Development of a pilot fluidised bed reactor system with a formulated clay–lime mixture for continuous removal of chemical pollutants from wastewater

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ABSTRACT

This study was to determine the prospective application of a newly developed fluidised bed reactor (FBR) system using a formulated clay–lime mixture for a large-scale wastewater treatment implementation. A lab-made FBR was designed to assess the application of this formulated clay–lime mixture for the removal of several potential pollutants present in wastewater streams. The operating conditions of the FBR system was first optimised in batch mode by individual experiments prior to progressing into the continuous scheme. The results revealed that the dye elimination was enhanced significantly, by which 99% removal of 30 mg L^{-1} dye can be achieved with 0.8 g L^{-1} loading and aeration rate of 1 L min^{-1}. This process was found effective in removal of anionic dye and phosphate while less favourable towards nitrate. This can be attributed to the different dominant removal mechanisms i.e. precipitation and adsorption. The potential reaction time of the formulated clay–lime mixture was found to be pH dependent where the removal performance was superior in strong alkaline conditions. Several municipal primary effluent samples were also treated using the developed FBR system in continuous operation mode. This system contributed an average 10–15% and 20–40% reduction of the nitrate and COD, respectively, while 100% removal of phosphate was obtained over the experimental period. This study demonstrated that the developed FBR system with the formulated clay–lime mixture can be a cost-effective alternative treatment process for a large-scale application for the treatment of industrial wastewater.

1. Introduction

Growing industrialisation leads to enormous consumption of vast amounts of hazardous chemicals in various industrial practices and results in growing environmental risks if discharged without proper treatment. Handling the effluent from textile manufacturing is one of the most problematic issues in wastewater treatment industries. This effluent often contains large amounts of suspended solids and toxic dye contaminants, and high chemical oxygen demand (COD) [1]. These dyes, even at a low concentration, can be aesthetically unpleasant and impede penetration of light into water bodies, thereby disturbing the ecological aquatic system [2]. The synthetic dyes generally contain azo-aromatic groups which are mostly mutagenic and carcinogenic to humans. They are also resistant against conventional biodgradative processes, due to their high physiochemical stability and recalcitrant nature [3]. Discharge of the untreated dye effluent can create serious environmental and public health problems.

Adsorption is a very simple and widespread method to eliminate pollutants from wastewater [4]. The use of activated carbon as an adsorbent has been well established and widely used in the wastewater treatment process [5]. However, its high cost and complicated regeneration process have led to search for alternative low-cost adsorbents such as activated carbon from cheap carbon sources [5,6] natural clays [7,8], biological waste products [9,10] etc.

Clay adsorption is considered the most economical option for dye removal [4]. The use of clay minerals is of great interest according to their variety of structural and surface properties, high chemical stability, and large specific surface area [11]. From our previous study, the application of different clay minerals for removal of congo red anionic dye was successfully demonstrated [7,8], in addition lime was introduced into the mixed clay to initiate a precipitation through Ca-dye interactions, resulting in an improved adsorption capacity [12]. This adsorbent mixture showed 10–20 times superior dye removal efficiency than natural clays themselves, also providing the potential of adsorbent recovery and long life span.

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This study aimed to develop a lab-designed pilot scale fluidised bed reactor (FBR) system to utilise a formulated clay–lime mixture for the removal of several nominated pollutants potentially present in wastewater streams. Optimisation of operating parameters influencing pollutant removal performance of the FBR system, i.e. adsorbent loading, aeration rate, reaction time etc. was undertaken to facilitate the continuous operating scheme. The removal performance of oxyanion phosphate and nitrate in the wastewater, as well as their interference effect on dye elimination were also determined. These nutrient containing compounds were of great concern in terms of eutrophication in waterways. Samples of primary effluent from a local sewage treatment plant were employed to investigate the removal capability of this formulated adsorbent mixture and the overall system performance, in which the reduction of selected parameters, i.e. COD, PO_4^{3-} and NO_3^- were taken into account.

