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ORIGINAL PAPER

Coagulation–flocculation process with metal salts, synthetic polymers and biopolymers for the removal of trace metals (Cu, Pb, Ni, Zn) from municipal wastewater

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Abstract

To ensure compliance with regulatory standards, it is important to examine the potential of treatment technologies to enhance trace metal removal from wastewater. This study investigated the effectiveness of coagulation–flocculation at removing trace metals from humus effluent with ferric chloride ($FeCl_3$), the synthetic polymer polyethyleneimine (PEI) and the biopolymers chitosan and floculan. Effluent samples were collected from a trickling filter treatment works operating in the UK and contained 21 ± 4 µg/L Cu, 0.8 ± 0.1 µg/L Pb, 4 ± 1 µg/L Ni and 43 ± 9 µg/L Zn. The influence of coagulant dosage and the velocity and time of the slow mixing stage were studied via a series of jar tests. Chitosan and PEI had a moderate effect on the removal of trace metals (≤ 35%). $FeCl_3$ removed 48% Cu, 56% Pb and 41% Zn at the optimised dose of 0.10 mg/L. At the optimised dose of 0.25 mg/L, floculan removed 77% Cu, 68% Pb and 42% Zn. The dominant mechanism for particle removal by $FeCl_3$ was enmeshment in the precipitates (i.e. sweep flocculation), whereas, for floculan, inter-particle bridging was the dominant removal mechanism. Overall, $FeCl_3$ and floculan were found to be most effective at removing trace metals from wastewater.

Keywords Coagulation–flocculation · Jar test · Wastewater · Copper · Zinc

Introduction

Metals such as Cu, Pb, Ni and Zn are frequently present in municipal wastewater at concentrations in the µg/L range. As a consequence of their potential to cause harm (Jaishankar et al. 2014), regulatory drivers require the mentioned metals to be removed during wastewater treatment. For example, in the USA, the Clean Water Act (CWA 1972) defines criteria maximum concentrations (CMC) and criterion continuous concentrations (CCC) for heavy metals to protect aquatic life and human health in surface water (USEPA 2017). In the European Union, the Water Framework Directive (WFD) (2000/60/EC) has recently specified bioavailability-based standards for Pb and Ni which are classified as priority hazardous substances. Bioavailability-based standards have also been specified for Cu and Zn, classified as specific pollutants under the WFD, in the UK (UKTAG 2008). Bioavailable metal concentrations are calculated using a biotic ligand model (BLM). This model converts a dissolved phase metal concentration into an equivalent bioavailable concentration by considering specific information on physico-chemical characteristics such as pH, water hardness and the concentration of dissolved organic carbon (DOC) (Di Toro et al. 2001). Whilst improving the environmental relevance, bioavailability-based standards are expected to significantly reduce acceptable metal concentrations in treated effluents (Peters et al. 2009). It is, however, difficult to reduce trace metal concentrations in wastewater due to the diverse nature

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of metal inputs to the sewer system, which makes it difficult for operators to identify and directly control the concentration of metals reaching wastewater treatment works (WWTWs). An understanding of metal sources is, therefore, often insufficient to be used to reduce metal inputs, and studies have shown that rates of removal vary considerably at WWTWs (Ziolko et al. 2011; Gardner et al. 2013). Faced with the expectation of more stringent regulation, many advanced treatment technologies are being operated for the removal of heavy metal ions from wastewater. Technologies include chemical precipitation, membrane filtration, adsorption or ion exchange. Issues have, however, been denoted with technologies in many instances found to be expensive and inadequate to achieve final effluent requirements.

Metal speciation in wastewater is an important consideration when choosing potential options to enhance metal removal. Traditionally, metals are considered to exist in two fractions: a soluble fraction that passes through a filter with a pore size of 0.45 µm and a particulate fraction which is retained on the filter (i.e. > 0.45 µm). At WWTWs, Cu and Pb are known to have a high affinity for the particulate fraction (Karvelas et al. 2003; Buzier et al. 2006) and, thus, can be removed by physical separation (Choubert et al. 2011). Conversely, Ni and Zn abound in the soluble fraction, which requires adsorption/ion exchange processes or chemical modification for their effective elimination (Martin et al. 1995). Such two-fraction distinction has been challenged by recent findings (Worms et al. 2010; Hargreaves et al. 2017, 2018) that indicate metals can adsorb or complex with organic material within the colloidal size fraction (1 kDa–0.45 µm). Such findings suggest that technologies capable of removing particles within the colloidal fraction have good potential to enhance metals removal from wastewater (Hargreaves et al. 2017).

One such technology is coagulation–flocculation (CF), a frequently applied process in the treatment of drinking water (Teh and Wu 2014) and the purification of industrial effluents (Teh et al. 2016). Coagulation with chemical coagulants involves combining insoluble particles and dissolved organic matter into larger aggregates which can be removed in subsequent sedimentation and filtration stages (Renault et al. 2009). Coagulants destabilise suspended and colloidal particles in wastewater by forming microflocs. These are aggregated by flocculation, which consists of a stirring/agitation procedure that encourages particles to clump allowing their removal in subsequent treatment stages (Tchobanoglous et al. 2003). Mechanisms through which particles and colloids are aggregated and, thus, removed can involve a combination of charge neutralisation, adsorption, entrapment and complexation processes (Alexander et al. 2012).

