



Removal of natural organic matter and ammonia from dam water by enhanced coagulation combined with adsorption on powdered composite nano-adsorbent

Surachai Wongcharee^{*}, Vasantha Aravinthan, Laszlo Erdei

School of Civil Engineering and Surveying, University of Southern Queensland, Toowoomba 4350, QLD, Australia



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ABSTRACT

Enhanced coagulation and adsorption were investigated in separate and combined processes to alleviate problems created by high levels of NOM (15 mg L^{-1}) and ammonia ($2.5 \text{ mg L}^{-1} \text{ NH}_4\text{-N}$) in dam water. Raw water acidification to pH 6.2 with optimised enhanced coagulation in jar tests achieved effective (68%) DOC reduction and satisfactory residual turbidity, aluminium, and colour, however removed only 5% ammonia. Adsorption on the nano-adsorbent (termed ACZ) led to 45% DOC reduction and excellent 58% ammonia removal in 30 min. Concurrent enhanced coagulation and complementary adsorption using only 80 mg L^{-1} alum and 150 mg L^{-1} ACZ doses showed high performance with 76% ammonia, 90% DOC, and 95% trihalomethanes formation potential (THMFP) reduction in 20 min time. Concurrent treatment can be simply implemented utilising readily available rapid mixers and flocculators, and operated on demand. Pre-adsorption and consecutive enhanced coagulation using the same alum and ACZ doses resulted in slightly better DOC but reduced (61%) ammonia removal. The results showed that concurrent treatment could safely resolve a challenging operational problem. ACZ combines the distinct advantages of zeolite and activated carbon in a single product, and may find additional uses in removing taste and odour, heavy metals, and synthetic organic matter from ground and surface waters.

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1. Introduction

Aquatic natural organic matter is composed of various groups of carbon and nitrogen-based compounds that originate primarily from plant and animal degradation products. For drinking water treatment, dissolved organic carbon is a commonly used surrogate parameter to quantify NOM content. Elevated levels of DOC in drinking water sources lead to operational, aesthetic and health-related problems. NOM creates problems in the production of drinking water by imparting taste, odour, and colour to raw water, increasing chemical demand for oxidation, coagulation, disinfection, and contributing to microbial regrowth in drinking water distribution systems (Thurman, 1985). DOC concentrations are a primary concern in drinking water treatment since NOM reacts with strong oxidants as a precursor of carcinogenic disinfection byproducts (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HAHs) (USEPA, 1999).

^{*} Corresponding author.

E-mail addresses: w0107942@uqmail.usq.edu.au (S. Wongcharee), Vasanthadevi.Aravinthan@usq.edu.au (V. Aravinthan), Laszlo.Erdei@usq.edu.au (L. Erdei).

Conventional water treatment usually includes coagulation–flocculation, sedimentation or flotation, filtration, disinfection, and pH adjustment. Among these processes, coagulation–flocculation has a critical role in removing colloidal particles, such as NOM (Bratby, 2006). Enhanced coagulation is the best available technology for large-scale potable water production (Edzwald and Tobiason, 1999), and involves dosages in excess of turbidity removal requirements. Nevertheless, the performance of enhanced coagulation depends upon the characteristics of NOM and treatment conditions, and even with the best effort recalcitrant portion remains to call for the use of supplementary processes (Sillanpää, 2014), such as adsorption.

Ammonia is another contaminant of concern in drinking water treatment and in distribution systems. It is formed naturally in the hypolimnion of reservoirs, present in anoxic groundwater but mostly originates from agricultural runoff and wastewater discharges. Ammonia in aqueous solution acts as a weak acid, comprising ionic (NH_4^+) and non-ionic (NH_3) species with a pKa value of 9.25, hence almost entirely present as the ionic (ammonium) form at neutral and acidic pH (Brezonik and Arnold, 2011). Although ammonia does not pose a direct health concern at low concentrations, its presence is undesirable in the distribution network. To prevent corrosion of copper pipes and fittings, nuisance growths of micro-organisms and increase of nitrite concentrations, the Australian Drinking Water Guidelines (NHMRC, 2011) recommend 0.5 mg L^{-1} limit, similarly to the EU Drinking Water Directive (European Union, 1998). Some EU member states, such as Denmark where systems operated with no residual disinfectant, enforce a much stricter $0.05 \text{ mg NH}_4 \text{ L}^{-1}$ limit (Wagner et al., 2018).

In conventional water treatment, ammonia reacts with the commonly used chlorine disinfectant to form chloramines. The results are increased chlorine demand coupled with reduced efficiency of disinfection, beside chloramines impart odour and taste to the produced water leading to consumer complaints. Ammonia can be oxidised to nitrogen gas using breakpoint chlorination. Unfortunately, this established method requires high chlorine doses, typically in 9–10:1 Cl: NH_3 -N ratios, and unavoidable reactions with NOM result in increased DBP formation. Disinfection by chloramination is an alternative low-cost control option if ammonia is normally present in raw water, although creating different health concerns due to nitrosamine DBP and nitrite formation (Krasner et al., 2013). Considering biological treatment options, low levels ($1\text{--}1.5 \text{ mg L}^{-1}$) of ammonia can be reliably treated by granular media rapid filters through nitrification even in cold water conditions (Kors et al., 1998), especially with the addition of copper in trace quantities (Wagner et al., 2016). In systems where ammonia is normally present in raw water at higher concentrations, nitrification on biological activated carbon (BAC) post-filters or fluidised bed units combined with aeration or ozonation may be necessary (Lytle et al., 2015). Other removal processes, including reverse osmosis, ion exchange, and advanced oxidation are effective but relatively complex and expensive, while air stripping at high pH is troublesome due to scale formation.

Compared to the above options, adsorption processes are simple, affordable, operationally flexible, and thus especially suitable to alleviate temporary or seasonally recurring problems caused by deteriorating raw water quality that normally occur for dam and river water sources. Adsorption can be performed with various materials, such as activated carbons, zeolites, aluminium oxides, silica compounds, biosorbents, and nano-adsorbents (Bergmann and Machado, 2015; Bhatnagar and Sillanpää, 2017; Huang et al., 2018). Adsorption is suitable for both NOM and ammonia removal, and can be used as a distinct unit process or in combination with other treatment processes. Granular adsorbents are normally used in fixed or expanded bed filters placed after rapid filtration or as top layers of existing filters. Polishing filtration is suitable to alleviate problems caused by pollutants permanently present in raw water by offering long contact times, easy handling, and possibility of regeneration (Çeçen and Aktaş, 2011). Powdered adsorbents may be added to the process train in slurry form at multiple locations, such as at the raw water intake (pre-adsorption), rapid mixers (concurrent adsorption and coagulation–flocculation), clarified water channels (post-adsorption) prior to the filters. The choice among these configurations depends on safety and performance requirements and plant operational aspects. The usual choice is pre-adsorption to increase detention (contact) times for the better utilisation of the adsorbent. Concurrent adsorption cum coagulation is operationally preferable, especially if sludge blanket or recirculating type clarifiers available to provide increased contact times. Post-adsorption prolongs contact times to backwash periods but set limits to the applicable adsorbent dosage, particle sizes, may interfere with filter hydraulics and/operation, beside eliminates clarification as a safety barrier in separating the spent adsorbent.

