Chemical and microstructural analyses for heavy metals removal from water media by ceramic membrane filtration

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ABSTRACT

This study aims to investigate the ability of low cost ceramic membrane filtration in removing three common heavy metals namely; Pb$^{2+}$, Cu$^{2+}$, and Cd$^{2+}$ from water media. The work includes manufacturing ceramic membranes with dimensions of 15 by 15 cm and 2 cm thickness. The membranes were made from low cost materials of local clay mixed with different sawdust percentages of 0.5%, 2.0%, and 5.0%. The used clay was characterized by X-ray diffraction (XRD) and X-ray fluorescence analysis. Aqueous solutions of heavy metals were prepared in the laboratory and filtered through the ceramic membranes. The influence of the main parameters such as pH, initial driving pressure head, and concentration of heavy metals on their removal efficiency by ceramic membranes was investigated. Water samples were collected before and after the filtration process and their heavy metal concentrations were determined by chemical analysis. Moreover, a microstructural analysis using scanning electronic microscope (SEM) was performed on ceramic membranes before and after the filtration process. The chemical analysis results showed high removal efficiency up to 99% for the concerned heavy metals. SEM images approved these results by showing adsorbed metal ions on sides of the internal pores of the ceramic membranes.

Key words | ceramic membranes, filtration, heavy metals removal, microstructural analysis, water media

INTRODUCTION

There are around thirty-five metals posing a threat to human health due to residential and/or occupational exposure, 23 of which are heavy metals (Mosby et al. 1996). Along with the industrial revolution, a great amount of industrial wastes discharging into sewage networks led to increasing heavy metals content in wastewater. Moreover, heavy metals in drinking water form a threat to human health. Populations are exposed to heavy metals through water consumption while some of these metals can bio-accumulate in the human body (Chowdhury et al. 2016). Among the heavy metals, As, Cd, Pb, Cr, Cu, Hg, and Ni are of major concern, mainly due to their presence with relatively high concentrations in drinking water and their effects on human health (ATSDR 2015). To minimize the risks of heavy metals, regulatory agencies have proposed the maximum allowable limits in drinking water (WHO 2011; USEPA 2014). Toxic chemicals such as heavy metals, if not treated properly, cause harmful effects to the organisms and the whole environment (Nziku & Namkinga 2013). Toxicity studies confirmed that they can directly impair the mental and neurological functions, influencing neurotransmitter production and utilization, and altering numerous metabolic body processes (Ogunfowokan et al. 2008). As, Cd, and Pb are the most produced metals from various sources and more problematic metal pollutants, they were extensively studied for public health impacts (Chowdhury et al. 2016).

The treatment of water polluted with heavy metals has become a challenging task for environmental engineers. There are several methods adopted to remove heavy metals from aqueous systems. The most widely used methods for removing heavy metals from wastewater are chemical or electrochemical precipitation, both of which pose a significant problem in terms of disposal of the precipitated wastes (Ozdemir et al. 2005). Ion-exchange...
treatments, as well, do not appear to be applicable due to their high costs (Pehlivian & Altun 2006). In addition, it has been reported that some aquatic plants (Keskinkan et al. 2004) and microorganisms (Tewari et al. 2005) have the capacity to adsorb and accumulate heavy metals, but the use of aquatic plants and microorganisms increases the chemical oxygen demand of wastewater (Argun et al. 2007). Brown algae are among the biosorberts more appointed for industrial applications due to their large uptake capacity (Ahluwalia & Goyal 2011). Dry alginate beads have been found to have a good potential for heavy metal biosorption from a real effluent and the metal ions could be easily desorbed (Silva et al. 2008).