2. Materials and methods

2.1. Materials

The formulated clay–lime mixtures made-up of Australian clay minerals, sodium bentonite (15%), kaolin (10%), zeolite (5%), and lime (70%) were prepared and pre-activated according to the optimised conditions reported in our previous study [12]. This adsorbent mixture demonstrated very rapid reaction with significant improvement in the dye removal efficiency, in relation to the individual clays themselves. Sodium bentonite with high montmorillonite content, dry milled white kaolin clay, and sand were obtained from Unimin Australia Ltd, and Escott zeolite was provided by Zeolite Australia Ltd. This zeolite contains clinoptilolite as the main crystalline component. Calcium hydroxide ($Ca(OH)_2$) powder was purchased from Unilab (Ajax Finechem). This slaked lime was a strong base material with high pH (12.5) and low solubility (1.2 g L^{-1} at 25 °C) in water.

Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, Labchem Ajax Finechem Australia), nitrate from potassium nitrate (KNO_3, Labchem Ajax Finechem Australia), and phosphate from potassium dihydrogen orthophosphate (KH_2PO_4, VWR England) solutions were prepared to 30 mg L^{-1} concentration by the addition of double-deionised water obtained from Barnstead nanopure Diamond Water ion exchange system with 18.2 MΩ cm resistivity.

The primary wastewater effluent was obtained from the Glenelg North municipal wastewater treatment plant, Adelaide, Australia. In this present study, the wastewater was characterised over a period of 2 weeks, during which two samples were collected each week and analysed in triplicate. The composition of the effluent was characterised as 280–320 mg L^{-1} for COD, 210–245 mg L^{-1} for NO_3^-, and 18–23 mg L^{-1} for PO_4^{3-}.

2.2. Reactor set-up

A lab-made fluidised bed reactor (FBR) was fabricated with Poly(methyl methacrylate) plastic column with a detachable conical bottom for ease of cleaning and scheduled maintenance. A gas sparger with an average pore size of 45 μm was fitted to the detachable conical bottom. The pilot FBR reactor consisted of three sampling ports positioned elevated in a row. The first port on the top part of the reactor was assigned for influent feeding. The middle host was taken as a sampling point that was connected to the sand bed column filtration. The last point was located at the bottom end of the reactor to ease the discharge of the effluent. The pressurised air was regulated by a flow meter (BOC, 1–15 L min^{-1}) to ensure constant aeration. To improve the hydrodynamic performance with homogeneous fluid flow of the FBR, a baffle ring was

also equipped just above the aeration disc to direct the flow of the solution in an up-flow mode through the reactor. This configuration provides a more intimate contact between the adsorbent mixture and solution.

The suspension from the fluidised bed reactor was subsequently transferred to the glass column of 3 cm diameter and with 30 cm height packed with two different sizes of sand. The column was equipped with a sintered glass disc filter to support the bed and sealed with a stopper to facilitate the pressurised condition during filtration. The column bed was initially filled with 3 cm of coarse sand (0.425–1 mm) to avoid possible blockage of the disc filter and subsequently filled with 7 cm of finely granulated sand (0.125–0.355 mm). Such configuration of the sand column allowed the clay particles and particulates formed by precipitation to be retained within the bed, while the residual CR and anion solution still easily passed through. From this packing practice, an average permeate flow rate of 10 mL min^{-1} can be obtained. The sand bed was set to be replaced when the column was half saturated to avoid the breakthrough condition, or when the flow rate was dropped to lower than 8 mL min^{-1} as a result of the particle blockage within the column bed. A schematic diagram of the fluidised bed reactor and sand filtration column is displayed in Fig. 1.

2.3. Experimental procedure

The removal of CR, and selective phosphate and nitrate ions by the FBR system with the formulated clay–lime mixture was investigated by two different schemes. An initial batch test was conducted to optimise an operating condition influencing the removal performance of the adsorbent mixture, and also to determine the prospective removal interaction toward different anion pollutants. Two and a half litres of the tested solution (30 mg L^{-1}) was pumped into the reactor, where the air was regulated and supplied constantly through the air sparger to generate fine bubbles. Then, the known amount of adsorbent was added into the reactor to initiate the removal process, before the suspension was transferred continuously to the sand column. This batch experiment was run for 2 h, in which the samples were collected from the column at predetermined time intervals and analysed for residual concentration.