Activated carbons in powdered (PAC) and granular (GAC) forms were introduced for removing odour and taste causing substances and became the most widely used adsorbents. PAC and GAC are effective in removing many organic constituents including DBP precursors from water but have low performance in ammonia removal. This is because activated carbons generally have hydrophobic, non-polar surfaces due to their preparation at high temperatures, and thus low affinity to polar substances (Halim et al., 2010). In contrast, zeolites have hydrophilic surfaces with specific ion exchange and adsorptive capacities that long have been used for ammonia adsorption (Gaspard et al., 1983; Hlavay et al., 1982) but show low performance in NOM removal. It would be advantageous to combine the complementary adsorptive properties of activated carbons and zeolites to enhance the removal of multiple pollutants. Accordingly, in a recent project we prepared a novel nano-adsorbent specifically intended for NOM and ammonia removal (Wongcharee et al., 2018a,b). The composite material (termed ACZ) is made from macadamia nut shell based mesoporous activated carbon (Wongcharee et al., 2018a,b) and synthetic faujasite that shows high affinity for ammonia (Montégut et al., 2016).

In the present study we report the removal of NOM and ammonia from challenging, poor quality dam water by enhanced coagulation with alum (aluminium sulphate) coagulant and adsorption on ACZ using independent and combined treatment processes.

Table 1
Dam water and laboratory raw water quality parameters.

Parameter	Dam water	Laboratory raw water
Turbidity (NTU)	3.00 ± 0.74	8.57 ± 0.48
pH	8.63 ± 0.14	6.2 ± 0.05
True colour (mg L ⁻¹ Pt Co)	4 ± 1.41	321 ± 9.19
UV ₂₅₄ (cm ⁻¹)	0.142 ± 0.02	0.874 ± 0.02
DOC (mg L ⁻¹)	7.64 ± 0.80	15.28 ± 0.81
NH ₄ (mg L ⁻¹ N)	0.39 ± 0.01	2.47 ± 0.06
Conductivity (mS)	1.017 ± 0.10	1.052 ± 0.10
Alkalinity (mg CaCO ₃ L ⁻¹)	113.0 ± 4.24	62.5 ± 3.54
THMFP (µg L ⁻¹)	249.5 ± 5.23	482.5 ± 9.19

2. Materials and methods

2.1. Stock solution preparation

Stock solution of humic acid (HA) was prepared by dispersing 0.1 g Sigma-Aldrich PGS10 commercial HA product in 0.2 L 1 mM (pH 11) NaOH solution and boiling for 30 min. Humic acid dissolved in alkaline media provided stable stock solutions, while boiling facilitated fast and simple preparation without altering the characteristic properties of HA (Janoš and Kozler, 1995). After cooling to room temperature, the volume was re-adjusted to 0.2 L using distilled water and the solution was analysed for dissolved organic carbon (DOC) and UV-Vis spectra. Ammonium chloride stock solution (1 g L⁻¹) was prepared by dissolving NH₄Cl (Ajax Finechem, Australia) in pure water. The solution was kept in a reagent bottle and also used for NH₄-N concentration calibrations.

2.2. Raw water quality

Raw water was collected from Cooby Dam, QLD Australia for the experiments. This dam is one of the alternative drinking water sources of Toowoomba. DOC and NH₄-N concentrations (Table 1) in the collected dam water were 7.64 mg L⁻¹ and 0.39 mg L⁻¹ respectively. However, a previous study (McIntyre, 2015) found that this dam, like other water sources used for drinking water supply in Australia and elsewhere, could provide raw water with elevated DOC and ammonium levels that created serious operational challenges. Therefore, the collected dam water sample was spiked with stock HA and NH₄Cl solutions to provide 15 mg L⁻¹ DOC and 2.5 mg L⁻¹ NH₄-N target concentrations for the laboratory raw water used in this study.

Extensive previous studies (McIntyre, 2015) conducted on the dam water found that for average raw water quality, about 60 mg L⁻¹ alum dose ensured effective turbidity reduction. Enhanced coagulation only was required for elevated DOC levels (>7 mg L⁻¹) in the raw water. The process was hindered by the relatively high pH and alkalinity of the raw water, resulting in only 29%–32% DOC removal at 90–95 mg L⁻¹ alum doses that barely met USEPA requirements (Edzwald and Tobiason, 1999). Alum coagulant alone could not cope with the high DOC concentration of the present study, and thus we looked for other means for effective treatment. Noting that the pH in the 5–8 range only has a small effect on ammonia removal by zeolites (Mazloomi and Jalali, 2016) we explored acidic process pH conditions for DOC removal. Screening tests found that acidification of the dam water to about 6.2 pH value substantially reduced the coagulant demand, ensured effective NOM removal and still permitted effective turbidity reduction. Using lower alum doses also reduced both the undesirable addition of sulphate to water and sludge production.

2.3. Nano-adsorbent and coagulant

The preparation and material properties of the ACZ nano-adsorbent are described in details elsewhere (Wongcharee et al., 2018a,b), and here suffices to present its main characteristics. The composite sample had 76% to 24% meso- to micropore ratio, 418 m² g⁻¹ specific surface area, and 45% by weight zeolite distributed on the active carbon carrier as nanocrystalline particles and their clusters. The granular product was grinded to below 200 mesh size and used without further treatment. Alum coagulant solution was prepared daily by dissolving 10 g of aluminium sulphate (Al₂(SO₄)₃·18H₂O, Ajax Finechem, Australia) in 1 L pure water.

2.4. Jar test experiments

The experiments were conducted in three stages by dosing (i) ACZ and alum individually, (ii) ACZ and alum concurrently, (iii) ACZ and alum in sequence. Jar test experiments were performed with a six paddle jar test apparatus (JLT6, Velp Scientifica) at controlled laboratory temperature (23–24 °C) using 1 L water samples in cylindrical jars. The basic procedure involved adding alum or ACZ alone to water samples mixed at 240 rpm. Rapid mixing was maintained for 2 min then the mixing speed was reduced to 30 rpm for flocculation or adsorption. Both alum and ACZ were dosed in

the 10–200 mg L⁻¹ range by 20 mg L⁻¹ increments. The stirring times varied from 30 to 150 min to simulate full-scale (water plant) conditions that may involve prolonged flocculation in cold weather conditions, and/or sludge recirculation with increased adsorption times.