There are some parameters affecting the metals removal such as aqueous solution pH, initial metal concentrations, the overall treatment performance compared to other technologies, and environmental impacts as well as economical parameters such as the capital investment and operational costs. The technical applicability, plant simplicity, and cost effectiveness are the key factors that play a major role in the selection of the suitable method for heavy metals removal. The factors mentioned above should be taken into consideration in selecting the most effective method for the metals removal process (Bobade & Eshtiagi 2015). Using membrane separation techniques in the treatment of contaminated water give high removal efficiency but they require a great membrane area and energy, so it has become an urgent need for developing new membranes based on low cost materials such as clays and apatite. Using such materials in wastewater treatment is an efficient solution, especially when they are burned to form ceramic membranes (Masmoudi et al. 2005; Khemakhem et al. 2007).

Ceramic membranes are categorized as one of the industrial porous materials. According to the International Union of Pure and Applied Chemistry, the porous materials are classified into three grades depending on the diameter of their pores (d). These grades include macro-porous (d > 50 nm), meso-porous (50 nm > d > 2 nm), and micro-porous (d < 2 nm). Moreover, depending on the pore diameter, the filtration process can be classified as: filtration (d > 10 μm), micro-filtration (10 μm > d > 100 nm), ultrafiltration (100 nm > d > 1 nm), nano-filtration (d = 1–2 nm), and reverse osmosis (d < 1 nm). In filtration and micro-filtration, the separation is accomplished mainly by sieving effect where particles whose size is larger than the pore size are trapped. While, in ultra-filtration, nano-filtration, and reverse osmosis where pore size is small, fluid permeability depends on the affinity of solute and solvent with the porous materials as well (Ohji & Fukushima 2012). For structural applications of ceramic materials, pores act as fracture defects that degrade the structural reliability, and therefore, ceramics should be sintered to their full density to attain high mechanical strength. On the other hand, such internal pores give advantages for filtration, absorption, catalysts, structural light weight, and thermal isolator (Messing & Stevenson 2008).

Thermal, chemical, and mechanical properties of ceramic membranes give them more advantages than polymeric ones (Chan & Brownstein 1991). Ceramic filters are in different shapes and sizes, which include disk filters and hollow candles (Mateiletea 2006). The main raw materials used commonly for manufacturing ceramic filters are clay and burnout materials. There is a number of innovative processes for making macro-porous ceramics, namely partial sintering, sacrificial fugitives, replica templates, and direct foaming (Ohji & Fukushima 2012). In partial sintering process, particles of a compacted powder are bonded due to the surface diffusion or evaporation–condensation processes and enhanced by heat treatments to form a homogeneous porous structure. In order to provide the desired pore size, the raw powder size should be geometrically in the range of two to five times larger than that of the coveted pore. In the process of sacrificial fugitives, porous ceramics can be obtained by mixing appropriate amounts of sacrificial fugitives as pore forming agents with the ceramic raw powder and evaporating or burning them out before or during sintering to create pores. Classification of agents forming pores divides into inorganic matters as fly ash (Ding et al. 2007), synthetic organic matters as organic fibers (Colombo & Bernardo 2005), natural organic matters as potato starch (Luyten et al. 2003), and liquid as water (Jia et al. 2007). In replica templates process, macro-porous ceramics having interconnected large pores or channels and open cell walls have been frequently fabricated. The templates need to have adequate flexibility, homogeneous open cell structure, and shape recovery ability. In the direct foaming technique, the ceramic membrane is foamed by incorporating air or gas and dried, and subsequently is sintered to obtain a consolidated structure.

Porous ceramics with high specific surface area are employed for absorptive and catalytic applications, where large area is needed for contacting with reactants. The applications of these porous ceramics have been applied for variety of filtration, adsorptions, and catalysts (Tolba et al. 2015). There are some investigations on combination of processes for the removal of heavy metal ions. Generally, it was found that combination of processes is more effective than
an individual process. For example, the combination of chemical precipitation and ion exchange treatments for the heavy metals removal from polluted solutions was adopted (Papadopoulos et al. 2004). The results showed that the combination of precipitation and ion exchange processes caused a higher nickel removal with an efficiency ranging from 94.2% to 98.3% while using the individual ion exchange treatment led to a lower removal of 74.8% (Feng et al. 2000). Another study relied on a single adsorption process for heavy metals removal by acid activated kaolin and the results revealed moderate removal efficiency (El-Molakap et al. 2013). Ceramic filters are effectively used for eliminating suspensions and Bacillus from wastewater because of their higher flux capability, sharper pore size distribution, better durability, and higher damage tolerance than those of organic hollow fibers (Jedidi et al. 2009).

