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.

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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,

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	–

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).

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.

Table 2
Parameters investigated for the removal of Zn(II).

Sample	Initial Zn(II) concentration (mg/L)	Mineral employed	Mineral concentration (g/L)	Grain Size (mm)	Sludge MLSS (g/L)	Contact time (min)	pH
Aqueous solution	50, 100, 150,250, 320, 400, 450	None	–	–	–	120	6
Sludge	50, 100, 150, 250, 320, 400 , 450	None Zeolite Bentonite Vermiculite	– 10 10 10	– <0.18	– 4.5	120	6
Aqueous solutions	320	Zeolite Bentonite Vermiculite Zeolite and bentonite Zeolite and vermiculite Bentonite and vermiculite	10 10 10 10 (5 and 5) 10 (5 and 5) 10 (5 and 5)	< 0.18	–	260	6
Sludge	320	Zeolite Bentonite Vermiculite Zeolite and bentonite Zeolite and vermiculite Bentonite and vermiculite	10 10 10 10 (5 and 5) 10 (5 and 5) 10 (5 and 5)	< 0.18	5.3	260	6
Sludge	320	Zeolite, bentonite, vermiculite	5, 7.5, 10, 15	< 0.18	6.2–7.9	120	6
Sludge	320	Zeolite and bentonite Zeolite and vermiculite Vermiculite and bentonite	10 (5 and 5) 10 (5 and 5) 10 (5 and 5)	< 0.18	3.7–5.0	120	6
Sludge	320	Vermiculite	5.0	< 0.18 0.18–0.5 0.5–1.4 1.4–2.0	3.7	120	6
Aqueous solutions	320	None	0	–	–	120	4, 5, 6, 7, 8, 9
Sludge	320	None Zeolite Bentonite Vermiculite	0 10 10 10	– <0.18	– 4.5	120	4, 5, 6, 7, 8, 9
Sludge	320	None Zeolite Bentonite Vermiculite	0 10 10 10	– <0.18	3.8–11.3 4.6–10.9 4.6–10.9 4.6–10.9	120	6

Prior to each filtration experiment the membrane module was chemically cleaned using the solutions NaOCl (1000 mg/L) and citric acid (4000 mg/L).

The level of membrane fouling was assessed by determining the clean membrane permeability k_o as well as the membrane permeability at any given time of the filtration experiment. The clean membrane permeability k_o was determined through filtration with clean water. The membrane permeability k represents the membrane condition at any given time after the initiation of the sludge filtration experiment. To compare the performance of the membrane each time the normalized permeability was calculated (k/k_o) and was corrected at 20 °C.

2.2. Materials

The natural minerals employed were zeolite, bentonite and vermiculite. Natural zeolite (clinoptilolite) and bentonite were supplied by S&B Industrial Minerals S.A., while vermiculite was supplied by Mathios Refractories S.A. The minerals were used in their natural form without any chemical modification. Zeolite and bentonite were supplied in powder form (<0.18 mm), while vermiculite was supplied in a grain size of 2.0–5.0 mm and was accordingly grinded and sieved to the appropriate size. These minerals have high ion-exchange and adsorption capacity. Zeolite consists of aluminum and silicate ions forming well defined channels. In the places where Si^{4+} is replaced by Al^{3+} the result is a net negative charge which is counterbalanced by exchangeable cations of Na^+, K^+ and Ca^{2+} [34]. Bentonite is a type of clay and consists mainly of montmorillonite. Its silicate layers result in a slightly negative charge; the latter is counterbalanced by Na^+, K^+ and Ca^{2+} which are exchangeable with heavy metals [35]. Vermiculite is a type of clay and its negative charge is also produced by the replacement of Si^{4+} by Al^{3+} and is neutralized with several cations. The cation exchange capacity (CEC) of zeolite was 188.40 meq/100 g, of vermiculite 120.65 meq/100 g and of bentonite 100.19 meq/100 g.

3. Results and discussion

This section analyzes the experimental results concerning the removal of zinc ions by the mineral–UF system in sludge and in aqueous solutions as well as the examination of membrane fouling. Activated sludge was employed as adsorbent. The system under examination can be applied in MBR systems treating industrial wastewater having high zinc concentration.

3.1. Zinc removal

Zinc removal was studied under the following conditions: (a) metal–mineral contact time and associated kinetics (b) initial Zn(II) concentration, (c) mineral particle size (d) pH value (e) type and dosage of minerals and (f) sludge MLSS concentration. The experimental results obtained under the various conditions are discussed.

3.1.1. Adsorption kinetics and mechanisms

The aim of this section is to determine the system kinetics and mechanisms both for aqueous solutions and sludge. System kinetics is assessed through the examination of three existing, well-known models: the pseudo-first-order, the pseudo-second-order and the Elovich model. The kinetics of adsorption describes the rate of zinc ions uptake on the minerals under examination. The kinetics of adsorbate uptake is required to select the optimum operating conditions for the batch process. The kinetic parameter, which is helpful for the prediction of adsorption rate, provides important information for designing and modelling the processes. The examination of system mechanisms was performed to determine the
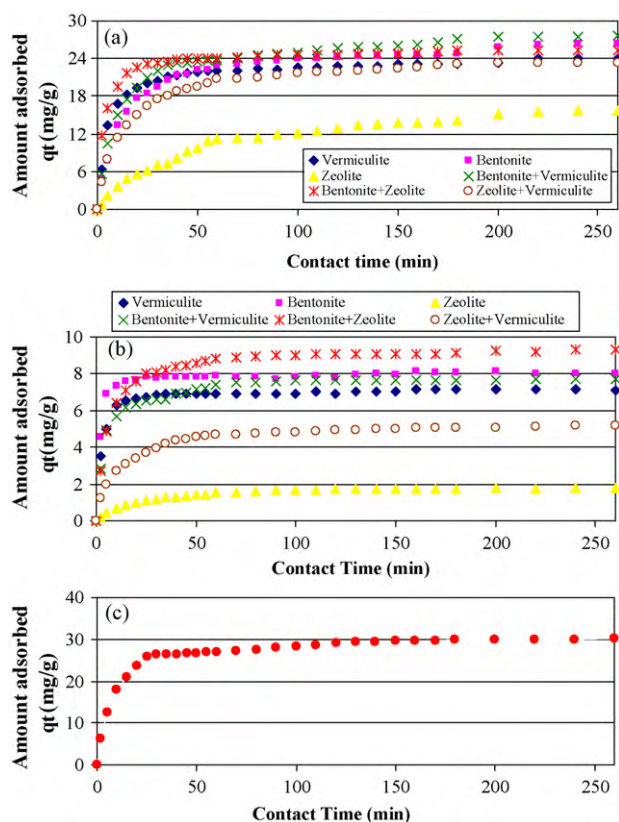