For concurrent treatment, the above basic procedure was followed, except that both alum and ACZ were added to jars simultaneously.

Lastly, for sequential treatment first ACZ was added to jars for pre-adsorption. Water samples were taken at 5, 10, 15, 20, 30, 45, 60, 90, 120 and 150 min for analyses. These time intervals at full-scale correspond to possible adsorption contact times in raw water transmission pipes. After collecting grab samples, the test followed the basic procedure with addition of alum.

Grab samples were collected with pipettes from 3 cm below the water surface and filtered on Whatman 1 paper to simulate filtered full-scale water quality for analyses. Removal percentages of DOC and NH₄-N were calculated from the initial and final concentration using the equation

$$\% \text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

while the adsorbed masses of DOC and NH₄-N q_e (mg g⁻¹) at equilibrium were calculated from Eq. (2)

$$q_e = \frac{C_0 - C_e}{m} V \quad (2)$$

with C_0 initial and C_e equilibrium concentrations of DOC or NH₄-N (mg L⁻¹), V (L) is the volume of water, and m (g) is the mass of adsorbent.

2.5. Analytical methods

Alkalinity was determined manually according to Standard Methods 2320B with sulphuric acid titration in the presence of methyl orange indicator, while pH was measured using an Eutech PC2700 meter. Ammonia was determined according to Standard Methods 4500-NH₃ D, using HI 902 instrument with HI-4101 gas sensing ion selective electrode. DOC was determined with a Shimadzu TOC-Vcsh analyser equipped with an auto-sampler (ASI-V) after filtration through 0.45 μm syringe filters. UV₂₅₄, UV₂₀₄, and SAC₄₃₆ absorbance were measured with a Jenway 6705UV/Vis spectrophotometer. Residual aluminium was determined with an AA-7000 Shimadzu atomic absorption spectrophotometer, while zeta potential was measured with a Malvern Zetasizer Nano ZS apparatus. True colour and trihalomethane formation potential (THMFP) were measured with a Hach DR2700 kit according to Standard Methods 8025 and 10132, respectively. Origin Pro v7.5 (OriginLab) software package was used for numerical data processing, modelling, and charting.

3. Results and discussion

3.1. Turbidity reduction by independent enhanced coagulation and adsorption processes

Fig. 1a presents the effect of alum and ACZ doses on the reduction of turbidity. While PAC dosing usually increases the residual turbidity of water, here adsorption on ACZ led to a modest turbidity reduction, up to 24.3% at the highest 200 mg L⁻¹ dose. For enhanced coagulation treatment with alum, the residual turbidity steeply decreased from 8.57 to 1.15 NTU when the alum dose increased to 80 mg L⁻¹, then increased to 2.66 NTU with increasing alum doses up to 140 mg L⁻¹, and again reduced from 2.66 to 1.98 NTU with the increase of alum dose up to 200 mg L⁻¹. The observed pattern indicates an initial charge neutralisation, surface charge reversal above 80 mg L⁻¹ dose, and finally sweep flocculation mechanism above 140 mg L⁻¹ dose. For sweep flocculation, particulate matter is removed by enmeshment or entrapment in the voluminous aggregates of aluminium hydroxide precipitate. This interpretation of turbidity reduction was confirmed by electrokinetic potential measurements.

Fig. 1b presents the evolution of the zeta potential measured at various doses (0–200 mg L⁻¹) of ACZ and alum in raw water. The initial zeta potential of about -20 mV showed monotonic increase with increasing doses of alum. Charge neutralisation was observed at about 80 mg L⁻¹ dose corresponding to the minimum turbidity value, while larger coagulant doses caused charge reversal to positive values.

ACZ addition had no significant on the zeta potential up until 40 mg L⁻¹ dose, then the initial -19.9 mV value fairly linearly decreased to -23.6 mV with increasing doses. This small change in zeta potential revealed small charge densities, indicating that increasing ACZ doses do not raise the coagulant demand significantly for its effective removal.

The reaction rate of alum with alkalinity is influenced by temperature and pH. In unfavourable conditions, the small and slowly aggregating aluminium hydroxide flocs can pass the filters to create sediment in the distribution network. Fig. 1d shows the effect of alum dose on residual aluminium content in treated water samples. The residual aluminium concentrations remained below 0.1 mg L⁻¹ at low doses but a nearly exponential increase is observed from about 90 mg L⁻¹ dose. Comparison of Fig. 1c and d reveals that the increase of residual Al concentration was caused by the low process pH values that rapidly increased the solubility of aluminium hydroxide precipitate. In contrast to alum, ACZ addition slowly increased the process pH during treatment according to Fig. 1c. This characteristic is advantageous for the stabilisation of supplied water to control scale deposition and internal corrosion in the pipe network.