The development of a high performance ceramic membrane technology has been stimulated by the need for submicron filtration of contaminated fluids in cost sensitive environmental applications. The purpose of this study is to evaluate the performance of ceramic membranes made from local low cost materials of clay and sawdust at three different mixing ratios in removing heavy metal ions from water media by filtration. The influence of pH, initial driving pressure head, and concentration of heavy metals on their removal efficiency by ceramic filters were investigated. Chemical and microstructural analyses on polluted water samples and ceramic membranes were carried out before and after the filtration process.

**MATERIALS AND METHODS**

**Ceramic membranes preparation**

The slip casting method for making porous ceramic membranes was implemented in this work according to the specified procedure in previous studies (Kabagambe 2010; Tolba et al. 2015). Sawdust was used as a pore forming agent based on the sacrificial fugitives process (Ohji & Fukushima 2012). The clay material was collected from an agriculture field near the Nile River in Kom-Ambo area (40 km north of Aswan city, Upper Egypt). A homogeneous clay mass was collected from a depth of 5 m below the ground surface. The clay mass was crushed, dried in an oven at 100°C for 24 h, and ground to a fine powder (particles size >425 μm). For mineralogical characterization, a powdered raw clay sample was scanned in the range 10–80 °2θ on X-ray diffractometer. In addition, the chemical composition of another powdered sample was studied by X-ray fluorescence (XRF) analysis. The sawdust was brought from a local wood workshop, dried in fresh air, and sieved through 425-μm openings sieve. A sensitive balance model ADAM EQUIPMENT ACH-30 was used in the preparation process. Different three mixes of clay and sawdust with sawdust percentages of 0.5%, 2.0%, and 5.0% by weight were prepared.

The dried powders of clay and sawdust were mixed well for 15 min. Then, an appropriate amount of water (20% by weight) was added into the mixture. Thereafter, the wet mixture was folded upon itself repeatedly until a smooth knead was formed. The knead mixture was casted in a 15×15 cm mold, compacted to perform the green body of the ceramic sheet with a thickness of 2 cm, and its upper face was formed to produce an ambient edge with a thickness of 1 cm. The green sheets were dried in fresh air away from direct sunlight for 15 days so that the internal moisture was expelled. The sheets were then sintered at a fixed temperature of 1,000°C for 6 h to produce ceramic membranes. The furnace was allowed to cool slowly through 12 h. The sintering process intensifies the compact and affects the microstructure of the ceramic. The fabricated ceramic membranes were found to have a sintered bonding that ensures a long life span; this bonding will not be separated even under challenging feed water conditions (Matteiletea 2006).

**Filtration experiments**

The prepared ceramic membranes were immersed in distilled water for 24 h before starting the filtration tests. Tests were conducted on ceramic filters with sawdust contents of 0.5%, 2.0%, and 5.0%. Hollow glass prisms with internal cross sectional dimensions of 10×10 cm and 30 cm height were used as upstream feeding containers. The glass prisms were fastened and sealed at the center of the ceramic sheets (15×15 cm) as shown in Figure 1. In this study, the removal of lead (Pb²⁺), copper (Cu²⁺), and cadmium (Cd²⁺) by ceramic filters was investigated. These metals were chosen as they belong to the most problematic metal pollutants (Chowdhury et al. 2016). Nitrate solution stocks of Pb²⁺, Cu²⁺, and Cd²⁺ at concentrations of 1,000 mg/L were used as metal sources. Aqueous solutions of these metals with concentrations of 5, 10, and 15 mg/L were prepared by diluting the stock solutions with distilled water and used as polluted media. The selection of these metal ion concentrations depends on their measured values in wastewater samples collected from the influent of Kima wastewater treatment plant. This plant receives
discharges from domestic communities and Kima chemical industry in Aswan city. All used chemicals were of analytical grade reagent and all experiments were carried out at laboratory ambient temperature of 29 ± 2°C. The metal concentrations were measured by spectrophotometer (Thermo, iCE 3000 SERIES).