The continuous operation of the FBR system was performed by a similar experimental procedure, except that the influent was continually fed to the reactor to maintain a constant volume of solution, without the addition of the adsorbent. This continuous flow operation was used to determine the potential reaction time of the formulated clay–lime mixture for upscale treatment process.

To simulate synthetic wastewater stream, the presence of multi-anions was taken into account to study the effect of a competitive environment on the removal efficiency of this FBR system. CR removal was assessed in the presence of phosphate and nitrate in continuous runs, respectively.

2.4. Analytical method

Dye concentration was determined colorimetrically by measuring maximum absorbance at 496.5 nm using a UV–visible spectrophotometer (model γ, Helios, UK). A calibration curve was plotted between absorbance and concentration of the dye solution to obtain an absorbance–concentration profile.

To determine phosphate concentration, the sample was tested with the standard kit (Total Phosphorous, 0–100 mg L^{-1}, Hach Lange GmbH, Germany) using a vanadium molybdate spectrometry method (spectrophotometer DR/4000, Hach Lange GmbH, Germany) [13,14]. The concentration of nitrate was determined using a persulfate digestion method provided by Hach Lange GmbH, Germany (Total Nitrogen 0–25 mg L^{-1}, spectrophotometer DR/4000) [15]. The residual organic contaminants were measured in term of
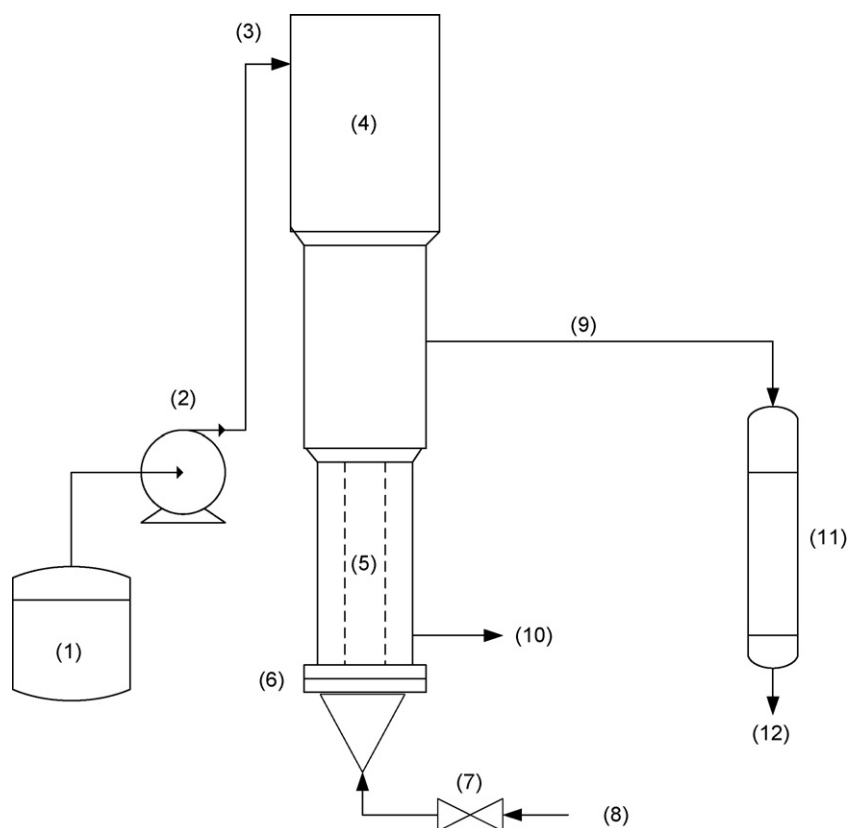
Fig. 1. Experimental set-up for fluidised bed reactor system: (1) solution vessel, (2) solution pump, (3) influent feeding point, (4) fluidised bed reactor, (5) in-house baffle ring, (6) air sparger, (7) compressed air regulation valve, (8) compressed air supply line, (9) suspension transferring line, (10) drainage point, (11) sand bed column, and (12) effluent sampling point.

chemical oxygen demand (COD) using Hach Lange GmbH, Germany (High range COD, 0–1500 mg L^{-1}, potassium dichromate oxidising agent, spectrophotometer DR/4000).