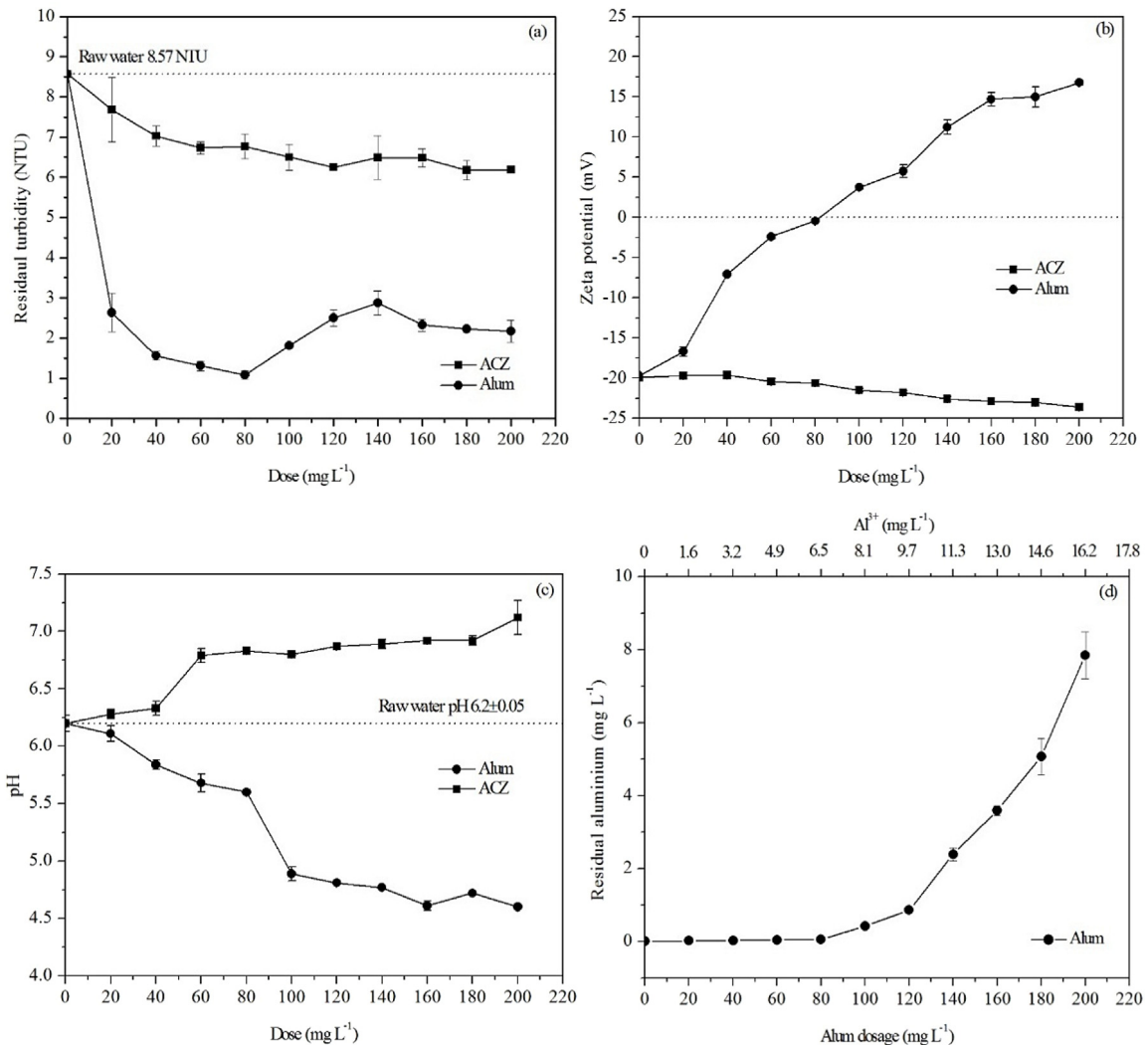


Fig. 1. Effect of alum and ACZ dosed individually on residual turbidity (a), zeta potential (b), pH (c), and residual aluminium (d) measured after 30 min.

3.2. DOC reduction by independent enhanced coagulation and adsorption processes

The reduction of DOC using enhanced coagulation and adsorption treatments is presented in Fig. 2.

Fig. 2a shows DOC reduction that depicts monotonic growth with declining rate as function of alum dose, reaching a 73% maximum value. This type of curve is generally observed for natural waters treated with inorganic coagulants. The operational limit of 69% at 90 mg L⁻¹ dose was constrained by the increasing residual aluminium level in treated water. NOM removal efficiency by coagulation–flocculation treatment depends on many factors, such as type and dose of coagulant, process pH, temperature, velocity gradients and durations, and especially the composition of the raw water. Coagulation–flocculation treatment preferentially and efficiently removes hydrophobic NOM fractions of high molecular weight (MW) with higher negative charge, while tends to leave lower MW, hydrophilic neutral organics in solution (Fabris et al., 2008; Sillanpää et al., 2018). Overall, enhanced coagulation was effective, considering the 68% reduction by 0.73 mg Al⁺ mg⁻¹ DOC specific coagulant dose.

DOC was significantly smaller for adsorption on ACZ. The removal shows monotonic increase with dose then reached a plateau of 45% removal for the largest doses. Adsorption of NOM on PAC, which is a component of the ACZ composite is very complex phenomena, influenced by factors such as the characteristic and concentration of NOM, structure and porosity of carbon, type and availability of surface functional groups, ionic strength and pH of water (Bjelopavlic et al., 1999; Newcombe et al., 1997). PAC has broad removal spectra for various aquatic pollutants, and able to adsorb neutral, smaller MW matter subject to pore size exclusion and surface screening effect by already deposited particles (Bhatnagar and Sillanpää, 2017). Therefore, spite of their typically large specific surface area, microporous carbons are

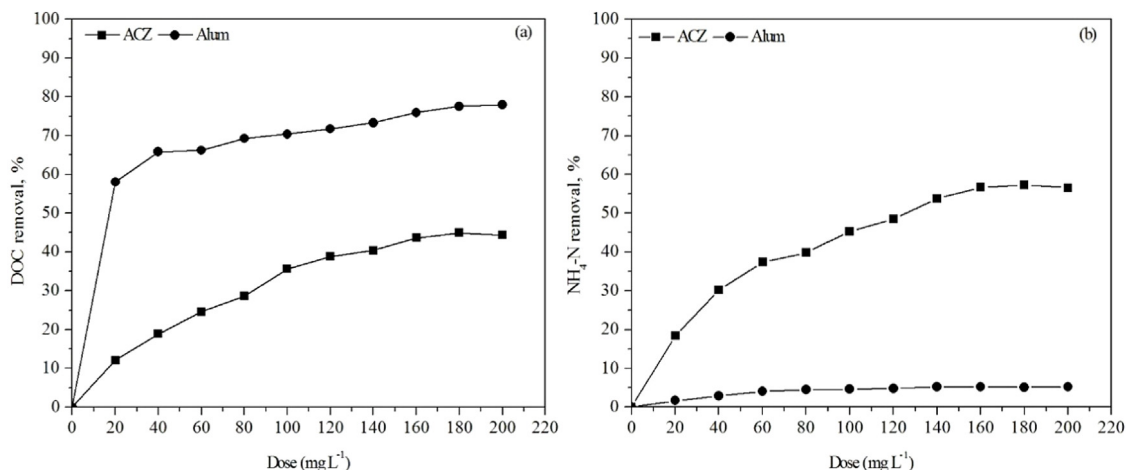


Fig. 2. Effect of alum and ACZ dosed individually on DOC (a) and NH₄-N (b) removal after 30 min.

often outperformed mesoporous products (Fabris et al., 2004; Knappe et al., 2004) such as that used in the preparation of the ACZ nano-adsorbent.

3.3. Ammonia removal by independent enhanced coagulation and adsorption processes

Fig. 2b presents the effect of alum and ACZ doses on ammonium removal efficiency. Enhanced coagulation treatment showed only 5.2% NH₄-N removal even at the largest alum dose. The poor removal of cationic ammonium ions is due to the like charge of metal hydroxide sols formed at coagulation. The observed small removal can be ascribed to sorption on other pollutant species such as NOM and silt having negative surface charge.

In contrast to alum, ACZ achieved very good ammonia removal performance. The ammonia removal rate shows a characteristic rise to saturation type trend with a plateau from around 160 mg L⁻¹ dose. The observed 58% maximum removal to 1.02 mg L⁻¹ value in 30 min contact time is remarkable considering the low 2.5 mg L⁻¹ initial concentration of adsorbate and presence of competing and interfering species in natural water (Huang et al., 2018). Together with additional removal by the rapid filters through nitrification, ACZ dosing can safely reduce ammonia levels below the 0.5 mg L⁻¹ (WHO and EU) guideline value in product water. The actual adsorption capacity at 200 mg L⁻¹ dose is 7.32 mg g⁻¹. This excellent performance is attributed to the faujasite nano-component of ACZ, since the parent PAC component of ACZ only had 1.32 mg g⁻¹ capacity in the same conditions.