Coagulants frequently used include inorganic salts such as ferric chloride ($FeCl_3$) or synthetic polymers such as polyethyleneimine (PEI). $FeCl_3$ has been utilised to enhance the removal of Cu, Pb, Ni and Zn from synthetic wastewater (Johnson et al. 2008) and aggregates particles by charge neutralisation and sweep flocculation (Duan and Gregory 2003). Charge neutralisation refers to the sorption of two particles with opposite charged ions, whereas sweep flocculation entails the enmeshment of particles in a growing hydroxide precipitate. Synthetic polymers agglomerate particles by inter-particle bridging. This phenomenon involves the sorption of particles onto polymeric chains by forming particle–polymer–particle complexes (Shak and Wu 2014). The loops and tails of adsorbed polymeric chains can protrude and attach to other particles in the medium, allowing bridging of particles to occur (Shak and Wu 2014). Synthetic polymers have also shown the ability to enhance metals removal. When it comes to the application of these products, a limited number of studies have reported on the removal of metal from municipal wastewater.

The use of salts and synthetic polymers may have consequences that are detrimental to the environment such as increasing non-target metal concentrations in treated wastewater, the production of large volumes of sludge and significant alterations to pH of treated wastewater (Renault et al. 2009; Vijayaraghavan et al. 2011). For these reasons, alternative reagents have been considered for CF treatment. Biopolymers such as chitosan and floculan are of great interest since they are natural low-cost products with environmentally friendly characteristics such as biodegradability, no toxicity and produced from a renewable resource (Renault et al. 2009). Chitosan possesses intrinsic properties including high cationic charge density and long polymer chains and, thus, has been applied in the treatment of different effluents (Renault et al. 2009). Floculan is an aqueous solution composed of up to 30% Tanfloc, a tannin-based product modified to include a quaternary nitrogen which provides a cationic character. Studies have identified that Tanfloc can enhance the removal of metals from polluted surface water (Beltrán Heredia and Sánchez Martín 2009). Nevertheless, investigations into the application of the more commercially available floculan for the treatment of wastewater are limited. Furthermore, it is noted that there is a scarcity of comprehensive studies that compare the effectiveness of natural coagulants, synthetic polymers and conventional coagulants. This gap in knowledge may hinder their potential for application to enhance trace metal removal at WWTWs. The aim of this study was, therefore, to compare the metal removal performance of the biopolymers chitosan and floculan with that of the conventional coagulant, $FeCl_3$, and the synthetic polymer, PEI.

Materials and methods

Wastewater samples

Coagulation–flocculation experiments were conducted with humus effluent for two reasons, namely the amount of

reagent required for coagulation is lower than that needed with primary effluent so that sludge production is minimised. Secondly, if dosed at this point the sludge generated can be removed in a subsequent sand filtration operated on site as part of the tertiary treatment. Humus effluent samples were collected from a full-scale WWTWs operating trickling filters in the UK. Samples were taken at least once each month over a 5-month study period (from May to September 2016). Samples were collected in 20-L plastic containers and were transported to, and were kept, in a refrigerated environment (4 °C) at Cranfield University laboratories.

Coagulants

The PEI was received as a 50% by weight solution from Sigma-Aldrich (Gillingham, UK). This was the branched chain form of the polymer with an average molecular weight of 750,000 Da (Cat No: 181978). A PEI stock solution (1 g/L) was prepared with deionised water. Chitosan powder, derived from shrimp shells (practical grade, Cat No: 417963), was also obtained from Sigma-Aldrich. A chitosan stock solution (500 mg/L) was prepared as described by Rizzo et al. (2008). Briefly, 100 mg of chitosan powder was dissolved in 0.5 mL of 2 M HCl solution (reagent grade, Fisher Scientific, Loughborough, UK) and 9.5 mL of deionised water; after 60 min, 190 mL of deionised water was added. A $FeCl_3$ solution (40%) was obtained from Darrant Chemicals (Lincoln, UK). Floculan solution was obtained from Lansdowne Chemicals (Oxon, UK).

Coagulation–flocculation experiments

The CF studies were conducted in a conventional jar test apparatus (Phipps and Bird, Richmond, USA), which allowed six beakers to be agitated simultaneously. Each jar test consisted of a batch experiment involving rapid mixing, slow mixing and sedimentation. Plastic beakers were filled with 1 L of humus effluent, placed on the floc illuminator and, once coagulant dosage was added, agitated at the preselected intensity of rapid mixing (100 RPM for 2 min). Once the rapid mixing was complete, the preselected intensity of slow mixing (40 RPM for 30 min) was immediately established. After slow mixing, beakers were removed from the floc illuminator for a 30-min sedimentation phase to take place. Subsequently, supernatant was withdrawn from about 25 mm below the surface with a syringe.

