the DOM and the fraction of HOC attached to it. Dedoxyltrimethylammoniumbromide (DDTMAB), one of the QAC was selected for its effectiveness in assisting PPL achieving 70% removal of the initial DOM (Adou Yedes, 1998; Adou Yedes *et al.*, 1999; Adou Yedes *et al.*, 2001).

In line with previous work, further investigations were undertaken to elucidate the optimum operating conditions of various parameters. This paper discusses the results of laboratory scale experiments on the effect of pH, ionic strength, surfactant dose and SS on the removal efficiency of a HS solution treated with DDTMAB, by PPL. The specific objectives assigned to this research are as follows.

1. To depict the parameters investigated.
2. To evaluate the effect of each parameter.
3. To find out the optimum operating condition of the system.

Materials and methods

Unless otherwise indicated, the water used in this research was obtained from an Advantec Water System (CPW-200 and GS-500) that provided distilled dionized water (DDW) using activated carbon and cation/anion exchange resin columns. From experiment to experiment, only one parameter was changed at a time; the others remained unchanged. Control samples were monitored through the experiments to evaluate, among other things, the effects of parameters other than PPL. All experiments were duplicated.

Reagents

All chemicals were of analytical reagent grade. Humic acid (HA) was used to represent the HS. Whenever needed a stock solution of HA was made by dissolving 4 g of powder HA (Aldrich Chemical) in 1 L of DDW. The 1 L solution was then partitioned in 4 parts of 250 mL each and rotated at 10,000 rpm at 14°C with Bekman Instrumenst’s centrifuge (Avanti J-25) for 3 hours to separate solids particles from the liquid. The saturated solution of HA was then filtered through a 0.45 mm glass fiber paper GS 25 (Advantec) using a Buchner funnel. In order to find out the HA concentrations in term of total organic carbon (TOC), samples were diluted to concentrations ranging from 1 to 10 mg TOC/L assuming that the initial 4 g/L yielded a concentration of approximately 2,000 mg TOC/L. The TOC values of the dilutions were measured with a Shimadzu 5000A TOC analyzer. The stock solution covered with aluminium foil, was stored at 4°C. At the same time, 1 g/L DDTMAB stock solution was prepared by dissolving 3 g of DDTMAB in 3 L of DDW. Precaution was taken to minimize surface foaming during the introduction of the required volume of surfactant. The white powder of DDTMAB was purchased with Wako Pure Chemical

Industries, and used without further purification. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from the same company. Stock solutions of NaOH (4 g/L) and 1% (v/v) HCl were prepared. Daiwa Ace, polypropylene foam produced by Daiwa Co., Japan was the adsorbent used in this research. Hereafter, Daiwa Ace will be referred as PPL. The PPL grain has a diameter comprises between 2.8 mm and 3.35 mm.

pH and DDTMAB dose effects

Due to the presence of ionizable sites on both the cationic surfactant DDTMAB and the negatively charge humic acid, the possible effect of pH on HA adsorption was evaluated. Different pH values were selected to study pH effect on the removal efficiency of PPL. The pH values were 4.0, 6.80 and 11.5. A 1 L solution containing 10 mg/L TOC of HA was prepared from the stock solution. Then, the pH of the humic acid solution was set to the pre-determined pH value. During experiments conducted at pH 4.0, the humic acid solution was adjusted using 1% (v/v) HCl whereas the 4 g/L NaOH served to rise the solution pH to 11.5. The pH value of 6.80 corresponds to the mean pH value of the unaltered HA solution. After pH adjustment, the humic acid solution was vigorously shaken by hand to have a well-mixed solution and then partitioned into 3 portions (A, B and C) of equal volumes. Different volumes of surfactant were then introduced into the 3 solutions.

