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Full Length Article

Application of Sayong Ball Clay Membrane Filtration for Ni (II) Removal from Industrial Wastewater

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Abstract

Wastewater containing heavy metals, such as nickel ions (Ni^{2+}), discharged from industry to water streams poses a serious threat because even at low concentrations, it does not naturally degrade and is toxic to human and aquatic life. This article reviews a novel technique for wastewater treatment using a Sayong ball clay (SBC) membrane to remove nickel from industrial wastewater. SBC powder was achieved through milling using a planetary ball mill (milling time; 10, 20 and 30 h), further labelled as SBC 10, SBC 20 and SBC 30, with a ball-to-powder of ratio 7:1 and rotation speed of 300 rpm. The physical characteristics of the apparent porosities, bulk density and shrinkage were investigated. XRD was used to study the phase, while FESEM was used to analyse the microstructure of the fired membrane. The FESEM microstructure indicates a decreased particle size (SB30). Filtration was conducted using a dead-end filtration system. The fabricated SBC 10, 20 and 30 membranes showed significant removal of nickel from industrial wastewater—88.87%, 82.96% and 85.13%, respectively. This study revealed that the SBC membrane is a promising membrane to remove nickel from industrial wastewater. The results also indicate the possibility of highlighting the introduced technique as a new technique for the treatment of industrial wastewater. As a new trend for waste management, pollution prevention could be applied in Malaysia as one of the advanced biotechnologies to solve various environmental problems.

Keywords: environmental management; wastewater treatment; waste processing; heavy metals

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1. Introduction

In this current era, environmental management; waste recycling, treatment, and disposal; pollution control and wastewater have become the most important issues atop the global agenda [1,2]. Countries that have experienced water pollution caused by toxic metallic, organic and metal–organic compounds have seen many catastrophic disasters, at both economic and environmental levels [3]. Heavy metal contamination in sewerage or water stream

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Table 1
Acute and chronic effect of heavy metals to human [6–13].

Metal	Acute	Chronic
Copper	Blue vomitus, GI irritation/haemorrhage, haemolysis, metal fume fever (MFF) (inhaled)	vineyard sprayer's lung (inhaled); Wilson disease (hepatic and basal ganglia degeneration)
Iron	Vomiting, GI haemorrhage, cardiac depression, metabolic acidosis	Hepatic cirrhosis
Lead	nausea, vomiting, encephalopathy (headache, seizures, ataxia, obtundation)	encephalopathy, anaemia, abdominal pain, nephropathy, foot-drop/wrist-drop
Manganese	Metal fume fever (MFF) (inhaled)	Parkinson-like syndrome, respiratory, neuropsychiatric
Nickel	Skin problem or rashes; nickel carbonyl: myocarditis, acute lung injury (ALI), encephalopathy	Occupational (inhaled): pulmonary fibrosis, reduced sperm count, nasopharyngeal tumours

is mostly caused by industrialization. One of the most common industrial activities contributing to this water pollution issue is the electro-less plating industry. In 1946, Brenner and Riddell described the term electro-less plating as a way of plating metallic substrates with nickel or cobalt alloys without the electric current external source benefit. In this process, heavy metals are used to obtain the best finishing of a product.

However, these processes produce industrial wastewaters that contain various toxic substances such as cyanides, alkaline cleaning agents, degreasing solvents, oils, fats and metals. Most of the metals including copper, nickel, chromium, silver and zinc are proved harmful when they are discharged without treatment [4]. During the final stage of the electro-less plating process, heavy metal effluent is produced. These heavy metal effluents are very hazardous to humans and the environment if not treated properly. Table 1 lists a few problems that are caused by polluted water containing these metals. Researchers have revealed that heavy metals have high solubility in aquatic environments and thus can be absorbed by living organisms [5]. A direct release of heavy metal effluent to sewerage or a river will pollute the neutral water flow and aquatic life. It can also cause acute and chronic toxicity to human physiology.

According to researchers, few technologies are used to remove suspended matter or metal from polluted water to produce potable water and prevent their release into the environment [14]. There are several techniques to treat heavy metal effluent such as chemical precipitation, coagulation–flocculation, floatation, ion exchange and membrane filtration. Precipitation is the most applicable among these techniques and is considered to be the most economical [15]. It is based on chemical coagulation by adding lime to raise the pH and aluminium or iron salt to remove colloidal matter as hydroxides. Although it is shown to be quite effective in treating industrial effluents, the added chemicals may induce secondary pollution effects.

These drawbacks together with the need for a low-cost treatment of wastewaters has encouraged many researchers to use other effective methods without chemical processing for the treatment of several industrial effluents [16]. Due to the limitation of the ion exchange process such as high cost of chemical resin, ceramic membrane is a potential method to filter wastewater containing heavy metal from electro-less nickel plating industries. Membrane technology has become a popular separation technology over recent years in many countries, plus membrane works without the addition of chemicals, using low energy and well-arranged process conductions [17].

Effluents from industry containing heavy metal such as nickel that exceed the permissible limit of the standard stated in Malaysia's EQA 1974 is the main subject in this research. The ion exchange technique is a popular method used in the industry, but it involves chemical resin and is very expensive. In one of the recent technologies, oxidized Multi-wall Carbon Nano Tubes (MWCNT's) were used as adsorbent for removal of Ni (II) from aqueous solutions, and this research resulted in enormous growth of research work considering the application of MWCNTs in the removal of heavy metal ions from industrial wastewater [18,19]. The results in this study proved that the adsorption mechanism is strongly dependent on the pH level and concentration of oxidized MWCNTs but less dependent on ionic strength. The same concept has been examined and validated by other researchers recently while focusing on ionic strength dependency for adsorption of Ni(II) on graphene oxides [20]. The results showed a strong dependency on pH and ionic strength for $\mathrm{pH} < 8$ and is independent for $\mathrm{pH} > 8$ value.