The percentage removal (%) of contaminants and the removal capacity of the adsorbent mixture were calculated using the following equations:

$$\% = (C_i - C_e) \times \frac{100}{C_i} \tag{1}$$

$$q = (C_i - C_e) \times \frac{V}{m} \tag{2}$$

where C_i is the initial concentration (mg L^{-1}), C_e is the concentration at adsorption equilibrium (mg L^{-1}), q is the amount of adsorbate uptake per unit of adsorbent, V is the volume of solution (mL), and m is the weight of the adsorbents (g).

3. Results and discussion

3.1. Dosage optimisation of the formulated clay–lime mixture

Our previous results suggested that the amount of adsorbent mixture should be approximately 1.0 g L^{-1} to ensure an optimum outcome [12]. However, to be economically viable, further investigation to find out an adequate loading of the mixture in the FBR system was also carried out. A range of adsorbent loading from 0.4 to 1.0 g L^{-1} was tested for the removal of CR and the results are shown in Fig. 2.

The results revealed that dye removal increased as the dosage of the formulated clay–lime mixture increased. This can be determined by measuring the residual dye concentration after the reaction. With 1 g L^{-1} of adsorbent loading, the residual concentration was maintained at the level of 0.1 mg L^{-1}, compared to 0.2,

0.6 and 1 mg L^{-1} obtained by use of 0.8, 0.6, and 0.4 g L^{-1} of the adsorbent mixture, respectively. It can be seen that there was no significant improvement in dye removal between 1.0 and 0.8 g L^{-1} of the mixture, in which over 99% removal was still able to be achieved in both cases. This removal capacity was equivalent to 37.2 and 29.9 mg g^{-1} for a loading of 0.8 and 1.0 g L^{-1}, respectively. Taking into account of the removal performance and the cost to produce the formulated clay–lime mixture, 0.8 g L^{-1} was selected as an optimum adsorbent loading and was applied for further experiments.
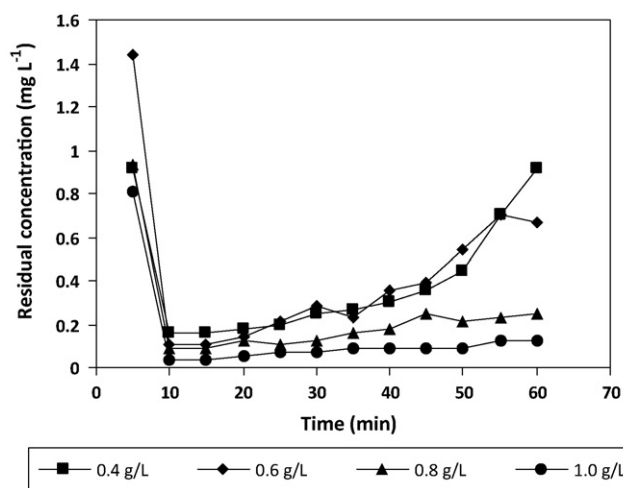

Fig. 2. The removal of congo red by the FBR system at different clay–lime mixture dosages (initial concentration 30 mg L^{-1}, aeration rate 2 L min^{-1}).
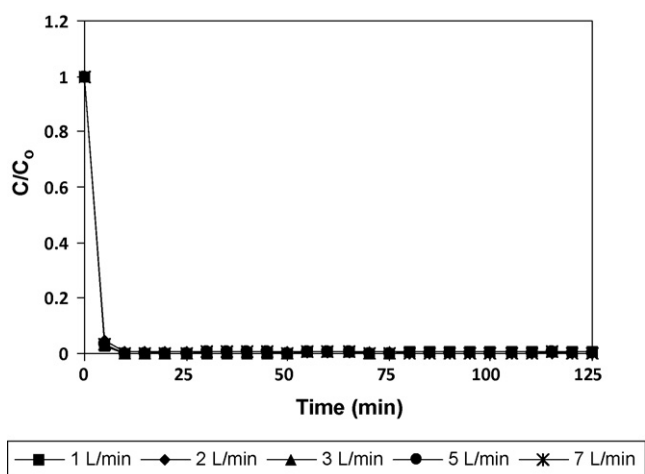
Fig. 3. The removal performance of congo red by the FBR system at different aeration rate (initial concentration $30\,\mathrm{mg\,L^{-1}}$, adsorbent dosage $0.8\,\mathrm{g\,L^{-1}}$).