Preliminary jar tests investigating a wide range of doses (0.25–8 mg/L for $FeCl_3$, 0.25–40 mg/L for floculan, chitosan and PEI and 0.10–2 g/L for PEI in 50% by weight solution) were carried out to identify whether the reagents were capable of achieving the desired metal removal, which is over 35% for at least two of the tested metals (Cu, Pb, Ni, Zn). Coagulants not capable of achieving this condition were eliminated from subsequent experiments for optimisation of coagulant dose and slow mixing conditions. In order to optimise coagulant dose narrow ranges of dose were selected for further investigation: 0.05–0.40 mg/L for $FeCl_3$ and 0.10–2 mg/L for floculan. In optimising coagulant dose, one beaker in each run had no coagulant added to it and was therefore treated by stirring only. This was used as the experimental control.

To identify the optimum slow mixing conditions, both agitation time and speed were assessed. In these experiments, the established optimum coagulant dose for either $FeCl_3$ (0.10 mg/L) or floculan (0.25 mg/L) was added to the jars and rapid mixing conditions (100 rpm for 2 min) remained constant. The slow mixing intensity was investigated in the range 0–50 rpm with a fixed agitation time of 30 min, whilst the duration of slow mixing was investigated in the range 0–50 min with a fixed agitation speed of 40 rpm. A beaker agitated by rapid mixing only was used as the experimental control.

Chemical analysis

Target metals (Cu, Pb, Ni and Zn) were measured with a Nexion 350D inductively coupled plasma-mass spectrometer (ICP-MS) from PerkinElmer (Beaconsfield, UK). The limit of detection for all the metals was 0.01 µg/L. Prior to ICP-MS analysis, samples were digested in a CEM-MARS microwave (CEM, Buckingham, UK). A Jenway 4330 pH and conductivity meter (Stone, UK) was used for pH measurement. Turbidity was determined with a Hach 2100N turbidimeter (Manchester, UK). Total chemical oxygen demand (COD) and total phosphorous (TP) concentrations were determined with cell test kits (Fisher Scientific, Leicestershire, UK). After vacuum filtration (APHA 2005) through 0.45-µm polyethersulphone membranes (Millipore, Livingston, UK), samples were analysed for dissolved organic carbon (DOC) in a TOC-V analyser (Shimadzu, Milton Keynes, UK). Zeta potential was analysed with a Malvern Zetasizer Nano ZS (Malvern, UK).

Data analysis

Statistical analysis of the obtained data was done with the software package Minitab 17. One-way ANOVA tests were performed to assess the differences in metal concentrations achieved at varying coagulant dosage and slow mixing conditions (i.e. time and velocity). Pearson's correlation coefficient tests were used to identify relationships between coagulant dose and the concentration of metals in treated effluent. The relationship between DOC and metal concentrations in treated effluent was also assessed. Correlation strength was determined to be weak (0.2–0.39), moderate (0.4–0.59) or

strong (> 0.59) using guidance from Evans (1996). All tests were conducted with a level of significance $p < 0.05$.

Results and discussion

Wastewater characteristics

Values for wastewater parameters analysed along with total metal concentrations measured in humus effluent samples are shown in Table 1. The abundance of target metals in terms of total concentration was Zn > Cu > Ni > Pb (see Table 1). Similar relative abundances and metal concentrations have been reported by other investigators at treatment facilities elsewhere in the UK (Gardner et al. 2013).

Selection criteria for trace metal removal

Both chitosan and PEI had a moderate effect on metal concentrations (≤ 35% reduction) at all dosage levels and, as a result, were eliminated from the subsequent testing regime (data not shown). Chitosan molecules include carboxyl and amino functional groups. In our experiments, the pH of the humus effluent was 7.3 ± 0.2 (Table 1). At such value, carboxyl groups are deprotonated becoming ($–COO^-$), whilst amino groups remain fully protonated as ($–NH_3^+$) (Macnow 2016). Thus, the chitosan molecules had both positive and negative charge but overall were electrically neutral, owing to the two charges neutralising one another (Macnow 2016). It was, therefore, anticipated that the electrostatic force between chitosan molecules and humus effluent particles was weak, hindering flocs' formation and explaining why removal of metals by CF with chitosan was constrained in this study.

It is recognised that the ability of polymers to remove metals is influenced by the presence of competing solutes and chelators such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). These competing substances are typically present in municipal wastewater (Shon et al. 2006) and limit the removal of metals by binding to available sites on the polymers. Since other studies (Almutairia and Lovitt 2012) have found that PEI has a poor ability to bind Cu, Ni and Zn in the presence of EDTA or NTA, it is thought that the removal of metals by CF with PEI in this study was limited by the presence of competing substances in the effluent. It is recognised that these substances may also have limited the extent to which chitosan removed metals.

