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Examination of zinc uptake in a combined system using sludge, minerals and ultrafiltration membranes

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ABSTRACT

This work investigates the feasibility of zinc removal from wastewater with the use of ultrafiltration (UF) membranes combined with natural minerals and sludge. Activated sludge obtained from a membrane bioreactor (MBR) was enriched with initial zinc concentration of 320 mg/L and specific concentrations of zeolite, bentonite and vermiculite. The mixture was agitated and placed inside a batch ultrafiltration unit where the filtration process took place. The effect of several parameters on zinc removal was investigated including the mineral type, quantity and grain size, the metal–mineral contact time and the associated kinetics, the pH value, the zinc initial concentration and sludge mixed liquor suspended solids (MLSS) concentration. The ultrafiltration membranes without any mineral addition were able to remove 38–78% of zinc ions due to biosorption on sludge flocs. The addition of minerals increased the Zn(II) removal efficiencies reaching in some cases more than 90%. Bentonite was the most effective mineral in zinc removal followed by vermiculite. Alkaline pH values favoured zinc removal due to enhanced chemical precipitation. A three-stage adsorption process was identified where the boundary layer diffusion process was followed by a two-stage intraparticle diffusion process. Powder size vermiculite was more effective than granular vermiculite in zinc removal. Minerals also resulted in membrane fouling mitigation since the membrane permeability drop was reduced. The combined sludge–mineral–ultrafiltration system can be effectively employed for the treatment of industrial wastewater.

1. Introduction

Zn(II) is a common heavy metal that contaminates waters through various industrial activities such as mining, metal coating, battery production and its use in paints, ceramics, wood, fabrics, drugs, sun blocks, deodorants, etc. [1–3]. Zinc is included in the list of priority pollutants proposed by the Environmental Protection Agency (EPA) and gives rise to serious poisoning cases when found in significant quantities. According to the US EPA the wastewater reuse limit for long-term use is 2.0 mg/L [4]. Various physico-chemical methods have been applied for the removal of zinc from aqueous solutions. These methods include chemical precipitation, ion exchange, adsorption, membrane filtration, reverse osmosis, electro-deposition and flotation. Each method has its own merits and drawbacks. Chemical precipitation, reverse osmosis and electro-deposition are considered expensive methods [5–9]. The use of low-cost adsorbents having high adsorption capacity is an attractive solution for zinc removal.

Several materials can be employed as adsorbents. Activated carbon is considered an effective adsorbent due to its extensive porosity and large available surface area [10,11]. The use of clays as sorbents to remove contaminants has been investigated since clay is less expensive compared to other materials such as activated carbon [12]. Some attempts have been made to utilize other low cost materials having high sorption capacity. Several researchers have investigated naturally occurring materials for the removal of heavy metals. Shawabkeh et al. [13] utilized chemically treated bentonite in order to study the removal of zinc from aqueous solutions. Bereket et al. [14] employed bentonite for the removal of Pb(II), Cd(II), Zn(II) and Cu(II) from aqueous solutions. Kaya and Ören [15] studied extensively the adsorption properties of natural and Na-enriched bentonite for zinc removal from aqueous solutions. Blöcher et al. [16] utilized an integrated system, which combined hybrid flotation, membrane separation and adsorption, using zeolite as a bonding agent for the removal of copper, nickel and zinc from wastewater. Mellah and Chegrouche [17] studied the removal of zinc from aqueous solutions using natural bentonite. Veli and Alyüz [18] investigated copper and zinc removal from aqueous solutions with the use of bentonite as adsorbent. Zamboulis et al. [19] employed an integrated, innovative process, which combined sorption with the use of synthetic ultrafine zeolite as sorbent and flotation for the removal of copper and zinc cations. Lazaridis et

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al. [20] applied a two-stage process, which was very effective for zinc removal from aqueous solutions. The first stage included the sorption of zinc ions onto zeolite and the second one the separation of the metal-loaded sorbent in a hybrid cell, which combined dispersed-air flotation and micro-filtration in one unit. da Fonseca et al. [21] utilized vermiculite as adsorbent to study the removal of Cd(II), Mn(II), Zn(II) and Cr(III) from aqueous solutions and Álvarez-Ayuso and García-Sánchez [22] utilized natural and Na-exchanged bentonite for the removal of Cr(III), Ni(II), Zn(II), Cu(II), and Cd(II) from wastewaters of galvanic industries. Sheta et al. [23] utilized natural zeolite and bentonite for examining the sorption characteristics of zinc and iron ions. Lin and Juang [12] investigated the removal of copper and zinc from aqueous solutions by employing surfactant-modified montmorillonite (with sodium dodecylsulfate) for the sorption process. Dimirkou and Doula [24] studied the removal of Mn(II) and Zn(II) ions from drinking water utilizing natural clinoptilolite and an Fe-over-exchanged clinoptilolite. Malamis et al. [25,26] employed ultrafiltration (UF) membranes and natural minerals for the removal of copper and chromium from industrial wastewater. Many researchers have used sewage sludge as a feedstock for producing sludge-based adsorbents that exhibit high metal cation capacity [27]. Floc-forming microorganisms in activated sludge flocs carry a substantial amount of negatively charged extracellular polymeric substances (EPS) that are confirmed to be capable of adsorbing a variety of metal ions from wastewater, playing an important role in complexing and removing heavy metals from solutions [28,29].