3.2. Optimisation of aeration rate

The mixing performance is the main parameter influencing the intimate contact between the pollutants and adsorbents, and ultimately determining the overall performance of the removal process. A certain aeration rate in an air-bubble reactor is essential for the adsorbent particles to be remained in suspension and also to minimise the operating cost. In general, the smaller the amount of air supply is used, the more economical the process would be. This is especially important for an industrial implementation. In this study the effect of aeration rate on the removal efficiency was carried out at a range of $1–7\,\mathrm{L\,min^{-1}}$.

From Fig. 3, it can be seen that the effect of aeration on the dye elimination was not significant. More than 99% of the dye removal can still be achieved at a low aeration rate of $1\,\mathrm{L\,min^{-1}}$. This result indicated that the aeration rate may not be a critical parameter in this FBR system due to the light particles of the adsorbent mixture and good mixing performance and hydrodynamics of the FBR system. A minimum aeration rate of $1\,\mathrm{L\,min^{-1}}$ was sufficient to maintain the suspended condition. Therefore, this aeration condition was chosen for the further experiments.

3.3. Removal of selected oxyanions by a fluidised bed reactor

In addition to the removal of CR, PO_4^{3-} and NO_3^- anions were also selected as surrogate anions to represent recalcitrant contaminant and common nutrients found in wastewater streams, respectively. The removal of these oxyanions is more difficult relative to that of cations due to their similar structure, and often coexists in nature with high concentrations [16].

It appeared that the removal of CR and PO_4^{3-} was superior to NO_3^- ions. The elimination of CR and PO_4^{3-} can be achieved in a fast pace. Fig. 4 demonstrated that over 95% removal of these two anions can be obtained within 15 min, followed by the complete removal at 45 min reaction time. The diminution of NO_3^- concentration, in contrast, was found to occur gradually in the first hour of contact time and then remained constant for the rest of the study period, in which maximum removal of approximately 45%, equivalent to $16.9\,\mathrm{mg\,g^{-1}}$ removal capacity, was obtained. This different extent in removal efficiency of the formulated clay–lime mixture toward the selected anions was likely due to the difference in their dominant removal mechanisms. It is suggested that the rapid removal of CR and PO_4^{3-} can be attributed to the precipitation between dissociated Ca^{2+} from the adsorbent and the PO_4^{3-} and dye anions as reported by Zhu et al. [17] and Vimonses et al. [12], respectively.

For instance, the proposed precipitation of PO_4^{3-} with lime to form Ca–P derivatives i.e. hydroxyapatite, can be presented as Eq. (3) [14,18].

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2 \tag{3}$$
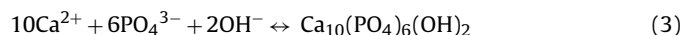
On the other hand, the NO_3^- was found to be less favoured in forming the precipitation with Ca^{2+}. The removal of NO_3^- may be mainly governed by adsorption onto the mixture surface, in which its adsorption efficiency was likely limited by the amount of mixture loading. This postulation was based on the steady reduction of the NO_3^- concentration in the reactor until it reached the adsorption equilibrium after 1 h. However, this NO_3^- removal efficiency by the mixture was found to be greater than the study reported by Mena-Duran et al. [19] using thermoactivated Ca-bentonite. This obtained batch result would assist prediction of the removal performance of the FBR system in further continuous operating schemes.

3.4. Anion removal in a continuous fluidised bed reactor system

To determine the feasibility of employing this process in large-scale wastewater treatment processes, its removal capability in a continuous system must be investigated.