A, B and C received respectively 2.5, 5 and 10 mg/L of DDTMAB. Thereafter, the 3 bottles were placed simultaneously on the mechanic mixer described by Adou Yedes (1998) and shaken for 10 minutes at the speed of 200 times per minutes. The 10 min shaking period was selected based on the result of a previous study on the effect of the shaking time (Adou Yedes, 1998; Adou Yedes *et al.*, 1999). At the end of the shaking, solutions A, B and C were used successively to run the corresponding column experiment. After taking some samples which served as influents, 50 mL of the solution were transferred in a syringe which was

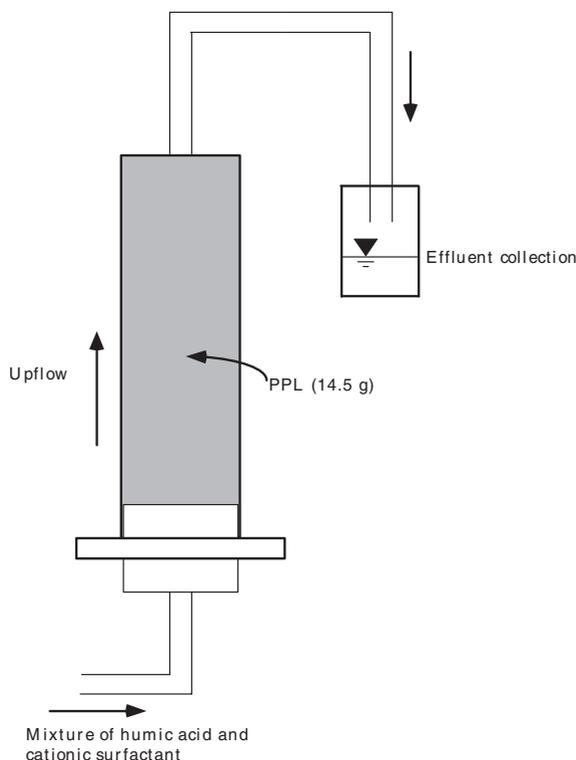


Figure 1 Continuous upflow set up with a syringe pump

later placed on the syringe pump set up (Figure 1). The syringe containing the feed was connected to another one filled with 14.5 g of PPL particles which sizes were comprised between 2.8 and 3.35 mm. The feed was then flown upward at the flow rate of 150 mL/h. The effluent was collected in a vial placed above the syringe pump and maintained in place by a support frame stand. Effluents and influents were analysed using a Shimadzu UV-VIS spectrophotometer (UV-2500PC) at a wavelength of 254 nm. The pH of the samples were measured with a Radiometer Analytical pH meter model, PHM210.

Ionic strength and SS effects

The effect of the ionic strength, which measures the number and strength of interactions between ions in a solution was evaluated. Furthermore, the impact of having the solid suspension in solution was investigated. A 3.5 L solution containing 10 mg/L TOC as HA was prepared in a reagent bottle. The ionic strength of the solution was adjusted to a fixed value in the range of 0 to 0.02 M by adding the corresponding quantity of sodium chloride (NaCl). After addition of NaCl, the solution was shaken by hands to ensure a well mixed solution. Then, 5 mg/L of DDTAMB were immediately added and the bottle shaken on the mechanic mixer 200 times per minutes for 10 minutes. At the end of the 10 minute period, the solution in the bottle was fractionated in two entities that were referred to as *Sol1* and *Sol2*. The partition was done to study the effect of the SS. The content of *Sol1* was filtered through a 0.45 μm glass fiber GS 25 (Advantec) of known weight, using a Buchner funnel apparatus to remove all suspended solids. Then, one after the other, 50 mL of the filtered solution were pumped up using the syringe pump set up described in a previous paragraph (pH and DDTMAB dose effect). Effluents and influents were collected for analysis. The glass fiber filter covered with the residue of SS was dried at 105°C for 2 hours with Tokyo Rikakikai, natural electric drying oven, NDO-601 5D. After that, it was cooled in a dessicator and weighted until a constant weight was obtained. The ionic strength of effluent and influent samples were determined from a calibration curve prepared beforehand using standard solutions of known conductivity and ionic strength. Conductivity was measured using C-173, a Horiba conductivity meter which was calibrated with a potassium chloride (KCl) standard solution. At the end of the testing with *Sol1*, the same procedure was repeated with *Sol2* at the exception that it was not filtered with the 0.45 μm glass fiber.