Fig. 1. Effect of contact time on the amount of zinc sorbed onto (a) minerals in aqueous solutions, (b) minerals in sludge and (c) sludge flocs (MLSS = 5.3 g/L) with no mineral addition at pH 6.

rate-controlling step. To accomplish this, the intraparticle diffusion model was compared against the experimental data.

The amount of zinc adsorbed onto minerals or sludge at time t, q_t (mg g^{-1}) was determined:

$$q_t = \frac{(C_0 - C_t)}{m} \tag{1}$$

where C_0 and C_t (mg/L) are the zinc concentrations initially (at time 0 min) and at time t, respectively, m is the amount of adsorbent (g/L). The amount of zinc ions adsorbed onto the minerals as a function of time for a fixed initial zinc concentration of 320 mg/L at pH 6 is given for aqueous solutions and sludge in Fig. 1(a) and (b) respectively. Initially, rapid adsorption of zinc ions onto minerals was observed (t = 10 min), probably due to the larger availability of free sites. This was followed by more gradual adsorption and the attainment of a state of equilibrium. Vermiculite and bentonite and their combinations reached equilibrium relatively quickly (within 60 min), while the adsorption rate of zinc on zeolite was slower reaching equilibrium after approximately 2 h. A contact time of 2 h was sufficient to attain equilibrium in all cases. No significant change in zinc uptake was observed with further increase in contact time. The amount of zinc adsorbed onto the minerals was significantly lower in the mixture of sludge (Fig. 1(b)) than in aqueous solutions (Fig. 1(a)). This is attributed to the increased competition between minerals and sludge flocs to capture the free zinc ions. In Fig. 1(c) the amount of zinc that is biosorbed onto sludge flocs is given as a function of contact time for MLSS = 5.3 g/L. Comparing the amount of zinc biosorbed onto sludge with the amount of zinc adsorbed onto the minerals, it can be seen that the former is higher than the latter for all minerals.

The experimental results were fitted to the pseudo-first-order, the pseudo-second-order and the Elovich equations both for aque-

Table 3a
Kinetic parameters for the adsorption of Zn(II) onto natural minerals.

Type of mineral	Aqueous environment									
	Pseudo-first order			Pseudo-second-order				Elovich		
	R_1^2	k_1 (min^{-1})	q_{1e} (mg g^{-1})	R_2^2	k_2 (g mg^{-1} min^{-1})	q_{2e} (mg g^{-1})	h_0 (mg g^{-1} min^{-1})	R_e^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})
Vermiculite	0.8850	0.0439	10.05	0.9993	0.0069	24.21	4.02	0.8565	78.04	0.351
Bentonite	0.9901	0.0368	15.76	0.9988	0.0031	27.10	2.26	0.9479	10.59	0.233
Zeolite	0.9803	0.0262	13.23	0.9951	0.0012	18.35	0.39	0.9825	18.67	0.250
Bentonite + vermiculite	0.8639	0.0215	16.09	0.999	0.0034	28.41	2.71	0.9384	17.04	0.239
Bentonite + Zeolite	0.8774	0.0237	6.33	0.9999	0.0119	25.58	7.78	0.817	1275.26	0.446
Zeolite + vermiculite	0.9893	0.0367	15.40	0.9997	0.0034	24.45	2.03	0.9642	8.78	0.255

Type of mineral	Sludge environment									
	Pseudo-first order			Pseudo-second-order				Elovich		
	R_1^2	k_1 (min^{-1})	q_{1e} (mg g^{-1})	R_2^2	k_2 (g mg^{-1} min^{-1})	q_{2e} (mg g^{-1})	h_0 (mg g^{-1} min^{-1})	R_e^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})
Vermiculite	0.7764	0.0215	1.03	0.9999	0.0688	7.19	3.55	0.6976	3716.45	1.920
Bentonite	0.5024	0.0111	1.34	0.9997	0.0765	8.10	5.02	0.6146	426278.42	2.316
Zeolite	0.9577	0.0178	1.12	0.9996	0.0312	1.91	0.11	0.9681	0.33	2.846
Bentonite + vermiculite	0.9042	0.0214	1.75	0.9999	0.0300	7.85	1.85	0.881	60.78	1.196
Bentonite + Zeolite	0.8606	0.0152	2.17	0.9999	0.0215	9.44	1.92	0.8593	28.60	0.880
Zeolite + vermiculite	0.9369	0.0166	2.12	0.9998	0.0193	5.34	0.55	0.9446	2.92	1.237

Type of mineral	Intraparticle diffusion											
	Aqueous environment						Sludge environment					
	R_{i1}^2	R_{i2}^2	R_{i3}^2	k_{i1} (mg g^{-1} min$^{-1/2}$)	k_{i2} (mg g^{-1} min$^{-1/2}$)	k_{i3} (mg g^{-1} min$^{-1/2}$)	R_{i1}^2	R_{i1}^2	R_{i1}^2	k_{i1} (mg g^{-1} min$^{-1/2}$)	k_{i2} (mg g^{-1} min$^{-1/2}$)	k_{i3} (mg g^{-1} min$^{-1/2}$)
Vermiculite	0.9797	0.9864	0.9655	5.5074	1.3439	0.2493	0.9945	0.9834	0.7875	2.2749	0.2368	0.0259
Bentonite	0.9872	0.974	0.9456	4.1552	1.6349	0.4095	0.9992	0.9284	0.5811	3.1170	0.2616	0.0275
Zeolite	0.9614	0.9833	0.9774	1.3439	1.9269	0.6155	0.978	0.9831	0.8661	0.2299	0.1509	0.0242
Bentonite + vermiculite	0.9941	0.9932	0.9832	4.6692	2.4675	0.496	0.996	0.9648	0.717	2.1831	0.3299	0.027
Bentonite + Zeolite	0.9891	0.9549	0.9473	7.3234	2.3151	0.1839	0.9924	0.9975	0.816	2.1456	0.936	0.1044
Zeolite + vermiculite	0.9959	0.9748	0.9459	3.5513	1.6396	0.3611	0.9998	0.9987	0.9151	0.8795	0.5334	0.0829