The affinity of PAC to ammonia can be increased by acidic treatment, albeit at the expense of reduced NOM removal capacity. Asada et al. (2006) prepared chars and activated carbons from bamboo and compared their performance with and without sulphuric acid treatment. The adsorption capacities of their best product for 1000 mg L⁻¹ PAC doses at 1–2 mg L⁻¹ equilibrium concentrations (similar to the effluent concentration of the present study) were about 1.2–4 mg g⁻¹, comparable to the performance of the untreated precursor PAC component of the ACZ nanosorbent (1.32 mg g⁻¹) of this work. In another study, Li et al. (2012) treated bamboo charcoal with nitric acid that improved ammonia adsorption performance by 40%. Nevertheless, their reported 0.65 mg g⁻¹ maximum adsorption capacity was relatively low and showed slow kinetics with 4 h contact time required for half-saturation.

Natural zeolites also can be modified using physical and chemical methods for enhanced ammonia removal. Published results (Lei et al., 2008; Xiao et al., 2015), however show that the benefits are only realised for high ammonia concentrations that do not occur in drinking water treatment.

3.4. Concurrent enhanced coagulation and adsorption treatment

The adsorption process offers a valuable complementary role to coagulation–flocculation by its ability to remove recalcitrant small MW and neutral species, thereby reducing coagulant demand while increasing overall NOM removal. Sections 3.1 and 3.2 established that 80 mg L⁻¹ alum dose resulted in very effective DOC removal at optimum 6.57 pH of coagulation with low residual aluminium concentration. The ACZ dose was selected chiefly regarding the residual NH₄-N levels, since this critical constituent is barely removed by the complementary coagulation–flocculation process. Jar tests found up to 58% ammonium removal with only a small improvement above 160 mg L⁻¹ ACZ doses, therefore a 150 mg L⁻¹ ACZ dosage was chosen for the combined treatment processes. The obtained results are summarised in Table 2, presenting the performance of individual and concurrent processes for comparison.

Table 2

Comparison of treated water quality parameters achieved by individual and concurrent processes (alum dose = 80 mg L⁻¹, ACZ dose = 150 mg L⁻¹, treatment time = 30 min).

Parameter	Raw water	ACZ alone	Alum alone	ACZ+alum
DOC (mg L ⁻¹)	15.28	8.85 (42.1%)	4.83 (68.3%)	1.546 (89.9%)
NH ₄ -N (mg L ⁻¹ -N)	2.47	1.04 (57.5%)	2.21 (4.45%)	0.600 (75.7%)
Turbidity (NTU)	8.57	6.50 (24.2%)	1.15 (86.6%)	0.950 (88.9%)
THMs (µg L ⁻¹)	483	144 (70.2%)	49 (89.9%)	24 (95.0%)
Colour SAC ₄₃₆ (m ⁻¹)	17.2	10.9 (36.6%)	5.6 (67.4%)	2.7 (84.3%)
Aluminium (mg L ⁻¹)	<0.010	<0.010	0.048	<0.010
SSAC ₄₃₆ (L mg ⁻¹ m ⁻¹)	1.13	0.713 (36.6%)	0.367 (67.4%)	0.177 (84.3%)
SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	5.72	4.23 (26%)	1.80 (68.5%)	1.21 (78.8%)
SUVA ₂₅₄ /SUVA ₂₀₃	0.717	0.690	0.610	0.512

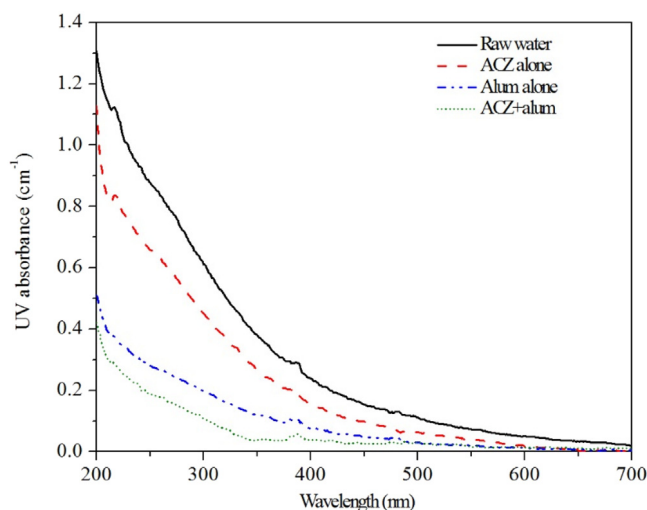


Fig. 3. UV-Vis spectra of water treated with individual and concurrent processes (ACZ dose = 150 mg L⁻¹, alum dose = 80 mg L⁻¹, initial DOC concentration = 15.28 mg L⁻¹, initial NH₄-N concentration = 2.47 mg L⁻¹, initial pH = 6.2, treatment time = 30 min).

Table 2 confirms that enhanced coagulation resulted in higher reduction of DOC, SAC₄₃₆ (brown colour) and turbidity, while adsorption on ACZ achieved much higher performance in removing NH₄-N (57.5%), together with a smaller but appreciable 42.1% DOC reduction.

The combined treatment process showed high performance in all aspects with excellent DOC (89.9%), NH₄-N (75.7%), turbidity (88.9%), and THMFP (95%) removal. The synergistic improvement of ammonia removal in concurrent treatment is remarkable and the reason will be elucidated in another section. The already low residual aluminium concentration measured after enhanced coagulation was further reduced to negligible levels. DOC reduction results are also mirrored in photometric parameters with effective SAC₄₃₆, SSAC₄₃₆ (84.3%) and SUVA₂₅₄ (78.8%) reduction, and illustrative changes in UV-Vis spectra (**Fig. 3**).

Fig. 3 shows that compared with individual processes, the concurrent process resulted in significant improvements over the entire spectra, which is consistent with results presented in **Table 2**. The specific absorbance SSAC₄₃₆ is an analogue of the more frequently used SUVA₂₅₄ and characterises the brownish colour of water. These parameters serve well as surrogates of aromatic compounds typical of the dominant humic fraction of NOM. DOC removal by enhanced coagulation can be reliably predicted by models based on initial DOC concentration, SUVA₂₅₄, coagulant dose, pH (**Edwards, 1997**) and can be calibrated to local conditions for minimising THMFP (**Van Leeuwen et al., 2005**). Coagulation preferentially removes high aromatic (phenolic) compounds, hence increases the relative concentration of hydrophilic (hydroxyl, carboxyl, ester and carbonyl) groups in treated water. Therefore, it was suggested (**Kim and Yu, 2005**) that the easily measured UV₂₅₃/UV₂₀₃ absorption ratio may be used as an indicator of THMFP. In the experimental conditions, however, this parameter showed worse correlation (0.77) with THMFP than DOC, UVA₂₅₄ and SAC₄₃₆ (0.91–0.96) indicating that this index is system specific, unlike the established and proven (**Golea et al., 2017**) surrogates.