Results and discussion

Effects of pH and DDTMAB concentration

During experiments conducted with a 10 mg/L TOC humic acid solution at pH 6.8 (pH of the HA solution), pH 4.0 (adjusted with HCl) and pH 11.5 (adjusted with NaOH), the removed UV ratio was evaluated. The results are shown in Figure 2. Figure 2 described the profile of the removed UV ratio in function of the solution pH at different initial concentration of DDTMAB. The concentrations of 2.5, 5 and 10 mg/L of DDTMAB were used. The concentration value of 5 mg/L was determined in a previous study as the optimum concentration of DDTMAB during its reaction with HA (Adou Yedes, 1998; Adou Yedes *et al.*, 1999).

The optimum dose is defined, as the concentration beyond it there is not any significant increase in removal efficiency with further addition of DDTMAB. Figure 2 shows that as the pH increases the removed fraction in term of UV increases for all three concentrations of surfactant. The efficiency of the system was strongly pH dependent. The maximum removal efficiency under any given concentration was achieved for the highest pH value tested. The increase in UV reduction was noticeable for all concentrations of DDTMAB.

The dependence of UV reduction on the pH of the solution could mainly be attributed to HA deprotonation at elevated pH. The change of pH from acidic to basic solution favored

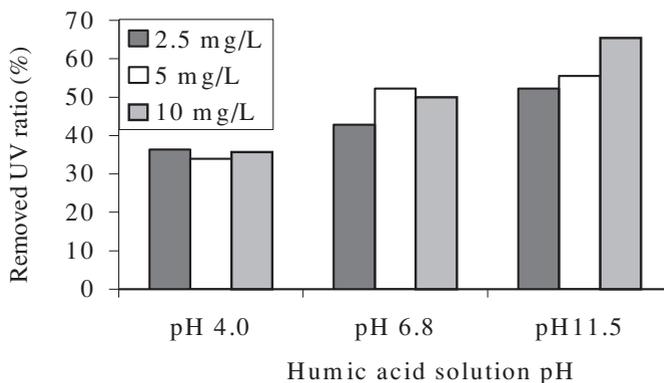


Figure 2 The pH effect on PPL removal of humic acid at different DDTMAB concentrations (PPL = 14.5 g, Flow rate = 150 mL/h)

the deprotonation of HA. The deprotonation of the humic acid molecules increased the density and number of negatively charged HA entities. Since DDTMAB remained positively charged even at higher pH values (Rosen, 1988), the number of HA molecules destabilized by charge neutralization increased with the pH. This phenomenon in turn led to the formation of a large number of suspended particles that aggregated. The aggregated particles could then easily be removed by PPL, which resulted in an increase in the removal efficiency as shown in Figure 2. The proliferation of negatively charged HA could have triggered the need for more concentration of DDTMAB. This may be the reason behind the fact that 10 mg/L of DDTMAB outranked the other concentrations at pH11.5 in term of removal efficiency. On the other hand, a decrease in pH enhances the protonation of carboxyl and other polar groups within the HA. The HA compound then behaved like an uncharged molecule and was no more engaged in the charge neutralization reaction with DDTMAB.

Cationic surfactants, because of their positively charged surface active moiety, can adsorb strongly onto most solid surfaces. However, lowering the pH may have changed the negative charge at the surface of PPL into a positive one or make it less negative due to the increase in number of protons which adsorbed onto it. This may have prevented the adsorption of single molecules of DDTMAB to its surface. DDTMAB molecules not retained by PPL may have contributed to the rise of the effluent UV, hence reducing the removal efficiency at lower pH.

Effects of ionic strength and SS

The ionic strength, according to Lewis and Randall (1921), describes the intensity of the electric field in a solution. NaCl is a strong electrolyte. It was assumed that 100% of NaCl formula dissociates in aqueous solution into ions. The added ionic strength was then computed using the following general formula:

$$I = \frac{1}{2} \sum_{i=1}^n C_i (z_i)^2 \quad (1)$$

In Eq. (1), C_i = concentration of the ion i (mol/L), z_i = charge of the ion i , and n = number of ions in solution.