3.4.1. Determination of the potential reaction time of the clay–lime mixture

In a continuous reactor system, it is essential to verify the potential reaction time of the adsorbent in order to design the treatment practice and operating time requirement. The variations in CR removal performance and pH against reaction time are presented in Fig. 5. The results demonstrated that dye decolourisation by the adsorbent mixture occurred very rapidly, by which 99% removal can be achieved within the first few minutes. Then, the removal was found to be sustained over 90% removal without re-loading of the adsorbents prior to a sudden decrease to 36% removal at 8 h. To explain this circumstance, the role of pH on dye removal was taken into account. The results indicated a correlation between the removal behaviour of the mixture and pH of the suspension. The formulated clay–lime mixture was reported to have a high alkalinity nature due to the presence of lime constituent [12]. This $Ca(OH)_2$ has a low solubility, of which the equilibrium solubility constant (K_{sp}) is about 5.5×10^{-6} [20]. Once the mixture was added into the reactor, the lime was slowly dissociated into Ca^{2+} and OH^-. The liberated Ca^{2+} was constantly consumed by precipitation with anionic dye molecules, while the suspension pH was gradually decreased due to the continuous dilution of the mixture concentration. The
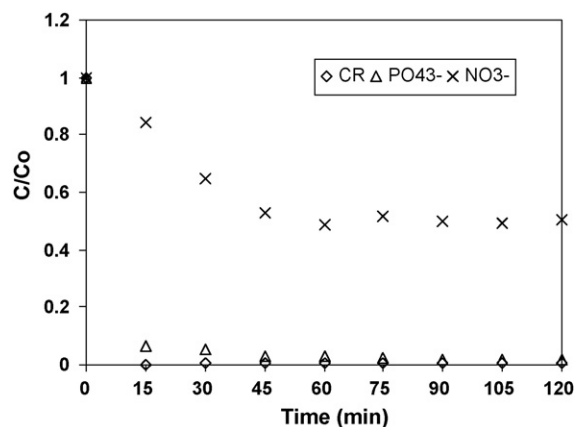

Fig. 4. Removal performance of selected anions by the FBR system (initial concentration $30\,\mathrm{mg\,L^{-1}}$, adsorbent dosage $0.8\,\mathrm{g\,L^{-1}}$, aeration rate $1\,\mathrm{L\,min^{-1}}$).
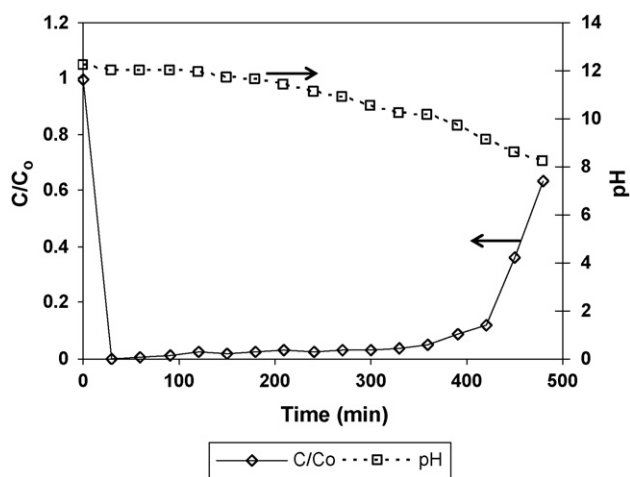
Fig. 5. Removal performance of congo red by the FBR system in continuous scheme against pH profile (initial concentration 30 mg L^{-1}, adsorbent dosage 0.8 g L^{-1}, aeration rate 1 L min^{-1}).

reduction of the suspension pH was used as an indicator to determine the residual mixture concentration retained in the solution, and therefore the cycle time. Fig. 5 shows that the decolourisation of CR decreased significantly when the suspension pH dropped to 8–9. This result corresponded well to our previous data, in which dye removal bottomed out at about neutral pH [12]. As a result, for further experiments, the validation of the formulated clay–lime mixture was estimated based on the solution pH of 10 (approximately 95% removal efficiency of CR), whereby below this limit the equivalent amount of the adsorbent mixture was re-loaded into the reactor.

3.4.2. Effect of co-existing anions

The interference effect of the competitive oxyanions on the removal of the CR, PO_4^{3-} and NO_3^- was taken into account and thus was investigated in a continuous scheme. This study was meant to simulate the actual situation, in which the anionic pollutants often coexist in wastewater streams.

