Separation of cadmium and copper from phosphorous rich synthetic waters by micellar-enhanced ultrafiltration

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ABSTRACT

In this study, micellar-enhanced ultrafiltration (MEUF) was proved to be a viable technique for the purification of phosphorous rich waters. The experiments were conducted in order to study the simultaneous removal of heavy metals from phosphorous rich synthetic waters by evaluating the effect of pH (3.5–5) and the feed concentrations of sodium dodecyl sulphate (C_{SDS}, 3.5–20 mM), phosphorous (C_{Phosph}, 0–1.3 g/dm^3), zinc (C_{Zn}, 0.8–2 mg/dm^3) and nickel (C_{Zn}, 2–4 mg/dm^3) on the rejection coefficients of cadmium and copper. Zinc and nickel feed concentrations had no statistically significant effect and the metal competition was negligible. pH, SDS and phosphorous feed concentration did show a significant effect on the MEUF process. Rejection coefficients up to 98% were achieved for both metals when no phosphorous was present and at SDS feed concentration of 20 mM. The phosphorous feed concentration showed a bigger negative effect on the rejection coefficient of copper at higher pH levels due to complex formation. At low pH values and in the presence of phosphorous the heavy metals were present as divalent cations and no complex formation was observed. In these conditions, copper rejection coefficients were very similar to cadmium, achieving up to 80% removal of heavy metals. At higher pH levels the presence of $Cu_3(PO_4)_2$ was more substantial and the rejection coefficients of copper decreased to 65%. The research presented in this manuscript could lead to novel uses of MEUF for the purification of nutrients from wastewater streams prior to their recovery, closing phosphorus cycles in anthropogenic systems.

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1. Introduction

Phosphorous (P) is a fundamental nutrient for living organisms and for crop production [1]. Studies indicate that food production and consumption systems are open in terms of phosphorous, resulting in losses to water and soil [2]. In excess, nutrients such as phosphorous often cause environmental problems such as eutrophication of aquatic ecosystems and pollution of groundwater. Most of the phosphate fertilizer production is achieved by processing phosphate rocks with sulphuric acid or nitric acid [3]. There is a concern that the exploitation of this non-renewable resource to meet the current demands is not sustainable. Therefore, in order to increase the life expectancy of the world's phosphorus resources, to make the fertilizer production more sustainable and to reduce the anthropogenic impact of phosphorous,

special attention has grown towards the recovery of phosphorous from waste [1,4,5].

Recently, research has been conducted to recover phosphorous from swine sludge and wastewater [6,7], sewage sludge [1,8] and ashes from monoincineration of sewage sludge [9]. The constraint is that industrial waste sources often contain pollutants such as heavy metals that can put in risk the further reuse of the recovered fertilizer product. Metal inputs to agricultural soils via mineral fertilizers are of great concern due to their potential risk to the environment and human health. When heavy metals are in the soil, they can accumulate in less soluble forms, be transferred to watersheds through leaching and erosion and enter in the food chain [10]. European Union member states have taken measures to reduce the metal content in fertilizers. In Finland, statutory requirement regarding the maximum cadmium concentration in phosphorous fertilizer is set to be 21.5 mg/kg P_2O_5 [11]. Therefore, heavy metals such as cadmium must be removed and separated from the phosphorous rich waste stream before the recovered phosphorous can be used as fertilizer.

In this study, micellar-enhanced ultrafiltration (MEUF) is proposed to be a viable technique to remove heavy metals from

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Nomenclature

A	membrane effective area (m^2)
b_i	linear coefficient
b_{ii}	quadratic coefficient
b_{ij}	interaction coefficient
b_o	constant coefficient
C_{Cu}	copper feed concentration (ppm)
C_{Cd}	cadmium feed concentration (ppm)
C_f	compound concentration in the feed (ppm)
C_{Ni}	nickel feed concentration (ppm)
C_p	compound concentration in the permeate (ppm)
$C_{Phosph.}$	phosphorous feed concentration (g/dm^3)
C_{SDS}	SDS feed concentration (mM)
C_{Zn}	zinc feed concentration (ppm)
DF	degrees of freedom
$F_{tabulated}$	Fisher test critical value
F value	Fisher test calculated value