ous solutions and for sludge for all minerals under examination. The Lagergren pseudo-first-order rate expression [36] is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) denote the amount of metal ions adsorbed at equilibrium and at time t respectively and k_1 (min^{-1}) is the rate constant of the first-order adsorption model. The pseudo-second-order kinetic model equation [37,38] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the second-order kinetic model. The pseudo-second-order model is based on the assumption that the rate limiting step is chemical sorption where valence forces are dominant through exchange or sharing of electrons between the sorbent and the sorbate [39]. Valence forces consist of inter-atomic, chemical forces characterized by relatively high bond energies and often require activation energy for bond formation.

In reactions involving chemisorption of adsorbate on a solid surface without desorption of products, adsorption rate decreases with time. One of the most useful models for describing such 'activated' chemisorption is the Elovich equation [40]. The Elovich equation can be written as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \qquad (4)$$

To simplify the Elovich equation, Chien and Clayton [41] assumed $\alpha\beta t \gg 1$ and by applying the boundary condition $q_t = 0$ at $t = 0$ Eq. (4) is linearized [42]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \qquad (5)$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}).

Fig. 2(a)–(c) shows the pseudo-second-order model describing the adsorption of zinc ions onto minerals in aqueous solutions, onto minerals in sludge and onto sludge in the absence of minerals respectively. Tables 3a and 3b summarizes the constants and the coefficients of determination R^2 for the three examined models. It is observed that the experimental data match closely to the pseudo-second-order model. However, further investigation is required to determine the system mechanisms. To examine this, the intraparticle diffusion model was applied.

The mechanism of adsorption between a solid and a liquid consists of three stages, one or any combination of which can be the rate-controlling step [43]:

(a) Boundary layer diffusion, where the solute is transferred from the bulk solution towards the external surface of the adsorbent.
(b) Intraparticle diffusion, where the solute is transferred within the pores of the adsorbent.
(c) Uptake of the solute by the active sites at the exterior of the adsorbent.

To investigate the rate-limiting adsorption step that governs the whole process the intraparticle diffusion model was considered. This model [43–46] is characterized by a lineal relationship among the amount of metal ions adsorbed q_t at a given time t versus the square root of time:

$$q_t = k_i t^{0.5} \qquad (6)$$

where k_i is the rate constant of intraparticle diffusion (mg g^{-1} min$^{-1/2}$).

If q_t versus $t^{0.5}$ plot is linear throughout its entire range and passes through the origin, then the sorption process is found to
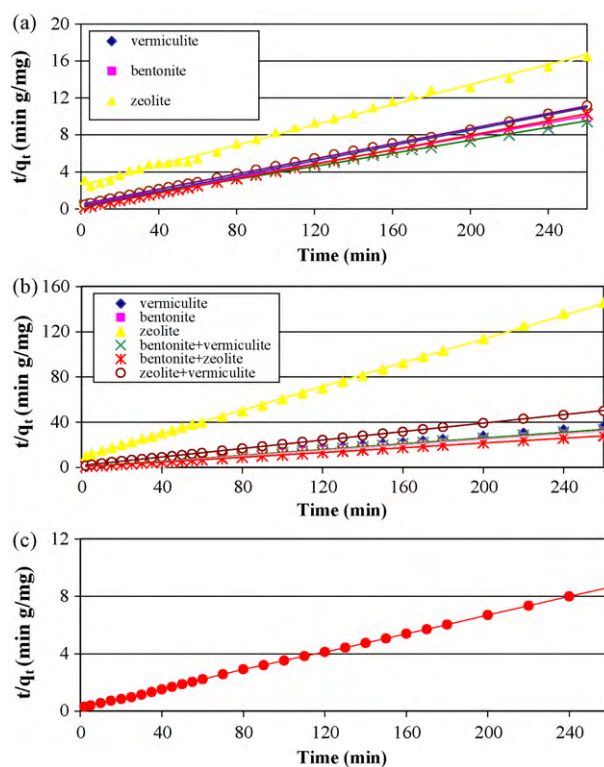

Fig. 2. Pseudo-second-order kinetic plots for the adsorption of Zn(II) ions onto (a) minerals (10 g/L) in aqueous solutions and (b) minerals (10 g/L) in sludge and (c) sludge (MLSS = 5.3 g/L) with no mineral addition at pH 6.

be controlled by intraparticle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. In Fig. 3(a)–(c) q_t is plotted against $t^{0.5}$ for minerals in aqueous solutions, minerals in sludge and for sludge with no minerals respectively. In the plots of q_t versus $t^{0.5}$ multi-linearity was observed in all cases. In particular, a three-stage process was identified. The slope of each linear portion shows the rate of adsorption. During the first stage rapid uptake of metal ions took place onto the external surface of the adsorbent with the diffusion rate being very high. In this stage the boundary layer diffusion was the rate-limiting step. The fast adsorption in this stage may be attributed to the large concentration gradient and availability of surface sites on minerals. The second stage is characterized by gradual adsorption, where intraparticle diffusion was the rate-limiting step. The second step refers to the adsorption of metal ions onto the mineral mesopores. In the third step, a state of equilibrium had been reached for which the intraparticle diffusion started to slow down and the rate of adsorption was extremely low, indicating adsorption onto micropores. The first stage of each plot is attributed to boundary layer diffusion, while the two other stages can be explained by intraparticle diffusion [47]. In the last two stages the adsorption rate reduced possibly due to pore blockage or steric hindrance exerted by the adsorbed zinc ions onto the minerals surface. The values of intraparticle rate parameters are given in Tables 3a and 3b. Comparing the intraparticle diffusion constants obtained for the same mineral and environment (i.e. sludge or aqueous solution) it is observed that the rate parameters decreased in the order k_{i1} (stage 1) > k_{i2} (stage 2) > k_{i3} (stage 3). Over long contact time periods intraparticle diffusion is the most important process.