Figure 3 depicts the variation of the residual UV ratio in function of the ionic strength of the solution. The same figure compares the efficiency of the system in the presence of suspended solids. According to the plot, the residual UV ratio increases with an increase in the ionic strength. At a given ionic strength value, the removed UV fraction was higher in SS

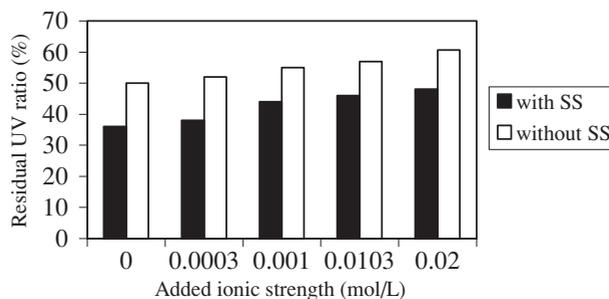


Figure 3 Comparison of residual UV ratio from SS free and SS containing influent

containing influent than in SS free influent. Furthermore, that difference increases as the ionic strength decreased. The decrease in UV removal ratio (the increase in residual UV ratio) observed as the ionic strength of the solution increases may be explained by two factors; the decrease in pH and the salting out (dehydration phenomenon) of the hydrophobic moiety of the surfactant. The addition of the electrolyte NaCl did induced a decrease in the pH as reported in Table 1. The acidic pH environment might have produced the same effect as described previously.

But the impact observed is too important (when compared to the effect achieved under a same pH value) to be uniquely explained by a proportional decrease in pH. Other factors such as the salting out effect might have contributed. Indeed, the presence of the dissolved NaCl must have favored a decrease in the solubility and availability of the hydrophobic organic solutes of DDTMAB ($C_{12}H_{25}N(CH_3)_3^+$) due to salting-out effect. As the concentration of NaCl ions increases, more and more water molecules take part in the hydration cells formed around Cl^- and Na^+ , and as a consequence less and less “free” water becomes available for forming cavities and icebergs around the organic solutes. As result of the partial “removal” of $C_{12}H_{25}N(CH_3)_3^+$ from solution, the reaction between HA and DDTMAB might have been hindered. The decrease in SS with increasing ionic strength described in Figure 4, agrees with the inability of the two compounds (HA and DDTMAB) to react. Therefore, the molecules of HA remained in solution and are transported to the effluent since PPL is not capable of removing them. Hence the weak removal efficiency observed. The fact that the removal efficiency is higher for SS containing influent is a proof that PPL can remove both the SS and solute complex formed during the reaction between HA and DDTMAB. It can be concluded that PPL works both as adsorbent (for solute complexes) and as filter (for SS).

Conclusions

This study provides an insight into the effect of influent chemistry on the removal efficiency of HA by PPL. The effects of the pH, ionic strength, surfactant dose and the presence of SS were investigated. The results showed that PPL removal of HA treated with cationic surfactant is pH dependent over the pH range of 4.0 to 11.5 investigated. At all tested concentrations of DDTMAB, the synthetic adsorbent efficiency increased with the pH. The

Table 1 Variations of pH, conductivity and ionic strength in function of the added quantity of NaCl

Added mass of NaCl (g/L)	0	0.018003	0.05845	0.600106	1.169
pH	6.93	6.67	6.55	6.5	6.24
Conductivity (mS/m)	0.75	1.5	10.2	100	200
Computed theoretical ionic strength (M)	0	0.000308	0.001	0.010267	0.02