Optimisation of coagulant dose for target metal removal

Rates of removal for target metals as a function of $FeCl_3$ dose are given in Fig. 1. An increasing dose of $FeCl_3$ enhanced the overall removal of metals (in particular of Cu and Pb) as higher concentrations of the salt result in ampler floc formation. When comparing $FeCl_3$ dosages, optimum removals for Cu (66%) and Pb (69%) were achieved at 0.20 mg/L as significantly lower residual concentrations of both metals were observed in treated effluent ($p < 0.05$). For Zn, the best removal (41%) was obtained after adding 0.10 mg/L $FeCl_3$ ($p < 0.05$). When it comes to Ni, a cumulative effect in its concentration was found as higher doses of $FeCl_3$ were added to the humus effluent (see Fig. 2). This relation proved to be linear as indicated by a strong positive correlation ($r = 0.959$, $p < 0.001$). Studies elsewhere (Buzier et al. 2006; Chys et al. 2013) have reported that $FeCl_3$ contains considerable Ni amounts and thus significantly contributes to the presence of the metal in treated effluent. This finding was, therefore, expected and indicates that, when used for the treatment of wastewater, $FeCl_3$ is a potential risk to compliance with environmental quality standards for Ni. Even though 0.20 mg/L provided the highest removal of Cu and Pb, a lower rate of addition was considered optimal for the purposes of this study in order to minimise the inadvertent addition of Ni. The optimum rate of addition was 0.10 mg/L,

Table 1 Humus effluent characteristics (mean ± SD)

Parameter	Value
pH	7.3 ± 0.2
Zeta potential (mV)	− 12.9 ± 0.4
Turbidity (NTU)	16.6 ± 7.1
COD (mg/L)	71.8 ± 15.7
DOC (mg/L)	17.9 ± 2.6
Total P (mg/L)	5.6 ± 0.7
Cu (µg/L)	20.5 ± 3.9
Pb (µg/L)	0.8 ± 0.1
Ni (µg/L)	3.7 ± 0.8
Zn (µg/L)	43.1 ± 8.9

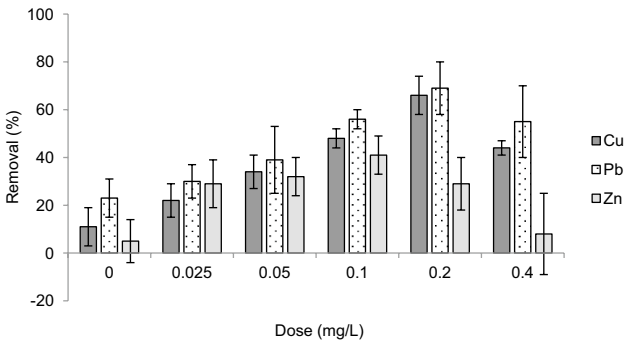

Fig. 1 Rates of removal for target metals as a function of $FeCl_3$ dose (mean ± SD)

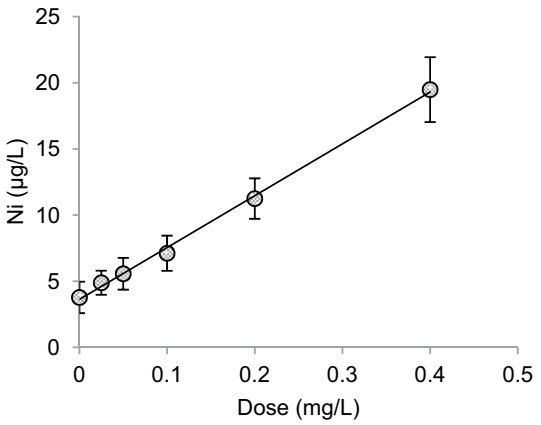

Fig. 2 Concentration of Ni in treated humus effluent as a function of $FeCl_3$ dose (mean ± SD)

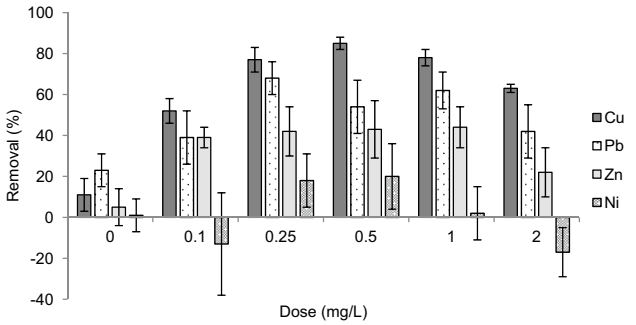

Fig. 3 Rates of removal for target metals as a function of floculan dose (mean ± SD)

which produced removal rates of 48% for Cu, 56% for Pb and 41% for Zn.

Rates of removal for the target metals as a function of floculan dose are shown in Fig. 3. The highest removal of Cu (85%) was observed at 0.50 mg/L, although no statistically significant difference ($p = 0.209$) was observed when humus effluent was treated with 0.25 mg/L floculan. The latter concentration was also the optimum dosage for the removal of Pb (68%). Removal efficiencies (41–44%) for Zn were similar ($p > 0.05$) for doses ranging between 0.25 and 1 mg/L. Given that reduction in Ni concentration was negligible for floculan at all doses ($p > 0.05$; Fig. 3), 0.25 mg/L was recommended as the optimum dose for the removal of target metals.

Performance efficiency

Metals

The concentrations of target metals in untreated humus effluent, the investigative control (i.e. CF with no coagulant added) and effluent treated with either $FeCl_3$ or floculan at the optimised dosages are presented in Fig. 4.