There are many examples of using coagulation with complementary adsorption on activated carbon (**Carriere et al., 2009; Kristiana et al., 2011; Szlachta and Adamski, 2009; Uyak et al., 2007; Younker and Walsh, 2016**) for improved organic matter and adsorbent with coagulants that convincingly show the benefits of combined treatment using enhanced coagulation and adsorption processes. Similarly, ammonia and organic matter removal by coagulation also were enhanced by the addition of zeolite adsorbents (**Albrektiene et al., 2017; Chmielewska, 2012**). Unfortunately, the literature is scarce

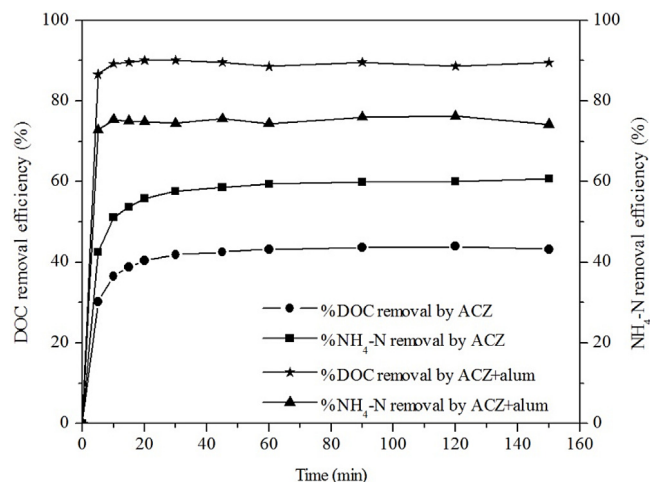


Fig. 4. DOC and NH₄-N removal over time by individual and concurrent enhanced coagulation and adsorption processes (ACZ dose = 150 mg L⁻¹, alum dose = 80 mg L⁻¹, initial DOC concentration = 15.28 mg L⁻¹ and initial NH₄-N concentration = 2.47 mg L⁻¹, initial pH = 6.2).

in studies presenting the more relevant use of both activated carbons and zeolites combined with coagulants for water treatment.

One of the pertinent investigations focused on ammonia and COD reduction, which is a long-standing problem for South China cities using river water sources polluted with wastewater discharges. Liao et al. (2015) used PAX coagulant (a polyaluminium chloride product) in combination with PAC and mineral zeolite grinded to 200 mesh size (PZ) using spiked raw water with comparable ammonia content (3.35 mg L⁻¹ NH₄-N). They found that PZ and especially PAC doses were limited due to excessive turbidity increase in treated water. Using up to 40 mg L⁻¹ PAX, fixed 40 mg L⁻¹ PAC and 2000 mg L⁻¹ PZ doses in different combinations, simultaneous application gave the best results, with up to 52% removal of COD and 49% of ammonia. Another study by Xue et al. (2018) examined removal of ammonia and N-nitrosamine precursors from synthetic and natural (river and ground) waters at 1.5 mg L⁻¹ normalised ammonia concentration. They used 50, 20 and 1000 mg L⁻¹ alum, PAC, and zeolite (mordenite) doses, respectively with the pH of water sample pre-adjusted to 7 value. Coagulation alone and with concurrent adsorption on PAC were ineffective but zeolite dosing to the jars achieved 67%–74% ammonia removal from natural and synthetic waters, respectively. The efficiency of removal was not significantly affected by temperature (2–40 °C) and pH (6–8) but the addition of lime had a negative effect due to the increased level of Ca cations and especially of the high pH, where ammonia was mainly present in dissolved gaseous form. Alum coagulation did not show negative effect on the concurrent adsorption processes, while PAC addition ensured the very effective removal of all N-nitrosamine precursors.

Although direct comparison of COD, N-nitrosamine precursor and DOC removals is not possible, all above presented results show that the combined use of zeolites, PAC, and ACZ with alum coagulant improves organic carbon removal that in turn reduces DBP formation. Ammonia removals directly comparable on removed mass per volume (concentration) basis rather than percentages. Calculating from the published data, the described studies achieved 1.56 and 0.55 mg L⁻¹ NH₃ removals from natural waters, whereas the present study 2.29 mg L⁻¹ while using 7–14 times less adsorbent dose. This finding confirms the high performance of ACZ that results from the nanocrystalline form of the faujasite component. Complete ammonia removal may not be possible from natural waters using this technology due to the presence of competing cations (K, Na, Ca, Mg) but the residual levels are low (only 0.6 mg L⁻¹ in the present study) that would be safely removed the filters downstream and/or breakpoint chlorination.

3.5. Effect of time on DOC and NH₄-N removal for concurrent treatment

The kinetics of pollutant removal is essential information for applications, and also provides insight into the mechanism of the adsorption process. Fig. 4 presents the results of DOC and NH₄-N removal over time for the individual and concurrent treatment processes.

When ACZ was used alone, DOC and NH₄-N removal rates were high and quasi-equilibrium values were reached in about 60 min time both for DOC (42%) and NH₄-N (59.3%). Moreover, 30 min contact time was sufficient to ensure the near complete (95%–96%) saturation of ACZ. In concurrent treatment, adsorption on ACZ composite and enhanced coagulation with alum was employed simultaneously. As shown in Fig. 4, the kinetic rates of removals increased substantially compared to the separate processes, and equilibrium values were achieved in 10 min for NH₄-N and in a remarkably short 20 min for DOC removal. Fast kinetics of ammonia removal were noted in earlier studies, especially for synthetic and modified zeolites (Alshameri et al., 2014; Shaban et al., 2017; Zhao et al., 2010). However, the relatively slow NOM

Table 3
Kinetic models and parameters of DOC and ammonia adsorption on ACZ.