The removal performance of CR, PO_4^{3-} and NO_3^- by the adsorbent mixture is illustrated in Fig. 6. The results showed that the elimination of CR and PO_4^{3-} took place rapidly, and achieved 100% removal after just a few minutes of mixing. This removal efficiency
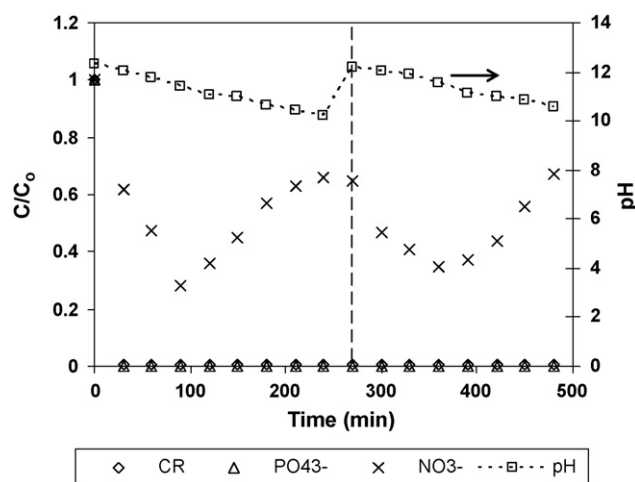

Fig. 6. Removal performance of co-existing anions by the FBR system in continuous scheme against pH profile (initial concentration 30 mg L^{-1}, adsorbent dosage 0.8 g L^{-1}, aeration rate 1 L min^{-1}).

was able to be sustained until the next batch of the adsorbent mixture was added (after 2.5 h). This implies that the effect of competitive anions on decolourisation of anionic dye and phosphate removal were insignificant, which was found to contradict the previous study by Zhu et al. [17]. In addition, a gradual decrease of suspension pH was observed along the experiment from pH 12 to 10 after 2.5 h contact time. It can be seen that the pH change did not hinder the elimination performance of the mixture toward these two particular anions. Such removal behaviour was found to be in contrast to that of NO_3^-. The reduction of NO_3^- content appeared to be less effective compared to the removal of CR and PO_4^{3-}, in which approximately 70% of the NO_3^- was gradually eliminated after 90 min before its concentration increased, and decreased again once the next batch of the formulated clay–lime mixture was added.

These results confirmed the postulation regarding the different controlled removal mechanisms proposed in the previous discussion. During the early stage of mixing, the clay and calcium derivatives, i.e. $CaCO_3$, could result in a high concentration of Ca^{2+} in the suspension. The anionic CR and PO_4^{3-} molecules were able to react with Ca^{2+} to form relatively insoluble complexes, which can be easily eliminated by filtration. On the other hand, NO_3^- has a chemically inactive nature in dilute aqueous solutions [21], and therefore was less likely to form Ca-nitrate precipitation. The removal of NO_3^- was, therefore, more dependent on adsorption to the material surface. However, these results revealed that the nitrate removal in the presence of co-existing anionic dye and PO_4^{3-} could be achieved up to 45% removal on its own. This may be explained by the complement adsorption or co-precipitation of the NO_3^- ions onto the surface of the flocs formed by the other calcium-anion compounds. Similar phenomenon was also reported by Liao and Randtke [22]. Such augmentation effect of co-existing anions on their removal efficiency supported the potential application of the adsorbent mixture for the real wastewater treatment.

3.5. Continuous removal of selected contaminants from primary wastewater

The primary effluent from Glenelg WWTP, Adelaide was employed to investigate the potential removal of contaminants in real wastewater using the developed FBR system with the formulated clay–lime mixture, and also to examine influence of the presence of compounds such as suspended solids on the removal performance of the FBR system. The removal performance was evaluated via water quality parameters of concern, such as organic compounds (COD and DOC) and nutrients (PO_4^{3-} and NO_3^-).

Fig. 7 shows that the removal of nutrient content from the real wastewater corresponded to the predicted profile from the previous experiment. Phosphate was found to be entirely eliminated within a short time, whereas the nitrate removal became less effective, by which only 10–15% removal can be achieved. This can be attributed to the presence of suspended solids and also the organic compounds in the effluent. These contaminants can create a competitive environment with NO_3^- for the adsorption sites, and hence reduce the overall removal performance.