Batch filtration experiments were carried out using volumes of 500 and 750 mL from heavy metal solutions to produce initial pressure heads of 5.0 and 7.50 cm, respectively. The solutions were poured into the glass prisms on the top side of the ceramic membranes. The tests were performed under falling head conditions that started at 5.0 or 7.5 cm height over the ceramic filter and decayed to zero at the end of the test. Plastic pots were placed under the ceramic membranes to receive the effluent. The initial flow rate through the ceramic filters was estimated from the volume of the collected filtrate within the first hour of the run. The effect of pH on heavy metals removal by ceramic membrane filtration was conducted by adopting three different values of pH, namely 5, 7, and 9. The desired pH was adjusted by the addition of 0.1 N nitric acid (HNO₃) or 0.1 N sodium hydroxide (NaOH). The effect of pH and heavy metals concentration on their removal by ceramic filters were studied under an initial driving head of 5.0 cm. On the other hand, the influence of the initial pressure head on both heavy metals removal and filtration rate through the ceramic filters was investigated at initial heads of 5.0 and 7.50 cm with heavy metals concentration of 5 mg/L. At the end of each run, the ceramic filter was subjected to a backwashing process with distilled water to remove the deposited ions. Accordingly, the same ceramic filter could be reused several times.

**Microstructural analysis**

Surface morphology of the ceramic membranes was investigated by scanning electronic microscope (SEM) images (JEOL JSM-5400 LV) before and after the filtration tests. To comply with the constraints imposed on the specimen size for SEM analysis, a small sample was cut from the membrane center and coated with gold under a vacuum pressure. The gold coating increases the conductivity of the materials. In the SEM chamber, each specimen was allocated in an electron beam to take its image at the desired magnification scale.

**RESULTS AND DISCUSSION**

**pH effect on heavy metals removal by ceramic membrane filtration**

pH of the water media has a considerable effect on heavy metals solubility. Therefore, heavy metals treatment by
Hydroxide precipitation is controlled by adjusting pH of the solution so that the metals will form insoluble precipitates. The effect of pH on heavy metals removal by ceramic membrane filtration was investigated by adopting three different values of pH, namely 5 (acidic), 7 (neutral), and 9 (alkaline), which were adjusted by HNO₃ or NaOH solutions. Tests were performed on ceramic filters with sawdust contents of 0.5%, 2.0%, and 5.0%. For comparison, the experiments were carried out in a constant temperature room at 29 ± 2°C, a constant heavy metals concentration of 5.0 mg/L, and an initial driving pressure head of 5.0 cm. The filtration run was terminated when a volume of 500 mL had passed through the ceramic filter, i.e. the driving pressure head became zero. The filtration tests lasted 24.2, 22.0, and 18.1 h for ceramic filters with 0.5%, 2.0%, and 5.0% sawdust contents, respectively. The metal ions removal efficiency was calculated according to the following common equation:

\[
\text{Removal efficiency (\%) } = \frac{C_i - C_e}{C_i} \times 100
\]  

where \( C_i \) and \( C_e \) are the metal ion concentrations in the influent and effluent aqueous solutions, respectively. The results of the effect of pH on the removal efficiency of \( \text{Pb}^{2+}, \text{Cu}^{2+}, \) and \( \text{Cd}^{2+} \) from aqueous solutions by ceramic filters with sawdust percentages of 0.5%, 2%, and 5% are presented in Figure 2(a)–2(c).