$J_{rel.}$	Relative flux
J_V	Permeate flux (dm^3/m^{2}h)
J_w	Water flux (dm^3/m^{2}h)
MS	mean square
p	p-value, probability
PRESS	prediction residual sum of squares
Q^2	response variation percentage predicted by the model
R	rejection coefficient (%)
R^2	coefficient of determination
R^2_{adj}	adjusted coefficient of determination
SD	standard deviation
SS	sum of squares
X_i	factor coded level
X_iX_j	interactive variables
Y	predicted response, predicted rejection coefficient (%)

phosphorous rich wastewaters. In MEUF, the anionic surfactant forms large amphiphilic aggregate micelles when it is added to aqueous streams at a concentration higher than its critical micelle concentration (CMC). The heavy metal cations can be mostly trapped by the micelles due to electrostatic interaction and thus retained by the ultrafiltration membrane. Anionic phosphates will not be trapped by the micelles and they will pass through the membrane to the permeate obtaining the separation from the heavy metals. In addition, the metal cations not trapped by the micelles and the surfactant monomers will also pass through the ultrafiltration membrane to the permeate side.

This research was conducted in collaboration with a fertilizer company, which was interested in recovering phosphorous from their phosphorous rich drainage waters. The phosphorous rich drainage waters are mainly formed when the rain waters infiltrate and wash a heterogeneous gypsum landfill of the company, a landfill that contains heavy metals such as cadmium, copper, zinc and nickel. As a consequence, the drainage waters of the company contain variable concentrations of heavy metals, which need to be removed from the waters prior to their utilization in-site. MEUF has been before established to be more efficient in solutions with diluted metal concentrations [12]. The aim of this research was thus to study the feasibility of MEUF for separating simultaneously heavy metals such as cadmium and copper from phosphorous rich synthetic samples and to find the important factors affecting the simultaneous removal of cadmium and copper from phosphorous rich synthetic waters. The simultaneous removal of heavy metals from synthetic samples by MEUF has been previously studied [13–15]. In addition, MEUF has also been applied for the removal of nutrients such as nitrates and phosphates from synthetic samples using cationic surfactants [16]. However, to the knowledge of the authors, this is the first study where MEUF has been applied to separate heavy metals from phosphorous rich waters in order to purify nutrient rich waters for further recovery and reutilization.

2. Material and methods

2.1. Chemicals and analysis

Sodium dodecyl sulfate (SDS, purity > 99%), zinc chloride (ZnCl$_2$, extra pure 99.99%) and cadmium chloride (CdCl$_2$, extra pure 99.99%) were obtained from Fisher Scientific. Copper chloride (CuCl$_2$, purity > 99%) and nickel nitrate (Ni(NO$_3$)$_2$, purity > 99%) were purchased from Across Organics. Sodium phosphate monobasic (NaH$_2$PO$_4$, purity > 99%) was supplied by Sigma Aldrich.

Chemicals were used as such without further purification. Synthetic samples were prepared using deionised water. The pH was adjusted by 0.1 M NaOH and 6 wt.% HNO$_3$.

Heavy metal concentrations were measured by atomic absorption spectroscopy (Perkin Elmer, AAnalyst 4100). Phosphorous concentrations were analysed by ICP–OES (Perkin Elmer, Optima 5300DV). SDS concentrations were measured by a Total Organic Carbon (TOC) analyser (Sievers 900).

2.2. Micellar-enhanced ultrafiltration

The ultrafiltration experiments were carried out in a batch stirred cell (Amicon 8400 stirred cell, Millipore), at room temperature and pressure of 3 bar. Applied overpressure was achieved by nitrogen gas. The stirring speed was maintained constant at 375 rpm to obtain effective agitation and vortex approximately one-third of the depth of the liquid as recommended by the supplier. The flat sheet membranes used were 10 KDa Amicon regenerated cellulose (PL series, Millipore) with a membrane effective area of 0.00418 m^2. The initial feed volume was 200 cm^3 and the ultrafiltration experiments were carried out until 100 cm^3 of the total sample was filtered. After the MEUF experiments and cleaning the membrane, water flux was re-calculated in order to observe the degree of possible membrane damages. More details of the procedure are explained in our previous publication [12].

2.3. Critical micelle concentration of SDS

The critical micelle concentration (CMC) of SDS was determined by measuring the conductivity of the system (model 20, Denver Instruments). Additionally, the effect of the presence of electrolytes (added as NaH$_2$PO$_4$, C$_{Phosph.}$ = 1.3 g/dm^3) on the CMC of the surfactant was also measured.

2.4. Statistical experimental design

The statistical experimental design used in this study was a fractional factorial design of resolution V, which means that all the main effects and two-factor interactions can be estimated without confounding. The curvature diagnostic plot developed showed that the linear model exhibited a strong curvature. Therefore, the fractional factorial design was complemented by adding extra experiments to estimate the effect of the quadratic terms and to improve the model.