Despite the extensive literature available on zinc removal, no studies have been performed using UF combined with additives of natural origin for zinc removal. UF membranes are employed in membrane bioreactor (MBR) systems for the separation of the treated effluent from sludge, thus delivering an effluent of superior quality [30–32]. The membrane pore size is very small (0.01–0.1 μm) and effectively retains sludge flocs and colloids. Consequently, zinc ions that are attached to sludge flocs are retained by the system and do not contaminate the final effluent. The addition of low-cost natural minerals with high adsorption capacity is expected to increase further the amount of zinc retained.

The aim of this work is to examine the removal of zinc in a combined system employing sludge–minerals–UF membranes. In addition, this work examines membrane fouling of the system, which is considered the main operational drawback of UF membrane technology.

2. Materials and methods

2.1. Experimental system

The experiments were conducted in a 6.7 L cylindrical reactor where the membrane UF module was immersed. The membrane module consisted of hollow fibres made of PVDF, having a nominal pore size of 0.04 μm. Coarse bubble aeration was continuously supplied to the membrane module at a rate of 8 L/min so that membrane fouling was minimal. Fine bubble aeration was continuously supplied to sludge (10 L/min) to maintain the mixture under suspension throughout the filtration experiments. Sludge was obtained from a MBR system treating municipal wastewater. The MBR system operated at steady state conditions and the sludge characteristics are summarized in Table 1. Activated Sludge samples were enriched with Zn(II) so that the final concentration prior to the conduction of the experiments was 320 mg/L. The concentration of 320 mg/L was chosen as it is a reasonable concentration of zinc found in industrial wastewater. The concentration was kept constant for all the experiments in order to be able to investigate the effect of various parameters. Fixed concentrations of bentonite, zeolite or vermiculite were added to sludge and the pH value of the mixture was adjusted to 6.0 using HNO_3; this way chemical precipitation was minimized. Some experiments were conducted at pH 8.0, the aim being to examine zinc removal at conditions similar to the operation of MR. The mixture was placed for 2 h under strong agitation at room temperature using a Heidolh RZR 2041 mechanical stirrer for the ion exchange process to take place. The mixture was then placed into the batch UF reactor and a 60-min filtration experiment was conducted at constant suction pressure of −30 kPa. Permeate was collected and measured to determine the filtered volume. The zinc concentration was measured in samples that were taken at the time intervals of 20, 40 and 60 min. This experiment was repeated using sludge with no mineral addition for comparison purposes. The parameters that were examined during the experimental procedure were: (i) the initial Zn(II) concentration, (ii) the metal–mineral contact time (iii) the pH value, (iv) the type of mineral, (v) the mineral concentration, (vi) the mineral grain size and (vii) the sludge mixed liquor suspended solids (MLSS) concentration (Table 2).

Table 1
Initial sludge characteristics.

Parameter	Mean values	Variations
pH	7.32	6.9–7.8
MLSS (g/L)	5.3	3.7–7.9
MLVSS (g/L)	4.6	3.4–6.7
Colloidal matter COD (mg/L)	25.3	20.8–33.2
NO_3–N (mg/L)	53.6	49–65
NH_4–N (mg/L)	<0.5	–

The impact of the initial Zn(II) concentration on the process was investigated by preparing aqueous solutions with concentrations in the range of 50–450 mg/L and by filtering these solutions through the UF membrane unit. Adsorption kinetic studies were conducted in 500 ml glass flasks on a magnetic stirrer at constant temperature (25 °C), both for aqueous solutions and for sludge enriched with zinc. The experiments were conducted at constant pH 6, with initial zinc concentration of 320 mg/L, mineral dosage of 10 g/L and mineral particle size <0.18 mm. Continuous, strong agitation was provided during the experiments (800 rpm). Samples were taken at different time intervals for a period of 260 min, the suspensions were filtered through 0.45 μm membranes and then analyzed for Zn(II) residual concentrations. The effect of the pH value on Zn(II) removal efficiency was examined by adjusting the pH values of sludge samples and of aqueous solutions in the range of 4.0–9.0. The impact of grain size of vermiculite on the zinc removal efficiency was examined for grain sizes <0.18, 0.18–0.50, 0.50–1.4 and 1.4–2.0 mm.

The pH, MLSS, mixed liquor volatile suspended solids (MLVSS), NO_3–N and NH_4–N in sludge were determined using Standard Methods [33]. The colloidal matter was determined in terms of COD by subtracting the permeate COD from the COD value of the filtrate obtained through membranes with pore size 1.2 μm The zinc concentrations were measured by the Atomic Absorption Spectrometer VARIAN AA24OFS.

SEM and EDX analysis were performed on membrane fibres using the Quanta 200 in order to investigate element depositions at the membrane interior. These membrane fibres had been subjected to extensive filtration with the mixture of sludge enriched with zinc without mineral addition and with the addition of 10 g/L zeolite. The effect of sludge MLSS concentration on Zn(II) removal was examined by allowing sludge to settle for several hours and removing the supernatant. The resulting sludge had high MLSS concentration (11.3 g/L) and was subsequently diluted with wastewater effluent in order to obtain sludge samples having different MLSS concentrations. The sludge samples were enriched with 320 mg/L Zn(II) and then filtered through the UF membranes.