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Removal of calcium ions from industrial wastewater

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ABSTRACT

This study deals with the removal of cadmium and cyanide from galvanic industry wastewaters. The use of the electro dialysis technique for the treatment of a synthetic wastewater containing approximately $0.0089 \text{ mol L}^{-1}$ cadmium and 0.086 mol L^{-1} cyanide was studied using a five-compartment electro dialysis cell. The extraction of cadmium and cyanide depends on the applied current density and it is limited by the precipitation of cadmium on the cation-exchange membrane in the diluate central cell compartment. © 2009 Trade Science Inc. - INDIA

1. INTRODUCTION

Calcium ions are commonly found in natural environments where it often precipitates as carbonate minerals e.g. calcite and dolomite. Previous studies of such carbonate precipitates suggested both the presence of bacteria, and specific interactions of these micro-organisms with the precipitated minerals. The general mechanism of microbiological carbonate precipitation (MCP) has been described as the ability of micro-organisms to alkalise (increase of pH and dissolved inorganic carbon (DIC)) an environment through various physiological activities (for review, see Riding and Awramik^[1]). In this regard, one of the best-described mechanisms is the enzymatic hydrolysis of urea, yielding ammonia and carbon dioxide. The latter will react further to carbonate, thus forming favourable conditions for CaCO_3 precipitation^[2,3].

Microbial calcification has already been used in several biotechnological applications such as a technique for the restoration of sandstone monuments^[2-4] and the mineral plugging of soil pores and subsequent control of groundwater (and pollutant) flow^[5,3]. This study investigated the potential application of MCP for

the removal of soluble calcium from real industrial wastewater. Calcium-rich wastewater ($500\text{--}1500 \text{ mg/L}$, Ca^{2+}) results from industries such as paper recycling, bone processing and citric acid production, and also from landfill leachates^[6,7]. Calcium ions in wastewater cause several operational problems with widespread economic implications. These include severe scaling in pipelines and reactors, due to calcium precipitation as gypsum, phosphate and/or carbonate, and malfunctioning of anaerobic reactors^[7]. Existing chemical crystallisation reactors are based on the addition of a base (NaOH or $\text{Ca}(\text{OH})_2$) in the presence of nucleation sites (e.g. sand grains). Such reactors are, however, often expensive, complex, and sometimes give rise to highly alkaline effluents. To the best of our knowledge, ureolytic MCP has never been used as such, and the aim of this paper is therefore to present results from initial experiments in this regard, as well as perspectives for future applications.

2. MATERIALS AND METHODS

2.1. Batch experiments

Wastewater

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Raw wastewater was obtained from a paper recycling facility and used on the day of collection. The average composition of the wastewater during the experimental period was: pH 6.6 (± 0.2); volatile fatty acids (VFA) 1291 (± 232) mg/L; soluble chemical oxygen demand (CODs) 3096 (± 517) mg/L; soluble calcium 489 (± 39) mg/L; ammonium-nitrogen 11 (± 5) mg NH_4^+ -N/L.

Urea concentration

Batch experiments were used consisting of 250 mL Erlenmeyer flasks with 100 mL raw wastewater and urea (Sigma) concentrations of 0, 0.1, 0.5, 1, 2, 4, 8 and 16 g/L, respectively. These were incubated aerobically (28°C and 100 rpm shaking) for 5 days, and sampled at completion of the experiment. Soluble calcium was analysed with flame atomic adsorption spectrometry (FAAS) (Perkin-Elmer AAS 3110, Perkin-Elmer, Belgium), after filtration (0.22 μm Millipore) and acidification with 0.1 N HNO_3 . pH and ammonium (NH_4^+ -N) were also measured^[8].

Hydraulic retention time (HRT)

Urea was added to final concentrations of 0 (control), 0.5 and 1 g/L in 100 mL wastewater samples in 250 mL Erlenmeyer flasks and incubated for 4 days (28°C and 100 rpm shaking). Samples were taken at 0, 15, 25, 42, 68, and 88 h, and analysed as described above. All experiments were performed in triplicate.

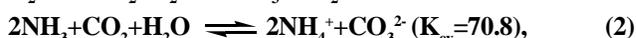
2.2. Semi-continuous reactors

Two semi-continuous calcification reactors (Reactors 1 and 2) were started with 1.5 L raw wastewater and a urea concentration of 1 g/L, while the two control reactors (Controls 1 and 2) were similar but without the addition of urea. These reactors were incubated (28°C and 100 rpm shaking) for 48 h. After this period, the "sludge" was allowed to sediment after which 1.35 L (90%) of the supernatant was removed and refreshed with raw wastewater and dosed with urea where applicable. Both the influent and the effluents from the respective reactors were analysed for pH, CODs, TSS, VSS^[8], and total and soluble calcium. After 18 days of operation, the HRT of one control (Control 1) and one calcification (Reactor 1) reactor was set at 24 h, while that of the others remained unchanged. The sludges from the reactors were examined with light

microscopy (Polivar, Reichert-Jung), and digital images were captured with a 1-CCD camera (Hamamatsu Photonics GmbH, Hersching, Germany).