3.1.2. Initial zinc concentration

Experiments were undertaken to investigate the effect of the initial zinc concentration on the metal removal efficiency both in sludge and aqueous solutions for UF systems (Fig. 4). The initial

Table 3b
Kinetic parameters for the adsorption of Zn(II) onto sludge flocs (MLSS = 5.3 g/L), with no mineral addition.

Pseudo-first order			Pseudo-second-order					Elovich		
R_1^2	k_1 (min^{-1})	q_{1e} (mg g^{-1})	R_2^2	k_2 (g mg^{-1} min^{-1})		q_{2e} (mg g^{-1})	h_0 (mg g^{-1} min^{-1})	R_e^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})
0.9613	0.0232	12.400	0.9998	0.0044		30.96	4.21	0.8822	30.78	0.23

Intraparticle diffusion					
R_{i1}^2	R_{i2}^2	R_{i3}^2	k_{i1} (mg g^{-1} min$^{-1/2}$)	k_{i2} (mg g^{-1} min$^{-1/2}$)	k_{i3} (mg g^{-1} min$^{-1/2}$)
0.9946	0.9722	0.9315	5.4749	0.5153	0.1404

zinc concentration varied between 50 and 450 mg/L. As expected the removal of zinc ions by the UF system in aqueous solutions was negligible (4.0–6.1%), indicating that chemical precipitation was minimal at pH 6. In sludge the results show that the increase in

the initial concentration resulted in a decrease in the zinc removal efficiency; this reduction was not linear and was more pronounced at lower concentrations in the range of 50–250 mg/L. At lower initial zinc concentrations the available metal ions were few and were thus more effectively removed by the given flocs. On the contrary, the biosorption capacity of sludge increased with increasing Zn(II) initial concentration, particularly as the zinc concentration increased from 50 to 250 mg/L. This is reasonable, since at higher initial concentrations more metal ions were available for biosorption onto the given flocs.

The mineral addition (10 g/L zeolite, bentonite or vermiculite) resulted in further removal of zinc ions. However, it was observed that at low initial zinc concentrations (50–100 mg/L) the amount of zinc removed by minerals was low due to increased competition among the minerals and the sludge for the sorption of the few available zinc ions.

3.1.3. Mineral particle size

The effect of mineral (vermiculite) particle size (0.18–2.0 mm) on zinc removal efficiency was examined. The vermiculite particle size was the variable under examination, while all other parameters were kept constant. In particular, the vermiculite dosage was 5 g/L, the initial zinc concentration was 320 mg/L, the contact time was 2 h at strong agitation (800 rpm) and the mixture was kept at room temperature (25 °C) and at pH 6 throughout the experiments. Fig. 5(a) shows the variation of the concentration of zinc removed against mineral particle size. It can be observed that the decrease in vermiculite particle size resulted in an increase in the amount of zinc that was removed. This is related to the mineral's specific surface area. The smallest size vermiculite (<0.18 mm) had the largest specific surface area (= 20.82 m²/g), resulting in more active sites being available for the adsorption process. The largest
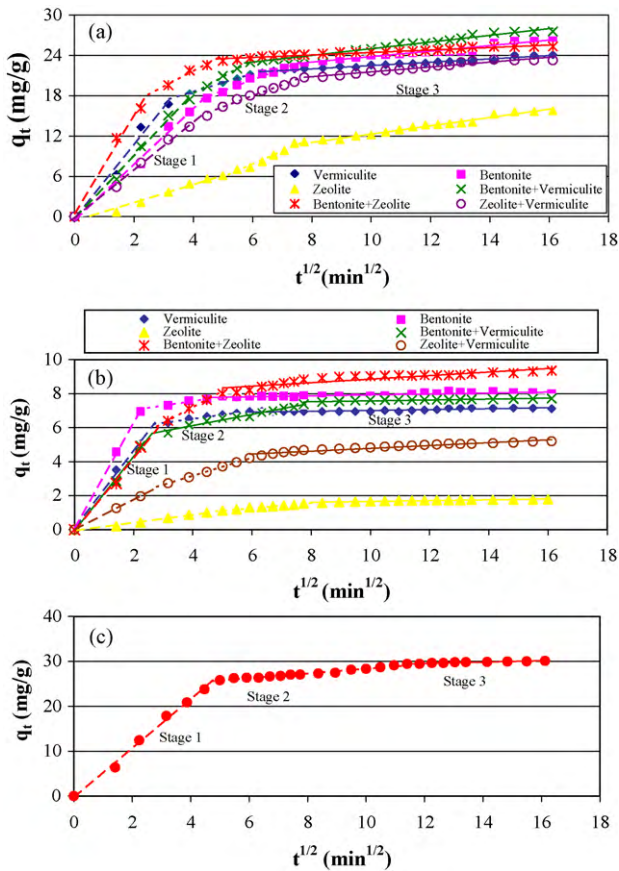

Fig. 3. Intraparticle diffusion plots showing the three adsorption stages for the adsorption of Zn(II) onto (a) minerals in aqueous solutions, (b) minerals in sludge and (c) sludge (MLSS = 5.3 g/L) at pH 6.
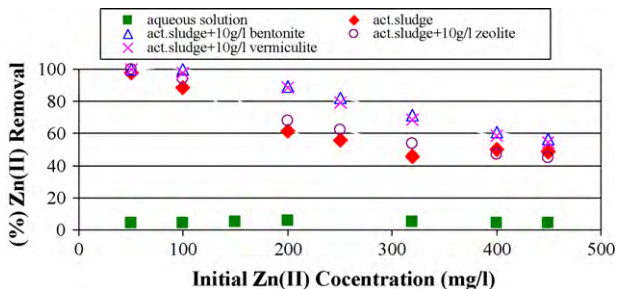