Sizeable amounts of Cu ($FeCl_3$: 48%, floculan: 77%) and Pb ($FeCl_3$: 68%, floculan: 56%) were removed from humus effluent with both $FeCl_3$ and floculan (see Fig. 4 panels a and b, respectively). Studies (Hargreaves et al. 2017, 2018) have reported that these metals are mainly bound to particulate and colloidal materials that readily adsorb to the surface of flocs. Hence, elimination of Cu and Pb by CF was expected. In fact, high rates of removal have been reported elsewhere for $FeCl_3$ (Cu: 81%, Pb: 88%; El Samrani et al. 2008) and plant-based biopolymers (Cu: 90%; Beltrán Heredia and Sánchez Martín 2009). Our removal percentages were substantially lower than those reported in other studies (El Samrani et al. 2008; Beltrán Heredia and Sánchez Martín 2009). This is most likely the result of significantly lower metal concentrations (< 25 µg/L Cu and < 1 µg/L Pb; Table 1) in the trickling effluent we used in our CF experiments compared with other studies (El Samrani et al. 2008: > 50 µg/L Cu and > 25 µg/L Pb; Beltrán Heredia and Sánchez Martín 2009: ~ 20 mg/L), which makes a high removal percentage more difficult to obtain.

In our case, residual concentrations of Cu after floculan addition were significantly lower ($p < 0.001$) than those found for $FeCl_3$ (Fig. 4a). This may arise since floculan removes organics with functional groups that Cu readily forms complexes with. This was supported by the strong correlation ($r = 0.935$, $p < 0.001$) observed between Cu and DOC concentrations in the treated effluent and implies that in CF with floculan removal in conjunction with DOC was a pathway for the elimination of Cu. Nevertheless, floculan is composed of polymeric chains along which functional groups such as amino and phenol groups are found. It is known that free Cu ions have a high affinity for these groups (Lu and Allen 2002; Hamza et al. 2017); therefore, complexation of Cu ions with these functional groups may also be a further point of removal.

As shown in Fig. 4c, residual concentrations of Zn were comparable for both $FeCl_3$ and floculan ($p = 0.976$). In both cases, a reduction in Zn was anticipated as findings were in agreement with those reported by others. El Samrani et al. (2008) recorded removal rates of up to 93% when using $FeCl_3$ as a coagulant in the treatment of combined sewer overflow. Beltrán Heredia and Sánchez Martín (2009) found that Tanfloc, the active ingredient in floculan, had the capacity to reduce Zn concentrations by 75% when treating polluted surface water. It was also noted by these authors that Cu (90%) was removed to a much greater degree than Zn (75%), with a similar trend observed in the present study for floculan (Fig. 4, panels a and c).

As Fig. 4d shows, floculan did not effectively remove Ni from humus effluent ($p = 0.429$). Given that Ni has a low affinity for particulate matter and in effluent at the neutral