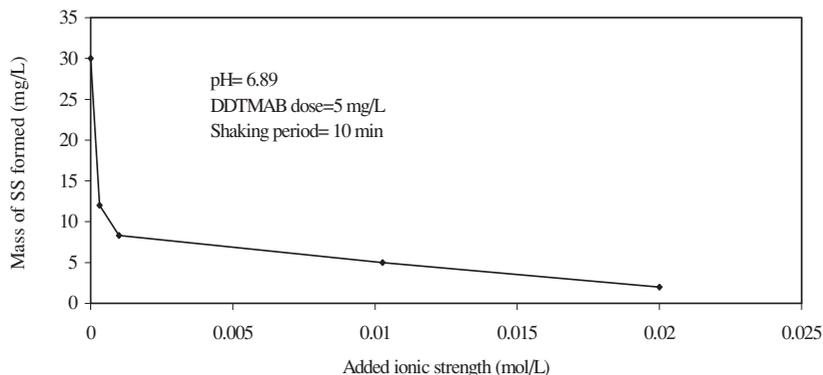


Figure 4 Variation of the mass of SS in function of the ionic strength

change of pH from 6.8 to 11.5 induced a PPL removal efficiency increase of 50% to more than 65% for a surfactant dose of 10 mg/L. At the same time, the efficiency gained for the previously determined optimum concentration of 5 mg/L of DDTMAB did not change much (52% to 56%).

The study suggested that the system would be cost efficient if operated at the pH prevailing in most wastewater, as any increase in pH will require a higher dose of surfactant and therefore generate more expenses for chemicals. Furthermore, the present study supports that increasing ionic strength can hinder the proper operation of the system by blocking the reaction between the cationic surfactant and the negatively charged HA molecules and therefore prevent the removal of HOCs bound to HA from solution. Finally, the study demonstrated that PPL can remove complex solutes and suspended solids formed during the reaction between the negatively charged HA and the cationic surfactant DDTMAB. The size of the two elements is yet another evidence that PPL can work as adsorbent and also as a filter medium.

References

- Adou Yedes, A.F. (1998). *Surfactant enhanced humic substances removal by adsorption onto a synthetic medium*. Masters thesis, Department of Global Environment Engineering, Kyoto University.
- Adou Yedes, A.F., Muhandiki, V.S., Shimizu, Y. and Matsui, S. (1999). Surfactant enhanced humic substances removal by adsorption onto a synthetic medium. *Proceedings of the Japan Society on Water Environment*, **33**(56), Sendai, Japan, 16–18.
- Adou Yedes, A.F., Muhandiki, V.S., Shimizu, Y. and Matsui, S. (2001). A new economical method to remove humic substances in water: adsorption onto a recycled polymeric material with surfactant addition. *Wat. Sci. Tech.*, **43**(11), 1–7.
- Benz, M. and Sontheimer, H. (1990). Description of the behavior of mixtures of unknown composition with activated carbon. *Proceeding of AWWA Water Quality Technology Conference*, USA.
- Boethling, S.R. (1984). Environmental fate and toxicity in wastewater treatment of quaternary ammonium surfactants. *Wat. Res.*, **18**, 1061–1076.
- Hirane, T. (1996). Personal communication. Daiwa Kogyo Co., Ltd., Tokyo, Japan.
- Jain, J.S. and Snoeyink, V.L. (1973). Adsorption from bisolute systems on activated carbon. *J. Wat. Poll. Cont. Fed.*, **45**, 2463–2479.
- Lewis, G.N. and Randall, M.J. (1921). *Am. Soc.*, **43**, 1111.
- Muhandiki, V.S. (1997). *A basic study on the removal of micropollutants from the effluent of municipal wastewater treatment plant*. Department of Global Environment Engineering, Kyoto University.
- Murin, C.J. and Snoeyink, V.L. (1979). Competitive adsorption of 2,4,3 trichlorophenol in the nanomolar to micromolar concentration range. *Environ. Sci. Tech.*, **13**, 305–311.
- Radke, C.J. and Pransnitz, J.M. (1972). Thermodynamics of multisolute adsorption from dilute liquid solutions. *Am. Inst. Chem. Eng. J.*, **11**, 121–127.

- Rosen, M.J. (1988). *Surfactants and Interfacial Phenomena*. Wiley, New York.
- Scamehorn, F.J. and Harwell, J.J. (1987). An overview of surfactant-based separation processes. In *Surfactants in Emerging Technology*, J.R. Milton (ed.), Marcel Dekker, New York.
- Srivastava, S.K. and Tyagi, R. (1995). Competitive adsorption of substituted phenols by activated carbon developed from the fertilizer waste slurry. *Wat. Res.*, **29**, 483–488.
- Swisher, R.D. (1987). *Surfactant Biodegradation*, Surfactant science series. Vol. 18.