Fig. 4. Variation of zinc removal for different initial metal concentrations in sludge and aqueous solutions at pH 6.
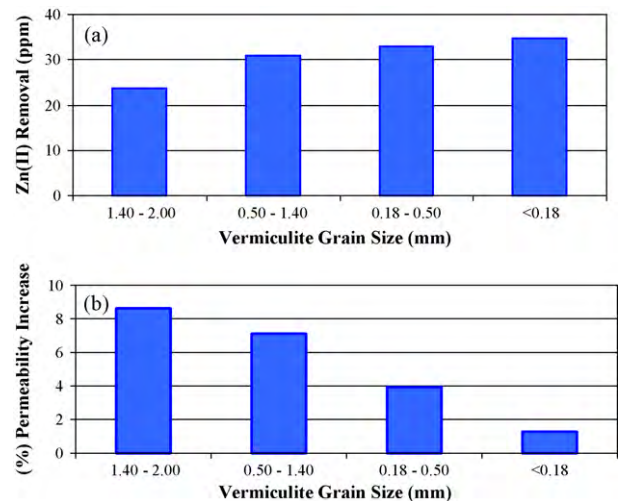

Fig. 5. Effect of vermiculite (5 g/L) particle size (a) on Zn(II) removal and (b) on membrane fouling at pH 6.
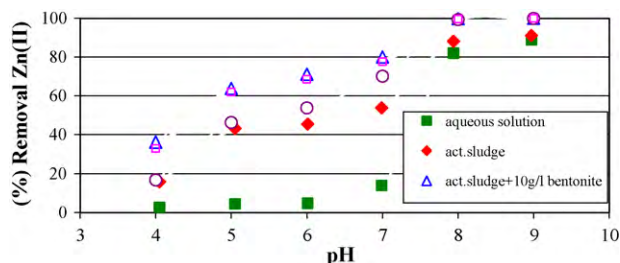
Fig. 6. Variation of zinc removal with pH in aqueous solutions, sludge and sludge with minerals.

size vermiculite (1.40–2.00 mm) had the smallest specific surface area (= 15.21 m^2/g). The results also showed that equilibrium had not been reached for vermiculite with grain size 1.4–2.0 mm for the contact time of 2 h. Longer time was required for the adsorption process to be completed for granular vermiculite due to the smaller surface area compared to powder form vermiculite. It was also observed that the grain size had little influence on the uptake process for grain size smaller than 1.4 mm, since the specific area variation for grain sizes smaller than 1.4 mm was relatively small.

Fig. 5(b) shows that by increasing the particle size of vermiculite, fouling mitigation increased; however, this increase was limited (<8%). Granular vermiculite (size 2.0–1.4 mm) was more effective than powder vermiculite in fouling mitigation, while it was less effective in zinc removal than vermiculite powder. It seems that sludge colloidal matter was more easily attached to granular vermiculite than to powder vermiculite, thus resulting in less membrane fouling.

3.1.4. pH Value

The pH value is an important parameter in biosorption and adsorption processes as it influences the speciation and solubility of the metal ions and the degree of ionization of the sorbate during the process [47]. The Zn(II) removal with the use of UF membranes was examined for the pH values of 4.0–9.0 for aqueous solutions and no mineral addition, for sludge samples with 10 g/L of mineral and in the absence of minerals. The experiments were conducted for initial Zn(II) concentration of 320 mg/L and for MLSS = 4.5 g/L. As it is seen in Fig. 6, the pH value had a significant impact on the zinc removal efficiency of the system. As the pH value increased from 4.0 to 9.0, the amount of zinc removed increased significantly. At low pH values (pH 4.0), Zn(II) removal was very low both for sludge and for aqueous solutions. At such low pH values the biosorption capacity was very low because large quantities of protons competed with metal ions for the available sorption sites. The sludge flocs became positively charged, thus reducing the attraction between the biomass and the zinc ions [48,49]. As the pH value increased to the levels of 5.0–7.0, the Zn(II) removal for sludge and no mineral increased to 43–54% due to enhanced biosorption, while for aqueous solutions it still remained low. As the pH value increased further to the levels of 8.0–9.0 high Zn(II) removal efficiencies were obtained (80–90%) both for sludge and for aqueous solutions due to enhanced chemical precipitation of zinc ions into $Zn(OH)_2$ (Fig. 6). Although the removal of zinc at pH 8.0–9.0 was significant both for sludge and aqueous solutions, the zinc concentration in the final effluent was still high. The use of sludge–UF at pH 9 produced a final effluent with zinc concentration of 28 mg/L. Therefore, minerals must be added to reduce further the lead effluent concentrations to values lower than the reuse limit values. This is clearly seen in Fig. 6 where the addition of 10 g/L mineral at pH 8 resulted in zinc removal efficiencies higher than 99.5% at pH 8 and the zinc effluent concentration satisfied the EPA reuse limit. The effect of minerals on zinc removal is further analyzed in Section 3.1.5.

Table 4
Zinc removal efficiencies for initial Zn(II) concentration of 320 mg/L.

Condition	Zn(II) removal efficiency (%)
Zn(II) + sludge	67.04
Zn(II) + sludge + 5 g/L zeolite	72.92
Zn(II) + sludge + 10 g/L zeolite	76.42
Zn(II) + sludge	65.26
Zn(II) + sludge + 7.5 g/L zeolite	71.72
Zn(II) + sludge + 15 g/L zeolite	78.60
Zn(II) + sludge	74.56
Zn(II) + sludge + 5 g/L bentonite	87.13
Zn(II) + sludge + 10 g/L bentonite	92.20
Zn(II) + sludge	68.50
Zn(II) + sludge + 7.5 g/L bentonite	82.36
Zn(II) + sludge + 15 g/L bentonite	89.70
Zn(II) + sludge	77.55
Zn(II) + sludge + 5 g/L vermiculite	88.38
Zn(II) + sludge + 10 g/L vermiculite	94.49
Zn(II) + sludge	50.65
Zn(II) + sludge + 7.5 g/L vermiculite	62.90
Zn(II) + sludge + 15 g/L vermiculite	71.60
Zn(II) + sludge	48.67
Zn(II) + sludge + 5 g/L zeolite + 5 g/L bentonite	63.09
Zn(II) + sludge + 5 g/L zeolite + 5 g/L vermiculite	62.72
Zn(II) + sludge + 5 g/L bentonite + 5 g/L vermiculite	64.92
Zn(II) + sludge	37.82
Zn(II) + sludge + 5 g/L vermiculite (1.40–2.00 mm)	45.24
Zn(II) + sludge + 5 g/L vermiculite (0.50–1.40 mm)	47.48
Zn(II) + sludge + 5 g/L vermiculite (0.18–0.50 mm)	48.13
Zn(II) + sludge + 5 g/L vermiculite (<0.18 mm)	48.65