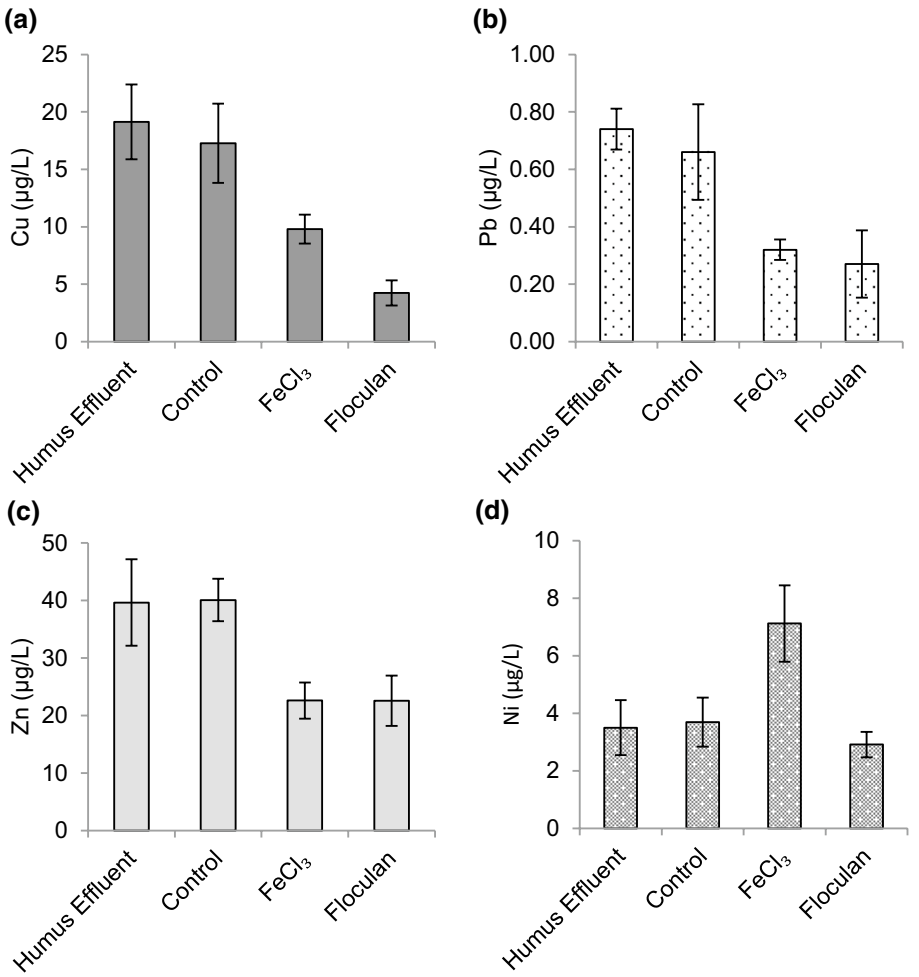

Fig. 4 Cu (**a**), Pb (**b**), Zn (**c**) and Ni (**d**) concentrations in humus effluent treated with $FeCl_3$ (0.10 mg/L) and floculan (0.25 mg/L) at the recommended doses outlined in this study (mean ± SD)

pH range observed herein (Table 1) a large proportion of soluble Ni typically exists in the mobile aqua ion form, such behaviour was expected. These properties reduce the ability of Ni to be adsorbed through the complexation process; thus, a pH > 11 is required for effective removal of Ni from the aqueous phase (Patterson 1985).

Turbidity removal

There are two main mechanisms for the removal of particles by $FeCl_3$ in the CF process, namely charge neutralisation and sweep flocculation (Duan and Gregory 2003). Given the sizeable amount of turbidity removed in conjunction with negative zeta potentials (see Fig. 5a), it is apparent that charge neutralisation did not play a significant role in the removal of particles from the humus effluent. For example, a dose of 0.10 mg/L $FeCl_3$ yielded a 75% turbidity removal with a corresponding zeta potential of − 12 mV. Increasing the dosage of $FeCl_3$ improved turbidity removal, although, when dosage beyond operational optimum was added, no further improvement was observed. In fact, when 0.40 mg/L $FeCl_3$ was added, a turbidity removal of 20% and a zeta potential of 4.39 mV were measured. This result is clearly explained by particle stabilisation. Sweep flocculation involves the enmeshment of particles in precipitates. This mechanism is not influenced by the properties of particles as negatively charged particles can become entrapped in precipitates (Crittenden et al. 2012). Hence, in our tests, sweep flocculation was assumed to be the main removal mechanism in CF treatment with $FeCl_3$.

In CF with floculan, zeta potential values increased as coagulant dose increased (see Fig. 5b). In this case, charge neutralisation played a role in particle removal from humus effluent. Floculan is composed of polymeric chains that adsorb onto the surface of particles because of interactions such as Coulombic, dipole, Van der Waals or hydrogen bonding. These interactions may occur at different points along the chain. Additionally, these chains extend and attach onto other particles which results in bridging between particles. Known as inter-particle bridging, this mechanism is widely recognised as the main process for particle removal by biopolymers (Shak and Wu 2014, 2015). Increasing the floculan dose from 0.10 to 0.25 mg/L did enhance the amount of turbidity removed from humus effluent (Fig. 5b).

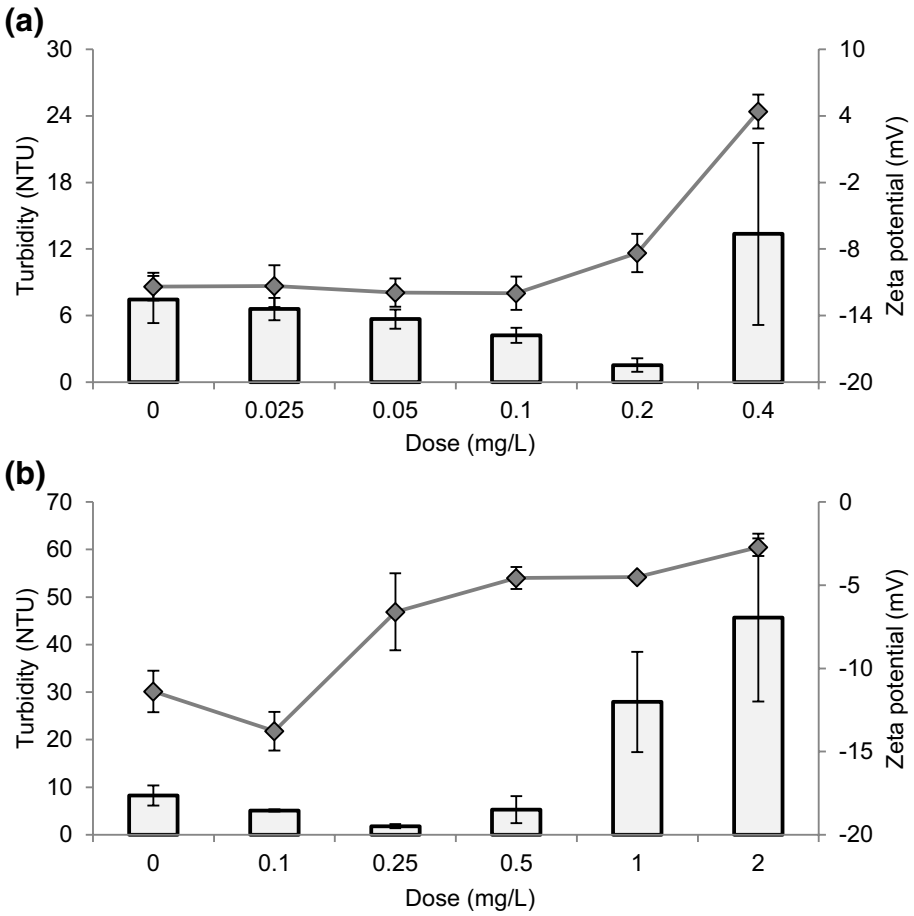

Fig. 5 Changes in turbidity (bars, light grey) and zeta potential (diamonds, dark grey) at different applied doses of $FeCl_3$ (**a**) and floculan (**b**) (mean ± SD)