Figure 2(a)–2(c) illustrate that \( \text{Pb}^{2+}, \text{Cu}^{2+}, \) and \( \text{Cd}^{2+} \) ions were effectively removed by ceramic filters with different sawdust ratios, especially at the higher values of pH (7 and 9). In general, the removal efficiency of these metals was more than 97% and the best efficiency with the different sawdust ratios occurred at pH 9. A similar study on the removal of heavy metals from aqueous medium using vermiculites achieved around 100% metals removal in alkaline conditions (Sis & Uysal 2014). The reason was partly attributed to the metal hydroxide formation and, consequently, the surface precipitation under alkaline conditions (Katsou et al. 2010). In addition, the affinity between the positive heavy metal ions and negative surface charges resulted from alkaline conditions greatly enhances the removal.
efficiency (Abdus-Salam & Adekola 2003). For ceramic membrane filtration, the observed high metals removal at pH 9 came from the double effect of two treatment mechanisms as the precipitation of insoluble metal hydroxides along with the membrane filtration. The results proved that the equilibrium capacity of the metals removal increased significantly as the pH of the solution increased. It is concomitant with a previous study on the removal of heavy metal ions from wastewater, which reported that the equilibrium capacity of copper and zinc removal by different adsorbents increased significantly, as the pH of the solution increased (Salam et al. 2011). Previous studies showed a formation of Pb(OH)\(^{-}\) occurs between pH 6 and 10 (Bradl 2004), precipitation of Cu(OH)\(_2\) starts at pH 6.3 (Pare et al. 2012), and formation of Cd(OH)\(^{-}\) happens between pH 8 and 12 (Ayres et al. 1994). Accordingly, to exclude the interference between surface ions precipitation and purifying mechanisms provided by ceramic filters, tests of heavy metals in the next parts were performed at pH 5 for Pb\(^{2+}\) and Cu\(^{2+}\) and at pH 7 for Cd\(^{2+}\).

Removal of heavy metals at different concentrations by ceramic membrane filtration

The influence of the concentrations of Pb\(^{2+}\), Cu\(^{2+}\), and Cd\(^{2+}\) on their removal efficiency by ceramic membrane filtration was studied. Tests were conducted at different metal ions concentration of 5, 10, and 15 mg/L and at pH 5 for Cu\(^{2+}\) and Pb\(^{2+}\) and pH 7 for Cd\(^{2+}\). For comparison, they were carried out in a constant temperature room (29 ± 2 °C) with an initial driving pressure head of 5.0 cm. Falling pressure head filtration tests were performed and the test was ended when the driving pressure head reached to zero, i.e. a volume of 500 mL of solution filtered through the ceramic membrane. As in the study of the effect of pH, these filtration essays lasted approximately 18–24 h for ceramic filters with different sawdust contents. Figure 3(a) presents Pb\(^{2+}\) removal efficiency by ceramic filters at three different sawdust percentages of 0.5%, 2.0%, and 5.0%. This figure reveals that there is no clear trend for the removal efficiency to be related with the ion concentrations of the aqueous solution in spite of the removal efficiency was constant and close to

Figure 3 | The removal efficiency of heavy metals from 500 mL aqueous solutions by ceramic membrane filtration at different metal concentrations and sawdust percentages; (a) lead, (b) copper, and (c) cadmium.
100%, in case of 2.0% sawdust. In Figure 3(b), Cu$^{2+}$ removal efficiency decreases as the initial concentration becomes higher for membranes with 5.0% sawdust and vice versa for the other membranes. Figure 3(c) states that the removal of Cd$^{2+}$ has a slight difference with its concentration for the three membranes. Mostly, the results indicate that the removal efficiency declines as the initial metal ion concentration goes up. This deficiency in the removal efficiency at the higher concentrations can be relayed to the capacity of the membrane pores that become relatively saturated with the adsorbed ions, therefore, the available adsorption sites are reduced. The same results were reported on the removal of heavy metals using low cost adsorbents (Salam et al. 2011).