At pH 8.0–9.0 the effect of sludge and aqueous solutions in zinc removal was not very different and the question that may arise is why use sludge as a biosorbent. This work investigated the effect of sludge since this system can be applied in MBR for the removal of zinc during biological wastewater treatment. Thus, the investigation of the removal of zinc in the presence of activated sludge is important. Such a system can be employed at pH 8 resulting in an effluent with very low zinc content. However, at highly alkaline environments (pH > 9) biomass activity is problematic and should be avoided.

3.1.5. Mineral type and dosage

The zinc ions removal was determined as a function of mineral type and dosage. Zeolite, bentonite and vermiculite were used, while the mineral dosage was altered, taking the values of 5, 7.5, 10 and 15 g/L. All other parameters remained constant (zinc initial concentration = 320 mg/L, pH 6, mineral particle size < 0.18 mm, strong agitation (800 rpm), contact time = 2 h and temperature = 25 °C). The UF membranes, when employed without any mineral addition for the filtration of sludge, were able to achieve zinc removal efficiencies in the range of 37.8–77.6% due to adsorption of metal ions onto the sludge flocs and their retention by the UF membranes (Table 4). Consequently, some amount of zinc was removed due to biosorption, but this was subject to significant variability. The latter is attributed to variability in the properties of sludge and particularly MLSS fluctuation. The lower range zinc removal efficiencies (38–51%) were obtained when sludge MLSS concentration ranged between 3.7 and 5.0 g/L, while the higher range zinc removal efficiencies (65–78%) were obtained when the sludge MLSS concentration ranged between 6.2 and 7.9 g/L (Table 4). The impact of sludge MLSS concentration on zinc removal is further investigated in Section 3.1.7. Other sludge properties, such as the variation of sludge colloidal matter were investigated, but could not be related to the change in zinc removal.

Table 4 shows the various zinc removal efficiencies for the minerals that were examined (zeolite, bentonite and vermiculite) and their concentrations. The addition of minerals with high ion

exchange and adsorption capacity increased the zinc removal efficiencies of this combined sludge–mineral–UF system. In this system zinc ions were removed through various mechanisms. These include: (a) biosorption of metal ions onto the sludge flocs, (b) ion-exchange and adsorption of metal ions onto minerals and (c) size exclusion of metal ions that were in insoluble form by UF membranes. The combined effect of the aforementioned mechanisms resulted in very high zinc removal efficiencies. In particular, the addition of 5, 7.5, 10 and 15 g/L of bentonite achieved zinc removal efficiencies of 87.1%, 82.4%, 92.2% and 89.7%, respectively. The addition of 5 and 10 g/L of zeolite and vermiculite resulted in Zn(II) removal of 72.9%, 76.4%, 88.4% and 94.5% respectively. It must be mentioned that the amount of zinc that is removed depends not only on the mineral type and concentration, but also on the sludge properties and the membrane condition. For example, the zinc removal efficiencies of the system with the addition of 15 g/L of vermiculite or 15 g/L of bentonite were lower than the respective 10 g/L due to the lower performance of the system in the former case, resulting from the lower MLSS concentration. However, in most cases, an increase was observed in zinc removal with an increase in mineral dosage. This was due to the availability of more ion-exchange and adsorption sites. Bentonite was the most effective mineral in the removal of zinc, followed by vermiculite and then by zeolite. The combined use of 5 g/L of vermiculite and 5 g/L of bentonite performed slightly worse than 10 g/L of bentonite or 10 g/L of vermiculite. The combined use of 5 g/L zeolite with 5 g/L vermiculite performed worse than 10 g/L of vermiculite, but better than 10 g/L of zeolite.

At pH 8.0 and MLSS = 5.0 g/L the addition of 10 g/L bentonite and 10 g/L vermiculite resulted in a final effluent having Zn(II) concentrations of 0.073 mg/L and 0.271 mg/L respectively which are below the US EPA [4] effluent reuse limit of 2 mg/L for irrigation. The results show that the combined use of UF membrane-minerals sludge can result in the production of a final effluent that can meet the US EPA reuse limit of 2 mg/L, therefore lifting the barriers for the potential reuse of industrial wastewater.

3.1.6. MBR application

MBR systems treating municipal wastewater usually operate at higher MLSS concentrations than the MLSS concentration that were examined in this work. High MLSS concentrations are associated with increased solids retention times (SRT) and thus result in the accumulation of heavy metals in the bioreactor. Thus, when treating industrial wastewater the MBR operation at high MLSS results in the accumulation of higher metal concentrations inside the bioreactor which can be detrimental to biomass. The system operation at lower SRT results in less metal accumulation and thus the biomass inhibition is lower. Furthermore, mineral addition inside the bioreactor has the advantage that a significant portion of metal ions are adsorbed onto the mineral; thus, the amount of metal ions that are retained by sludge flocs is lower and the overall biomass inhibition is lower.

Comparing the zinc removal efficiencies between an MBR system having MLSS = 5.3 g/L sludge + 15 g/L bentonite with an MBR system with MLSS = 15.1 g/L at pH 7, in the first system the zinc removal was 93%, while in the second system it was 81%. The COD effluent concentration was 47.4 and 41.8 mg/L, respectively, and the COD removal percentage 87.2% and 89.5%. It is evident that the first system performed better in terms of zinc removal, while the organics removal is similar and satisfactory in both cases.