Higher floculan doses provide more polymer chains to be contacted with particles to form particle–polymer–particle aggregates, thus leading to an increase in the quantity of flocs formed. However, an addition of dosage above the optimum would restabilise the particles due to surface saturation by the excess amount of absorbed polymer (Bratby 2006). This phenomenon will result in a decrease in the amount of turbidity removed, as observed herein for floculan dosage ≥ 0.50 mg/L (Fig. 5b).

Organic matter removal

When compared, amounts of removed DOC relative to COD were substantially lower for both $FeCl_3$ and floculan at the recommended dosage (Fig. 6). Such trend can be attributed to the limited DOC adsorption to flocs, owing to the hydrophilic characteristics of the floc surface and the electrostatic repulsion of DOC when in anionic form Wang et al. (2015).

The presence of DOC in effluent reduces the bioavailability of residual metal, and as such, DOC is one of the parameters input into the BLM to calculate bioavailable metal concentrations. Compared with $FeCl_3$, equivalent or greater removal extents for metals (Fig. 4) in conjunction with significantly ($p = 0.026$) greater concentrations of DOC in treated effluent (Fig. 6) indicate that floculan is likely to be more effective at reducing the bioavailability of residual metal in treated effluent. This is important given the current transition towards water quality standards which relate to the metals permissible bioavailable concentration.

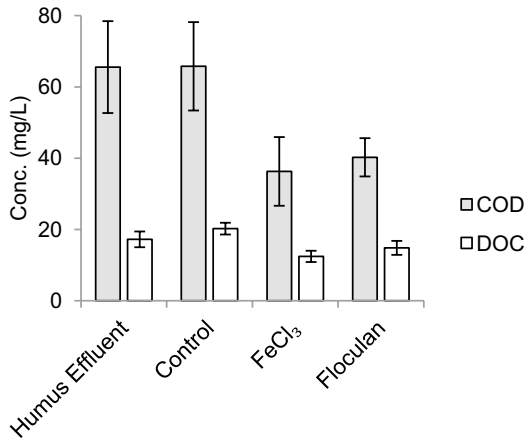

Fig. 6 COD and DOC concentrations in humus effluent treated with $FeCl_3$ (0.10 mg/L) and floculan (0.25 mg/L) at the recommended doses outlined in this study (mean ± SD)

pH of treated wastewater

The pH of treated wastewater was considered in this study as it may influence the economic feasibility of coagulants examined. At the recommended optimum dosage of $FeCl_3$, the pH of treated humus effluent was significantly ($p < 0.001$) reduced with a mean value of 6.6. The acidity of the ferric ions in this reagent explains the change in pH. With floculan, however, the pH of treated humus effluent remained fairly constant ($p = 0.080$) as values between 7.3 and 7.6 were observed. These findings indicate that pH correction of effluent prior to discharge would not be required when using $FeCl_3$ or floculan at the dosage recommended herein, as the discharge allowance for pH is typically between 6 and 9 (UKTAG 2008).

Phosphorous removal

The sizeable amount of TP removed by $FeCl_3$ (see Fig. 7) was expected, given that this coagulant readily precipitates P ions enabling effective removal (de-Bashan and Bashan 2004). Findings from the present study, therefore, indicate that $FeCl_3$ is a viable treatment option for the simultaneous removal of trace metals (Cu, Pb and Zn) and TP. Nevertheless, removal of P with floculan was negligible at all investigated doses (Fig. 7).

Effect of slow mixing conditions

Variation in the time (0–50 min) and velocity (0–50 rpm) of the slow mixing stage had no substantial effect on the removal of metals from humus effluent when treated with $FeCl_3$ or floculan. These findings suggest that flocs produced by both coagulants have similar resistance to breakage and indicate that the slow mixing stage was ineffective at enhancing metals removal.