Model	Parameter	DOC	NH ₄ -N	
PFO	$q_t = q_e (1 - \exp(-k_1 \cdot t))$	q_e (mg g ⁻¹)	43.29	9.642
		k_1 (min ⁻¹)	0.2217	0.2331
		R^2_{adj}	0.9887	0.9888
		RMSE	1.394	0.3078
		SSE	17.49	0.8525
PSO	$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + q_e \cdot k_2 \cdot t}$	q_e (mg g ⁻¹)	45.56	10.13
		k_2 (g mg ⁻¹ min ⁻¹)	0.0096	0.0458
		R^2_{adj}	0.9993	0.9997
		RMSE	0.3581	0.0495
		SSE	1.154	0.0221
General (rational) order	$q_t = q_e \frac{q_e}{[t \cdot k_r \cdot q_e^{n-1} \cdot (n-1) + 1]^{1/(n-1)}}$	q_e (mg g ⁻¹)	44.91	10.03
		k_r [h ⁻¹ (g mg ⁻¹) ⁿ⁻¹]	0.0203	0.0603
		n	1.765	1.837
		R^2_{adj}	0.9996	0.9999
		RMSE	0.2620	0.0351
Bangham	$q_t = k_b \cdot t^\vartheta$	SSE	0.5491	0.0099
		ϑ	0.1732	0.1921
		k_b	24.27	31.87
		R^2	0.9956	0.9977
		RMSE	1.072	1.123
SSE	4.598	3.783		

Note: experimental q_e values are 44.78 mg g⁻¹ for DOC and 9.99 mg g⁻¹ for NH₄-N.

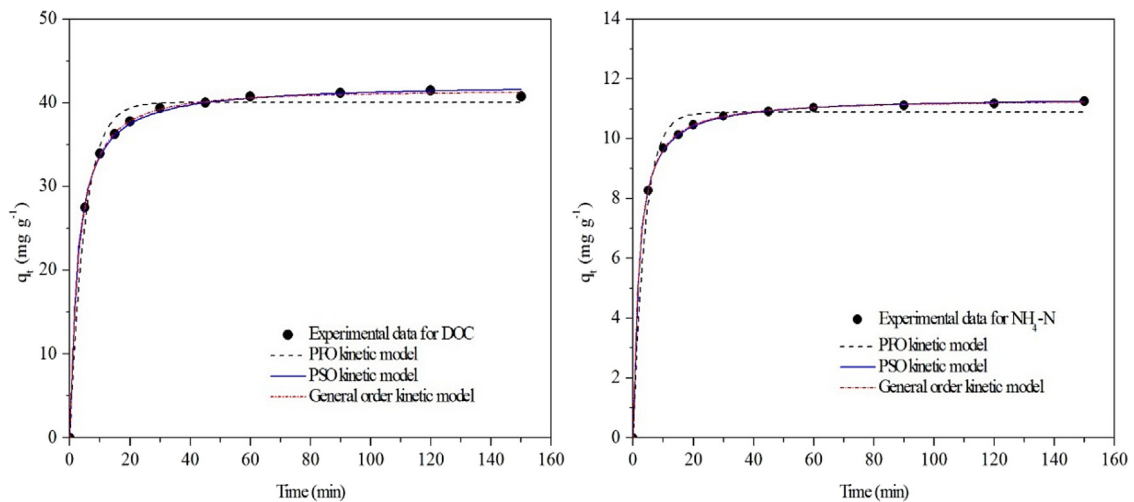


Fig. 5. PFO, PSO, and general order kinetic adsorption model plots of DOC and NH₄-N adsorption on ACZ.

removal rates often require prolonged contact times using pre-adsorption and/or sludge recirculation (Plourde-Lescelleur et al., 2015), and worth quantitative exploration by modelling. In this study, the pseudo first order (PFO), pseudo second order (PSO) and general (rational) order models (Liu and Shen, 2008) were examined according to Table 3. Experimental data were fitted to the selected models using nonlinear regression in Origin Pro software. Model performances were ranked by the adjusted coefficient of determination (R^2_{adj}), root of mean square error (RMSE) and sum of squared error (SSE).

Despite the complex natural water composition, the results show excellent fits for both DOC and NH₄-N removal. As expected, the general order model has the best statistics, together with a quite accurate prediction of adsorption capacity. However, the n orders of this model (1.765 for DOC and 1.837 for NH₄-N) are close to 2, for which value this model is equivalent to the PSO model. This finding indicates that the adsorption processes largely follow second order kinetics, as is typical for low adsorbate concentrations (Azizian, 2004). The plots in Fig. 5 confirm that it is difficult to notice visual differences between these two models, hence the use of the simpler PSO model is preferable.

The kinetic plots in Fig. 5 reveal that the adsorbent is nearly saturated (>96%) after 30 min for DOC and NH₄-N, therefore it is appropriate to consider the 0–20 min initial period in modelling. Fig. 6 present good fit to the Bangham

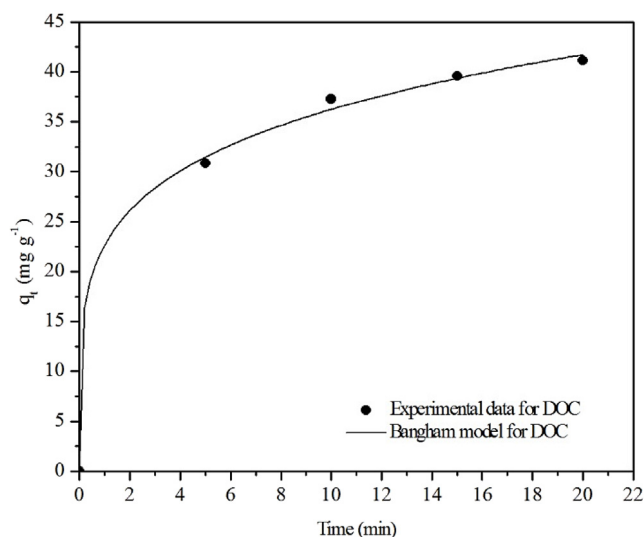


Fig. 6. Bangham model plot of NOM adsorption on ACZ adsorbent.

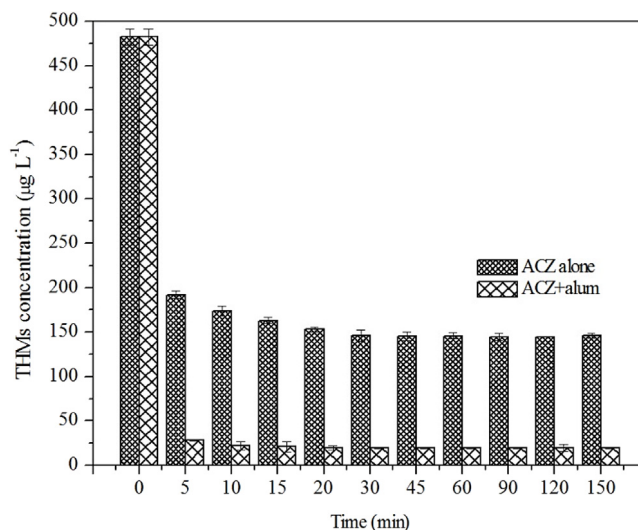


Fig. 7. Change of THMF in treated water over time for concurrent treatment (ACZ dose = 150 mg L^{-1} , alum dose = 80 mg L^{-1} , initial concentration of THMs = $482.5 \mu\text{g L}^{-1}$, initial pH = 6.2).

model (Largitte and Pasquier, 2016), indicating that the controlling mechanism of adsorption process is intra-particle diffusion.