3. RESULTS AND DISCUSSION

A biological catalysed precipitation process, based on urea hydrolysis, was investigated as a potential alternative to chemical carbonate precipitation. Urea degradation is a simplistic process, and since it is based on the working of the urease enzyme, which is common in many organisms, it can easily be integrated in an existing biological wastewater treatment system. Moreover, urea is a relatively inexpensive chemical and provides upon hydrolysis simultaneously a pH increase and DIC increase, both of which are essential to precipitation (1-3)



Previously reported applications of ureolytic MCP used urea concentrations between 10 and 20 g/L^[5,3]. In wastewater, the required precipitation is governed by the amount of calcium which is to be removed, while two other important effluent parameters to be considered are the maintenance of a near-neutral pH, and low nitrogen (ammonium resulting from urea hydrolysis) concentrations. Therefore, it is essential to find a combination of the most efficient as well as the lowest possible urea concentration. The raw wastewater used in these experiments contained about 12 mM Ca^{2+} . Based on (1), (2) and (3), it can be argued that a minimum

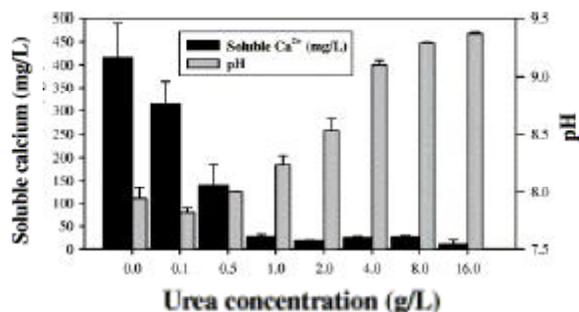


Figure 1: Soluble calcium (mg/L) and pH measurements of batch tests on raw wastewater dosed with different urea concentrations after 5 days incubation. Error bars indicate standard deviation (n=3)

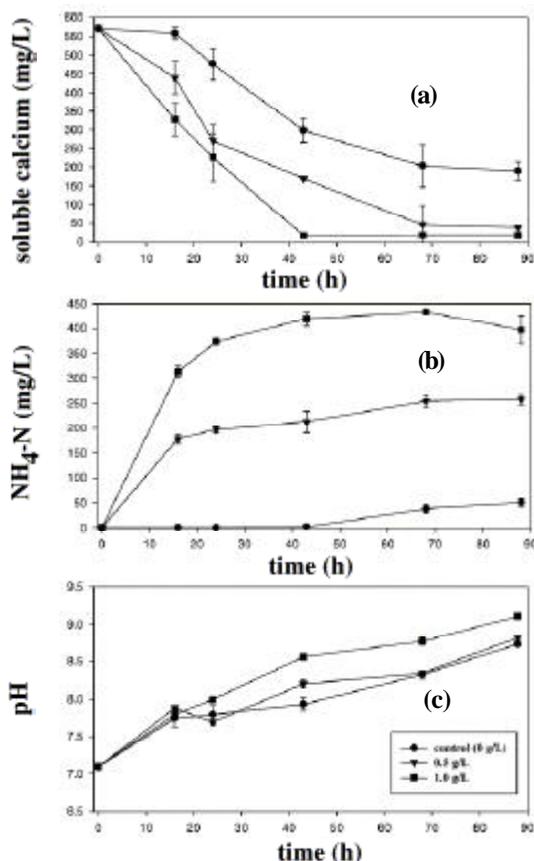


Figure 2: (a–c) Soluble calcium removal and evolution of ammonium and pH, respectively, in raw wastewater at two different urea concentrations during 4 days. Error bars indicate standard deviation (n=3)

of 12 mM urea (=0.72 g/L) is required to precipitate 12 mM calcium.

The most efficient concentration under the experimental conditions was indeed between 0.5 and 1 g/L urea (Figure 1), which concurs with the theoretical required amount. The pH increased with increased urea concentrations, but did not exceed 9.3, as a result of the ammonium buffer equilibrium (Eq. (4)).