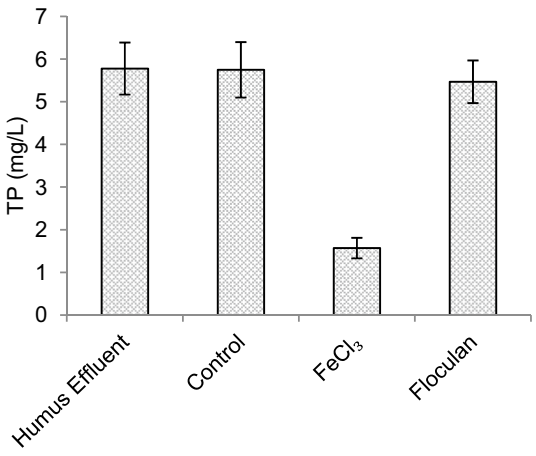

Fig. 7 TP concentrations in humus effluent treated with $FeCl_3$ (0.10 mg/L) and floculan (0.25 mg/L) at the recommended doses outlined in this study (mean ± SD)

Advantages and disadvantages of using CF with $FeCl_3$ or floculan for trace metal removal

Despite the constant development of new and improved treatment processes, CF still remains an important process for treating wastewater, owing to its simplicity in design and operation, low energy consumption and versatility (Teh et al. 2016). This technology can be applied as a primary, secondary or tertiary treatment and can be operated intermittently. Discontinuous operation enables CF to be used as a responsive treatment, which allows application when sudden spikes in metal load are detected. This is a distinct advantage of CF as a treatment option, as influent metal concentrations are known to fluctuate widely (Salihoglu 2013) due to the diverse sources of metals in the areas that WWTWs serve.

Previous studies have demonstrated that salts and biopolymers are effective for the removal of metal from industrial wastewater (Amuda et al. 2006; Shaheen et al. 2013). Findings from the present study demonstrate that elimination of trace metals in the µg/L range from municipal wastewater can be achieved with CF. At recommended dosage, both $FeCl_3$ (0.10 mg/L) and floculan (0.25 mg/L) were equally effective for the removal of Pb and Zn (Fig. 4 panels b and c, respectively) from humus effluent. Floculan, however, outperformed $FeCl_3$ in the removal of Cu (Fig. 4 panel a). Whilst elimination of Ni was negligible for floculan (Fig. 3), Ni concentrations were significantly increased in effluent treated with $FeCl_3$ (Fig. 2). Such findings indicate that floculan is a better option for the removal of trace metals from municipal wastewater.

At present, improving the sustainability and viability of the wastewater treatment process is a particular focus; thus, research interests have been shifted towards the use of biopolymers as coagulants (Renault et al. 2009). Floculan is a commercial product and is, therefore, more practical as a treatment option than non-plant sources such as chitosan, owing to a relatively high-volume market and thus bulk processing. Nevertheless, the cost of floculan (£0.65/kg; A. Lee 2017, personal communication) remains substantially higher than that of $FeCl_3$ (£0.16/kg; A. Major 2017, personal communication). The low cost of $FeCl_3$ is typically noted as the main advantage of this salt, and it has, thus, been used for decades as a coagulant Zeng and Park (2009). A further advantage of $FeCl_3$ was the simultaneous removal of metal and P from humus effluent, something floculan was not able to achieve (Fig. 7).

Further costs must be accounted for when using coagulants in wastewater treatment, in particular, the production of sludge that must be disposed. In CF with biopolymers, flocs formed by inter-particle bridging are dense

and closely packed generating low sludge volume and facilitating drying compared to sludge produced with salts (Renault et al. 2009; Lee et al. 2014). In addition, as biopolymers are biodegradable, the sludge generated can be efficiently degraded by micro-organisms (Renault et al. 2009). Given that floculan removed particles through the mechanism of inter-particle bridging (Section "Turbidity removal"; Hargreaves et al. 2018) and is biodegradable, it is expected that, compared with $FeCl_3$, sludge handling and disposal costs would be much lower in the application of floculan. This advantage may lead to a lower overall treatment cost.

The efficiency of CF with either $FeCl_3$ or floculan was greatly influenced by operating parameters including coagulant dosage (Figs. 1 and 2, respectively). It is, therefore, important to optimise process parameters before large-scale implementations (Teh et al. 2016). Nevertheless, commercialisation for use as a wastewater treatment agent will always be based primarily on whether at full-scale similar treatment performance at comparable (or reduced) cost with established chemical coagulants can be sustained.

Conclusions

This study was one of the first of its kind to study the effectiveness of the CF treatment process for the elimination of trace metals in the µg/L range from municipal wastewater. Investigation has demonstrated that both $FeCl_3$ and floculan were most effective for the removal of trace metals from humus effluent. Using recommended conditions for dosage ($FeCl_3$: 0.10 mg/L, floculan: 0.25 mg/L), both coagulants were equally effective in removing Pb and Zn. Floculan, however, yielded much better removal rates for Cu. Ni removal was negligible with floculan, whilst in effluent treated with $FeCl_3$, Ni concentrations were significantly increased. These findings depict floculan as a better wastewater treatment agent for metal management. Further tests are necessary to assess the performance and cost of floculan when applied in full-scale wastewater treatment.

High turbidity removals and consistent negative zeta potentials indicated that charge neutralisation did not play a significant role in the removal of particles from humus effluent when treated with $FeCl_3$. As such, the sweep flocculation mechanism, which is not influenced by the properties of particles (i.e. negatively charged particles can become entrapped in precipitates), was determined to be the dominant removal mechanism. Floculan, on the other hand, is composed of polymeric chains with cationic charge that neutralise particles and enables aggregation and removal through the mechanism of inter-particle bridging.

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