This finding indicates the possibility of product improvements. The length of diffusional pathway can be reduced by using smaller adsorbent particles to provide faster kinetics (Najm et al., 1990), and increase the specific surface area and adsorption capacity. Matsui et al. (2004) showed that grinding commercial PAC to micrometre-size range increased NOM removal capacity tenfold. About 80% of equilibrium capacity was reached within only 1 min of contact time, and further improvements were possible using submicron size PAC (Matsui et al., 2006). Those examples suggest that ACZ pulverised to finer particle sizes can be even more attractive for use in drinking water treatment plants, stormwater runoff treatment systems (Khorsha and Davis, 2017), and hybrid micro- and ultrafiltration systems utilising adsorbents (Ngo et al., 2000; Stoquart et al., 2012; Yuasa, 1998) with short detention times.

3.6. Effect of contact time on THMs formation for concurrent treatment

Fig. 7 presents the effect of contact time on THMs formation using ACZ adsorbent alone, and in concurrent application with alum coagulant.

The removal kinetics and trends of THMFP are similar to those observed for DOC and $\text{NH}_4\text{-N}$ contaminant removal. The THMFP was quickly reduced to $190 \mu\text{g L}^{-1}$ after a short 5 min contact time, and the final value of $145 \mu\text{g L}^{-1}$ was achieved in 30 min contact time. Therefore, using adsorption on ACZ could satisfy the (rather lax) $250 \mu\text{g L}^{-1}$ limit of the Australian guidelines (NHMRC, 2011).

The concurrent adsorption cum enhanced coagulation process resulted in a further and substantial reduction of THMFP. A short 5 min process time led to a low $30 \mu\text{g L}^{-1}$ value, and practically no change was observed after 20 min time. The $24 \mu\text{g L}^{-1}$ final value easily meet the 100 and $80 \mu\text{g L}^{-1}$ limits set by the EU Drinking Water Directive European Union (1998) and USEPA (1999), respectively. The results clearly demonstrate that the concurrent treatment is capable of the rapid and very effective removal of DBP precursors from poor quality dam water.

3.7. Effect of dosing sequence on DOC and $\text{NH}_4\text{-N}$ removal

The previous sections illustrated that concurrent adsorption and enhanced coagulation achieved high performance, easily meeting statutory requirements. Many water plants already have dosing facilities located upstream of the water treatment plant (at the raw water intake, for example) and prefer to use pre-adsorption followed by consecutive enhanced coagulation. This dosing sequence increases the contact time and thus better utilises the adsorbent.

For pre-adsorption studies were conducted with same 150 mg L^{-1} ACZ and 80 mg L^{-1} alum doses used for concurrent treatment. The results showed that overall DOC removal by sequential treatment was only marginally higher than for concurrent treatment, even for the longest pre-adsorption time of 150 min. The best overall result was 93.6% versus the 90% removal achieved for concurrent treatment, which are quite comparable considering standard determination errors. More importantly, pre-adsorption achieved about 15% lower ammonia removal than concurrent treatment. In fact, there was no significant improvement in overall ammonia removal (61%) compared with adsorption on ACZ alone (58%).

Similar findings were reported by Liao et al. (2015, 2016) who investigated the effect of sequential dosing of zeolite and PAC relative to coagulation and flocculation. They found that addition of zeolite at each dosing point increased the residual turbidity, and only concurrent treatment provided acceptable results. The effect on COD and UV_{254} removal varied with the dosing location of zeolite. The best results and improvements were obtained at the earliest addition that provided the longest adsorption time, while significant deterioration was observed for addition in the late (ongoing flocculation) stage. In contrast, poor ammonia removal (22%–28% for 2 g L^{-1} dose) was observed for early zeolite addition, while concurrent application with alum showed the best, about 48% removal rate.

Both the present and the above studies found that pre-adsorption treatment removed less ammonia than concurrent treatment. It long has been known that ammonia uptake by zeolite involves both ion exchange in micropores and surface adsorption (Jorgensen et al., 1976). For pre-adsorption treatment, sorption of NOM constituents on dosed zeolite (and zeolite component of ACZ) leads to surface screening effect that reduces the number of sorption sites available for ammonia uptake. For concurrent treatment, the adsorption and coagulation–flocculation compete in NOM removal but the two processes have very different kinetic rates. Hydrolysis and precipitation of the dosed coagulant is extremely fast (Licisko, 1997) with a resulting rapid charge neutralisation and complexation of NOM constituents. Therefore, the comparatively slow sorption on zeolite takes place in an environment depleted of reactive NOM species. The reduced concentration gradient then results in reduced NOM and increased ammonia uptake on zeolite compared with the pre-adsorption process.

4. Conclusion

We investigated the performance of enhanced coagulation and adsorption processes in separate and combined treatments to remove challenging levels of NOM and ammonia from potable water source.

Enhanced coagulation with alum showed efficient turbidity, colour, SUVA, and DOC reduction by dosing only $60\text{--}90 \text{ mg L}^{-1}$ coagulant. The low dosage was attained by pre-acidifying the raw water 6.2 pH, which together with inherent acidity of the coagulant, resulted in optimum pH of coagulation. For full-scale operation would worth to explore the use of acidified alum that is less expensive than the purified premium grade products. As expected, however, coagulation–flocculation was ineffective in ammonia removal.

Adsorption on ACZ showed appreciable DOC reduction and remarkable ammonia removal, the latter exceeding the efficiency of PAC, zeolites, and other materials reported in the literature for drinking water treatment. The high performance achieved in 30 min time was attributed to the composition and material characteristics of the nano-adsorbent.

Concurrent treatment involving simultaneous enhanced coagulation cum adsorption processes combined the complementary merits of the individual processes, and achieved excellent performance. Removals of target pollutants were faster than those found for individual processes. The adsorption capacity of ACZ was fully utilised in only 20 min, a short detention time readily provided by the flocculator units in conventional water treatment plants.

Combined treatment using pre-adsorption on ACZ and consecutive enhanced coagulation showed no significant improvement in DOC removal but reduced ammonia removal compared to concurrent treatment. This result suggested that sorption of NOM reduced ammonia uptake on the faujasite component of ACZ, and this hindering effect was counteracted by concurrent coagulation.

Both NOM and ammonia adsorption on ACZ followed pseudo second order kinetics, and NOM removal kinetics was controlled by intra-particle diffusion. These findings suggest that grinding the ACZ to finer particle sizes should provide

rapid kinetics, suitable for hybrid treatment processes using short detention times, as well as increased adsorption capacity. ACZ is multi-purpose adsorbent that combines the advantages of zeolite and activated carbon in a single, powdered or granular product that may find additional applications in water treatment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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