The impact of zinc on biomass toxicity is well established by other researchers and has also been examined in this work. Lin et al. [50] found that up to 40 mg/L the addition of zinc did not adversely affect biomass activity. Kurmac [51] found that Zn(II) did not affect biomass growth for concentrations up to 128 mg/L. In this work it was found that the concentration of 320 mg/L at pH 8 resulted in
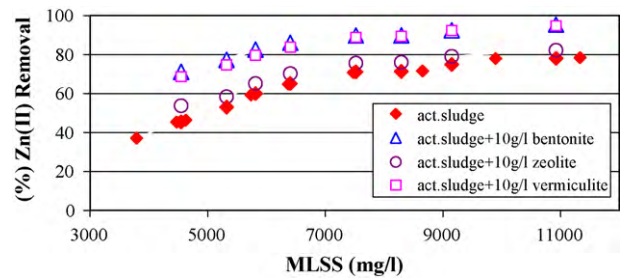

Fig. 7. Effect of sludge MLSS concentration on Zn(II) removal at pH 6.

70–80% inhibition of heterotrophic biomass. However, even with such inhibition the activated sludge could effectively remove zinc ions through biosorption.

3.1.7. Effect of sludge MLSS concentration

The impact of sludge MLSS concentration on zinc removal was investigated under constant sludge pH value (=6) with no mineral addition. MLSS had a profound impact on the zinc that is removed by the system. As it is observed in Fig. 7, high MLSS values favoured zinc removal. The MLSS increase from 3.8 up to 11.3 g/L had a significant impact on zinc removal as it increased from 37% to 78%.
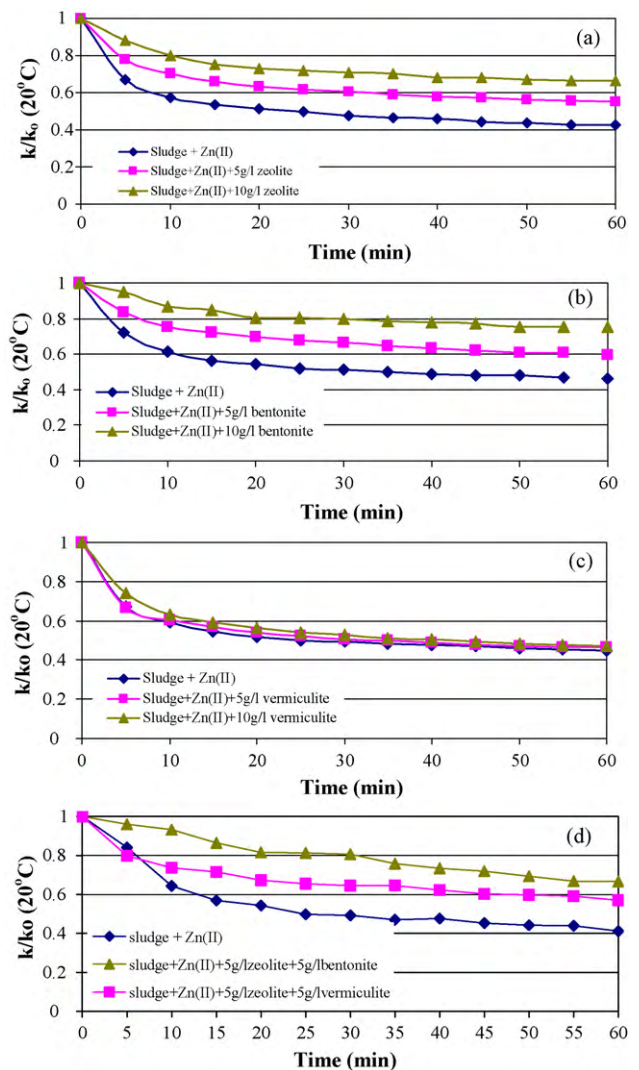

Fig. 8. Normalized permeability reduction due to filtration of sludge with (a) zeolite, (b) bentonite, (c) vermiculite and (d) combined use of minerals at pH 6.

The increase in zinc removal was greater when MLSS concentration increased from 3.8 to 7.5 g/L, compared to the zinc removal increase when MLSS concentration increased from 7.5 to 11.3 g/L. The high MLSS values could effectively remove more zinc ions, since the available biosorption sites increased and thus more metal ions were attached to sludge flocs and were thus retained by the UF membranes. The increase of metal removal due to increased biosorbent solids concentration has also been reported in other studies [26,52].

As it is expected the addition of minerals in sludge resulted in increased removal of zinc for all the examined MLSS range (Fig. 7). The MLSS concentration of Fig. 7 refers to the suspended solids concentration of sludge exclusively and not to the mineral solids concentration. This way it is easier to depict the effect of mineral addition with respect to zinc removal. However, the adsorption capacity of minerals was lower at higher MLSS concentrations. For example at MLSS = 10.92 g/L (+10 g/L bentonite) the adsorption capacity of bentonite was 5.51 mg g^{-1}, while for MLSS = 4.55 g/L (+10 g/L bentonite) it was 8.22 mg g^{-1}. This is reasonable since at higher MLSS concentrations there were more sites available for biosorption, thus creating more competition among the mineral and sludge active sites for the sorption of available metal ions.

The sludge remaining after the treatment process contains higher zinc concentrations than the required limit of 2500–4000 mg Zn(II)/kg of dry weight set by Directive 86/278/EEC for sludge application to land. Thus, the produced sludge is considered hazardous and must be treated prior to its disposal. This can be achieved through acid treatment to redissolve the metals followed by electrodeposition.

3.2. Membrane fouling

The greatest operational problem associated with MBR systems is that of membrane fouling. It is therefore essential to examine the impact of each mineral on fouling. Membrane fouling was assessed through the calculation of the ratio of membrane permeability at a given moment k to the initial clean membrane permeability k_o, corrected at 20 °C. Fig. 8(a)–(e) shows the decrease in membrane permeability due to the 60-min filtration of sludge in which minerals were added. In all cases, it can be observed that sludge with no mineral addition exhibited the worst performance, as it resulted in the highest reduction in permeability. Therefore, the addition of minerals resulted in fouling mitigation. This is explained by the adsorption of colloidal matter onto the mineral surface. The minerals retained a large proportion of colloidal matter that would otherwise foul the membrane. When the mineral concentration was increased fouling was reduced. This is reasonable since the available adsorption sites increased and as a result, more colloidal matter was retained by the mineral. Another plausible explanation for the reduction of membrane fouling in the presence of mineral particles is that the sludge flocs become more porous. Zeolite was the mineral resulting in the greatest fouling mitigation, followed by bentonite. The addition of vermiculite only marginally impacted on membrane fouling.