A urea concentration of 1 g/L was clearly more effective than that of 0.5 g/L in terms of the required

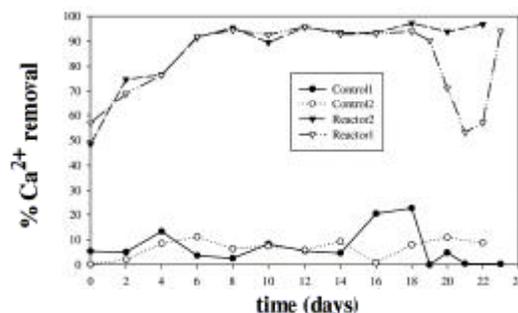


Figure 3: Evolution of soluble calcium removal in the semi-continuous reactors. Controls 1 and 2 duplicate control reactors. Reactors 1 and 2 represent duplicate treatments with urea. In the period 0–18 days, the hydraulic residence time was 48 h in all reactors. From day 18 it was lowered to 24 h for Reactor 1 and Control 1

HRT (Figure 2a). Both concentrations resulted in about 50% removal after 24 h, but after 48 h, the 1 g/L concentration showed more than 90% removal while the 0.5 g/L samples only showed about 60% removal. (Figure 2b) suggests that a significant percentage of the urea was degraded in both samples after 24 h. The moderate Ca²⁺ removal at this time could be due to a lack of sufficient crystal nucleation sites, which accelerates the crystallisation process. Based on the results of both batch experiments, it was opted to continue with a working urea concentration of 1 g/L and a HRT of 48 h in the semi-continuous reactors. Both (Figures 1 and 2) suggest that at 1 g/L urea, a final pH of about 8.5 could be expected.

For all the semi-continuous reactors, COD removal was around 60% (TABLE 1). Ammonium levels were on average slightly lower than expected (1 g urea equals 468 mg NH₄⁺-N), which could be ascribed to a combination of volatilisation and microbial uptake processes. Ammonium production together with eventual carbonate precipitation has significant influences on the eventual pH. Whereas the former results in a pH increase, CaCO₃ precipitation leads to acidification^[9]. Therefore, the pH measured at 24/48 h intervals might

TABLE 1: Average values and standard deviation of all parameters for the influent and the four semi-continuous reactors as measured from 6 days onwards after start-up

	Influent	Control 1	Reactor 1	Control 2	Reactor 2
pH	6.6±0.3	7.4±0.3	7.8±0.3	7.4±0.2	7.9±0.4
Ca ²⁺ (mg/L) ^a	482.7±3.6	452.0±33	147.0±63	445.4±48	105.2±66
Ca ²⁺ (mg/L) ^b	471.1±22	453.7±69	31.8±7	440.2±72	28.7±12
CODs(mg/L)	3075±522	1319±465	1653±465	1236±340	1267±127
NH ₄ -N(mg/L)	12.0±5	2.1±3	418.5±19	2.5±3	409±32

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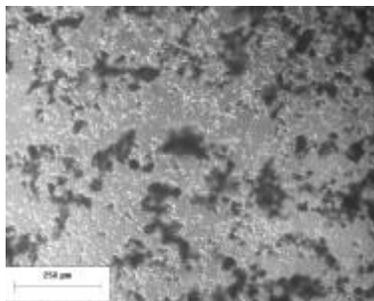


Figure 4 : Sludge from the calcification reactor (Reactor 1), characterised by small calcareous flocs and free-swimming bacteria

not necessarily reflect the fluxes occurring in-between (TABLE 1). However, as measured, the effluent pH for the calcification reactors remained below 8 for most of the experimental period.

(Figure 3) shows that calcium removal in the crystallisation reactors exceeded 90% from day 6 onwards. This “start-up period” is considered to be due to the development of a calcifying sludge, with increased urease activity and a build-up of crystal nucleation sites. At a pH below 8.0, little CaCO_3 precipitation could be expected, as a result of the bicarbonate buffer equilibrium ($\text{pK}_a=10.3$). COD/VFA removal, together with subsequent DIC increase and pH fluxes, were similar in the control and calcification reactors. This suggests that the key to the precipitation process was the urea-hydrolysis products. As measured, the resulting pH increase seemed insufficient to account for all the precipitation observed. The DIC resulting from urea hydrolysis seems little (about $16.7 \text{ mM CO}_3^{2-}$) in comparison with that from COD/VFA degradation (about 56 mM CO_2). However, as (1) and (2) indicate, this DIC is immediately available as carbonate, thereby forming the key to the precipitation reaction. It is therefore proposed that the value of using urea for precipitation is the direct availability of carbonate ions, even at moderate pH values.

(TABLE 1) also shows that not all insoluble calcium was retained under the current operational conditions in the reactors. The CaCO_3 suspended in the effluent was also reflected in the VSS/TSS measurements. While the VSS remained more or less constant in both the calcification and control reactors (between 300 and 500 mg/L), the TSS increased in the calcification reactors up to 900 mg/L (results not shown).

Microscopic examination of the calcifying sludge revealed the presence of small, but dense calcareous flocs (Figure 4).

4. CONCLUSIONS

- A novel application of ureolytic microbiological carbonate precipitation was proposed to remove soluble calcium from industrial wastewater.
- The main objective of this work was to explore the feasibility of urea-based microbial carbonate precipitation as an alternative Ca^{2+} -removal technology. The doses of urea applied, the retention times of, respectively, calcification and sedimentation, and the management of the biocatalytic sludge need to be further investigated and optimised.
- Positive results from these preliminary experiments certainly warrant further development of this process.

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