**Effect of the pressure head on heavy metals removal and filtration rate by ceramic membranes**

The water pressure head acting on the surface of the ceramic membrane directly affects the filtration rate. The solution flow rate presents an important performance parameter for ceramic filters because their applicability is greatly relying on it. To check the influence of the driving pressure head on the filtration rate and removal of heavy metals by ceramic filters, two experiments were carried out with different initial pressure heads of 5.0 and 7.5 cm. The volumes of the aqueous solutions to be filtered in the experiments were 500 and 750 mL. The tests were carried out under falling pressure head conditions, starting at the initial head and terminating at zero head. To exclude the effect of the surface precipitation, values of pH were adjusted to 5 for the surface precipitation, values of pH were adjusted to 5 for both Pb$^{2+}$ and Cu$^{2+}$ and 7 for Cd$^{2+}$. The experiments were conducted in a constant temperature room (29 ± 2°C) and with influent metal concentration of 5 ppm. Tests were carried out on ceramic filters with sawdust contents of 0.5%, 2.0%, and 5.0%.

The initial flux through the ceramic membranes was estimated from the filtrate volume within the first hour of the filtration test. Under initial gravitational pressure head of 5.0 cm, membranes with 0.5%, 2.0%, and 5.0% contents of sawdust showed initial filtration rates of 41.36, 45.28, and 55.27 mL/h, respectively. At this initial head, the ceramic filters produced 500 mL of filtrate through 24.2, 22.0, and 18.1 h for 0.5%, 2.0%, and 5.0% sawdust contents, respectively. In case of 7.50 cm initial head acting on filters that have 0.5%, 2.0%, and 5.0% sawdust contents, the initial water fluxes were found to be 50.66, 55.46, and 67.69 mL/h, respectively and the runs continued for 29.6, 27.0, and 22.2 h to produce 750 mL of filtrate. In a previous study, gravitational ceramic filters that had cylindrical shapes were used to treat grey water and showed filtration runs with lengths varied from 0.74 to 2.0 days. The filters were backwashed and used several times for a period more than six months (Hasan et al. 2015).

Chemical analysis results illustrated an enhancement in the removal of Pb$^{2+}$ and Cu$^{2+}$, with increasing the driving pressure head acting on ceramic membranes with the three sawdust ratios as presented in Figure 4(a) and 4(b). Moreover, the filters produced high removal efficiencies close to 100% for Cd$^{2+}$ with the two tried pressure heads as shown in Figure 4(c).

**Surface morphological structure of the manufactured ceramic membranes**

The surface morphology of locally manufactured ceramic membranes was examined by SEM. Figure 5(a)–5(f) illustrate SEM images from the surface of sintered ceramic membranes at magnification scales of 200× and 500× before the filtration process. The images show that there is a rough surface structure as the pores are irregular in their sizes, shapes, and distribution. It was reported that an agent must be mixed homogeneously with the ceramic raw powder to have regular and uniform distribution of pores (Ohji & Fukushima 2012). In addition, it can be observed that depressions covered most of the membrane surface and micro cracks began to appear. These depressions might be produced from the manual compaction while the micro cracks were likely to have been deformed during the firing process and/or induced from the preparation chopping for SEM specimens.

Figure 5(a) shows the surface structure of a membrane with 0.5% sawdust at magnification of 200× with the biggest number of pores on the surface. The size of the pores was relatively small with diameters less than 8.5 μm. Figure 5(c) illustrates the surface morphology of another membrane with 2.0% sawdust at magnification scale of 200×. The number of pores diminishes, whereas their size seems to be bigger with an average diameter of 15 μm. The morphology of 5.0% sawdust ceramic membrane at magnification of 200× has a different shape with the minimum number of pores and the largest size with diameters up to 50 μm as depicted in Figure 5(e). By increasing the magnification scale to 500×, a small and narrow micro crack can be observed in Figure 5(d) on the surface of the membrane with 2.0% sawdust. For the membrane with 5.0% sawdust, a long micro crack line with a bigger width can be seen in Figure 5(f). Practically, it was observed that...
Figure 4 | Influence of the initial pressure head on the removal efficiency of heavy metals with concentration of 5 mg/L by ceramic membrane filtration at different sawdust ratios; (a) lead, (b) copper, and (c) cadmium.