In addition to the nutrient removal, COD reduction was observed, demonstrating 20–40% COD removal over 6 h. Generally, the natural clays posses a charged surface due to isomorphous substitution in their crystal lattice, and therefore enable efficient adsorption of the ions and polar molecules [23]. However, the application of the clay for removal of non-ionic organic pollutants might be limited.

It was observed that the addition of the formulated clay–lime mixture can induce a significant amount of floc formation which was quickly settled in the early minutes of contact with the effluent. Taking the role of the lime constituent into account, this may
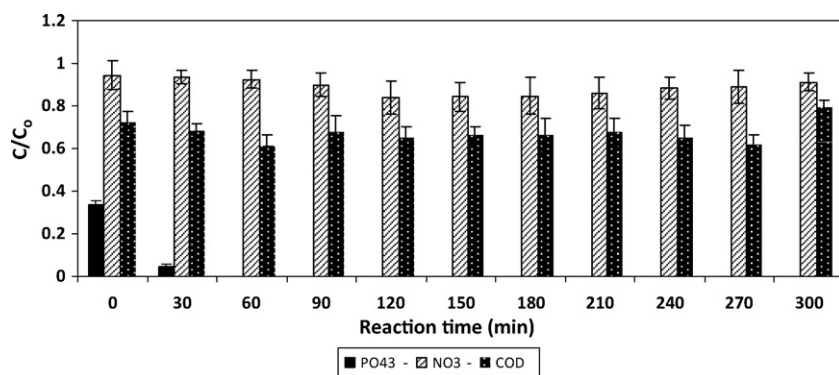
Fig. 7. Removal performance of PO_4^{3-}, NO_3^-, and COD from primary effluent by the FBR system (adsorbent dosage $0.8\,g\,L^{-1}$).

suggest that the COD reduction may also contribute to the Ca derivatives and its dissociations in solution. Several studies have addressed the importance of lime in the removal of polluting matters by coagulation and flocculation [24,25]. It is suggested that lime can promote the removal of organic compounds through the polymerisation and precipitation of long chain fatty acids [25]. The organic compounds which are moderately hydrophilic and contain carboxyl, enol, and phenol functional groups can bind with Ca^{2+} and easily adsorb or precipitate, while the rest tends to remain in solution [22]. The optimal performance of the liming condition was reported to be at strong alkaline level (pH 12) [24,25]. The results from the present study well supported these findings. In addition, the enhancement of COD removal by the clay and lime mixture prior to biological treatment was also reported by Beccari et al. [26].

From the above results, although the removal efficiency of the adsorbent mixture toward COD and NO_3^- was not significant, relative to PO_4^{3-}, this study still revealed the potential employment of this system (FBR with the formulated clay–lime mixture) as the post-treatment process for the wastewater industry, making the treated wastewater as a reusable water source.

4. Conclusion

The removal of selected anionic pollutants by the newly developed fluidised bed system with a formulated clay–lime mixture was studied. The optimum conditions of the FBR system were found to be at low aeration rate of $1\,L\,min^{-1}$ with an adsorbent mixture loading of $8\,g\,L^{-1}$, indicating the economic viability of this treatment process. The batch experiments revealed high removal efficiency with over 99% removal of congo red and phosphate within 15 min treatment time; while nitrate reduction was less significant, where only 45% removal was obtained. This could be explained by variation of the dominant mechanisms. The anionic dye and phosphate can react with partially dissociated Ca^{2+} to form insoluble precipitates. The behaviour of nitrate in contrast was less interactive with Ca^{2+}, and thus its removal was likely attributed to the adsorption on the mixture surface. The cycle reaction time of the formulated clay–lime mixture was found to be pH dependent, in which the removal was more effective at strong alkaline condition. The removal capability of the formulated adsorbent mixture was also examined using the real primary wastewater. It was shown that phosphate can be completely eliminated, while the fluctuation in COD and nitrate removal was experienced in the range of 10–15% and 20–40%, respectively. The successful operation of this pilot FBR system suggested a prospective large-scale application as alternative low-cost treatment process for the wastewater industry, especially for the removal of toxic anionic dye and phosphate in industrial wastewater.

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