In order to assess the components that were mainly responsible for fouling, SEM and EDX analysis were performed at the membrane fibre. The results of Fig. 9(a) and (b) showed that some fouling was attributed to zinc itself. However, the elements that contributed mostly to membrane fouling were carbon and oxygen. These ele-
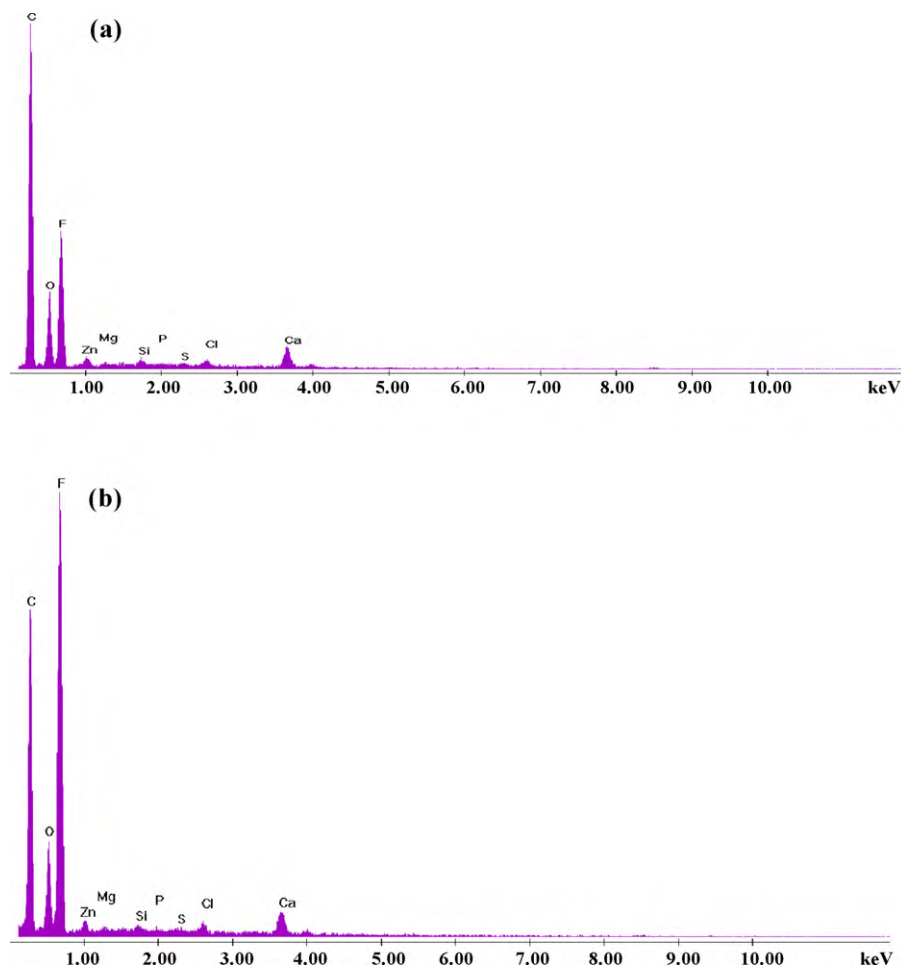

Fig. 9. EDX analysis at the membrane fibre (a) interior and (b) surface.
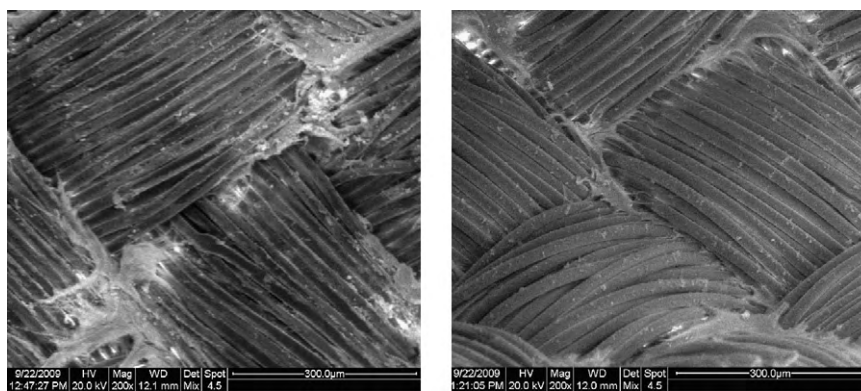
Fig. 10. Membrane fibres interior exposed to filtration with zinc (a) with no mineral addition and (b) with the addition of 10 g/L zeolite.

ments were attributed to the deposition of biomass products on the membrane surface and interior. The fluoride detected was from the membrane material. Fig. 10(a) and (b) shows the interior of two membrane fibres where filtration of (a) sludge with no mineral addition has taken place and (b) sludge with the addition of 10 g/L zeolite has taken place. It is evident that in the case of sludge with no mineral addition fouling was higher.

4. Conclusions

This work has shown that the combined system of sludge–natural minerals–UF membranes is a feasible system for the removal of zinc from industrial wastewater. The results show that the amount of zinc that is removed greatly depends on the sludge MLSS concentration. The examined system could achieve Zn(II) removal efficiencies higher than 90%. Bentonite was found to have the highest zinc uptake followed by vermiculite. Furthermore, high pH (>7) and MLSS (>5.0 g/L) values and increased mineral dosages enhance the zinc removal process. The use of sludge and minerals at an alkaline environment (pH 8) can result in attaining the EPA effluent reuse limit. Increasing initial concentration resulted in a decrease in the zinc removal efficiency. A three-stage adsorption process was identified where the boundary layer diffusion process was followed by a two-stage intraparticle diffusion process. Mineral addition resulted in membrane fouling mitigation with zeolite having the best performance followed by bentonite.

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