Figure 5 | SEM images from the surface of ceramic membranes before filtration; (a) and (b) with 0.5% sawdust, (c) and (d) with 2.0% sawdust, and (e) and (f) with 5.0% sawdust. The upper and lower images were magnified to 200× and 500×, respectively.
the prevalence of wide cracks through membranes with 5% sawdust led to a fabricated fragile membrane with less life-span and more possibility of damage. In contrast, micro cracks disappear from the image of the membrane with 0.5% sawdust as in Figure 5(b). In addition, images with the magnification scale of 500× show an agglomeration of the membrane fabricating materials due to the manual compaction. These observations are assured by the reported data about depressions and micro cracks that were found on most of the surface of ceramic filters manufactured from Seeta and Ntaawo clay (Kabagambe 2010).

**Microstructural analysis of membrane pores after filtration**

As the magnification scale of images maximizes, the interior pore spaces become clearer. Figure 6 presents images from pores of ceramic membranes with different sawdust ratios after filtration at magnification scale of 1,500×. The figure illustrates that through the filtration process, the positive ions of heavy metals were adsorbed on the sides of the membrane pores. Such membranes usually contain active OH− functional groups on the surface of their pores that bind the heavy metal ions. Even if the metal ions are much smaller than the membrane pores, metals can be removed by the adsorptive active sites. Adsorption of metals in pores varied according to the pore shape and size as it can be depicted from Figure 6(a)–6(c) for membranes with 0.5%, 2.0%, and 5.0% sawdust, respectively. Morphology differences can be observed among membranes with the three-mentioned ratios of sawdust.

**The membrane microstructure before and after filtration tests**

SEM images of the ceramic membranes may indicate some differences between before and after the filtration experiments. Figure 7(a) and 7(b) illustrate comparable SEM images of ceramic membrane with 2.0% sawdust magnified at 2,000× before and after the filtration process. Before the
filtration test, the membrane surface contained clay crystals only as shown in Figure 7(a). After filtration, delighted adsorbed metal ions on the sides of the pores can be clearly seen in Figure 7(b) along with the surface wetness. The negative charges on the surface of ceramic pores attracted the metal ions that carry positive charges resulted in surface adsorption. From Figure 7, it is clear that the interior pores surface after the filtration test became darker than before it. Although the long time between the filtration test and taking SEM images, the interior pores’ surface remained

Figure 8 | XRD pattern of the raw clay powder.

Figure 9 | XRF pattern of the raw clay powder.
wet and proved that the membrane retains water from the filtration process.

X-ray diffraction and fluorescence studies

The mineralogy of the supported metal oxide of the raw clay powder that has been used for making the ceramic membranes was characterized by X-ray diffraction (XRD) pattern-ray. The results are presented by the diffractogram shown in Figure 8, which has diffraction peaks attributed to quartz (SiO₂). In addition, the results of XRF analysis on the clay powder are illustrated in Figure 9 that confirms the presence of quartz (SiO₂) as the major component. The chemical composition of the natural clay powder is given in Table 1, which demonstrates that the majority of the used clay (86.64%) consists of quartz (SiO₂), hematite (Fe₂O₃), and calcium oxide (CaO).

<table>
<thead>
<tr>
<th>Element</th>
<th>Proportion (wt. %)</th>
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<tr>
<td>SiO₂</td>
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</tr>
<tr>
<td>F₂O₃</td>
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<tr>
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<tr>
<td>MnO</td>
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</table>

Table 1 | Chemical composition of the raw clay powder from XRF analysis

(4) SEM images indicated that the morphology and both size and shape of internal pores of ceramic membranes could be controlled by changing the ratio of the burn out materials in the mixture.

(5) Increasing the sawdust contribution in ceramic membranes substrates produces fragile ceramics with significant interior cracks, while not frequently affect the metals removal efficiency.

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