Green technology and promising techniques are important to filter the effluent before it can be discharged to the water stream and then processed at a Wastewater Treatment Plant (WTP) for human use and consumption. Clay-based membrane was studied to filter effluent containing nickel taken from a real industrial setting. This research analysed the potential of Sayong Ball Clay (SBC) membranes in wastewater treatment aimed for heavy metal removal considering Ni[II] as an example.

2. Materials & Methods

All chemicals and reagents used were of analytical grade. Three wastewater samples were collected between March and December. The duration was aimed to maintain the consistency of nickel content in spent final rinse water bath from the electro-less plating process in the industry.

X-ray diffraction was employed to the study mineralogical category of the SBC milled at different milling durations (10, 20 and 30 h) using a Bruker D8 Advance X-ray Diffraction (XRD) machine. The phase identification analysis was performed in the range from 10° to 50° of 2θ at a wavelength of 1.5406 Å with operating voltage of 15 kV and CuKα1 anticathode filter. The surface area of the absorbent was measured by a surface area and pore analyser machine by Thermo Scientific. A fabricated image of SBC membrane was evaluated using the Brunauer–Emmett–Teller (BET) method.

2.1. Preparation of samples

Three (3) wastewater samples were collected between March and December (labelled as wastewater 1, 2 and 3, respectively). The duration was aimed to maintain the consistency of nickel content in spent final rinse water bath from the electro-less plating process in the industry. The nickel (mg/l) from industrial influent and effluent was taken and compared using fabricated SBC membranes.

2.2. Saying ball clay (SBC)

SBC is a type of clay that can be found at Sayong District in Perak State, Malaysia. Ball clay is a kaolinitic sedimentary clay that commonly consists of 20–80% kaolinite, 10–25% mica and 6–65% quartz. Ball clay is also referred as a secondary clay; it has been transported away by natural watercourses from the area or geology in which it was generated.

2.3. Preparation SBC Membrane

Ball milling is an important step to obtain fine SBC powders ranging from 100 to 2500 nm or 0.1 to 2.5 μm. A model Retsch PM100 planetary ball mill machine was used for this purpose. During the early stage, the raw SBC was sieved to obtain 50 μm powder. Furthermore, the powder was milled for 10, 20 and 30 h and labelled as SBC 10, SBC 20 and SBC 30, respectively. The ball mill offers a very attractive advantage of avoiding the loss of volatile elements in the procedure of synthesis of powders with their uniform composition [20]. The advantage of ball milling compared to inert gas condensation is that the average grain size can be controlled easily by varying the milling time [21].

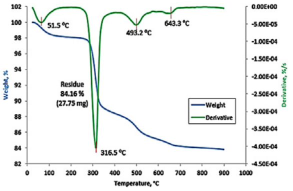

Fig. 1. Thermo-gravimetric analysis of SBC and starch mixture.

The particle size distribution and its concentration were determined by using dynamic light scattering (DLC) with a Zetasizer Nano, Melvern Instruments. The SBC 10, SBC 20 and SBC 30 powders were then mixed with 25 wt% cassava starch for 3 h by using a roller mixer model LRM-30. Cassava starch acted as a pore former for the membrane. Mixed powder of SBC and cassava starch was compacted by using the uniaxial pressing technique. Three types of SBC membranes were pressed with pressure of 50 MPa and holding time of 10 min. The pressing technique was performed by using the uniaxial cold compaction method (Instron machine model 600DX). Firing is a consolidation process of material by heat without melting it to the point of liquefaction. The SBC membrane was fired by using a high-temperature muffle furnace (model KSL-1800X).

Fig. 1 shows the Thermo-gravimetric analysis (TGA) of SBC and starch mixture. TGA and DTA were carried out to analyse the effective firing temperature, produce a stable fired SBC membrane and generate a firing profile. Weight reduction was performed in two stages. The first weight reduction of the sample was performed when the temperature increased to 500 °C with 15.48% at 4.2946 mg. Reduction occurs due to burning process of starch and water elimination from the sample. The dehydroxylation process of clay minerals was performed at 643.3 °C. Insignificant weight loss was observed at 800 °C. From the result, the minimum firing temperature for SBC is 900 °C.

2.4. Sayong Ball Clay Filtration Performance

The effectiveness of fired-clay-based membrane can be measured by testing it using a filtration system. The

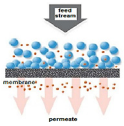

Fig. 2. Dead-end filtration.

filtration testing module used in this study was the most basic one, which is the dead-end filtration module. Fig. 2 shows the dead-end filtration process, which illustrates the liquid or gaseous particle flow through the membrane.

This process usually requires pressure from the feed stream. Only selective particle sizes can pass through the membrane pores to produce permeate and the filtered residue is accumulated on the surface of the membrane. The dead-end filtration is a batch process in which the residue on the filter reduces the filtration capacity through clogging. Next, remove the residue on the membrane surface using a flush back system.

2.5. Nickel ion analysis

The concentration of metal ions was determined by a Spectrophotometer Instrument (model HACH DR1900). The metal standards were checked with standard reference material obtained from the Malaysian Standard, EQA 1974. The ASTM standard used was Nickel—Standard ASTM D1886-14 and Copper.

Atomic Absorption Spectroscopy (AAS) was used to measure the nickel content. Atomic absorption methods determine the energy amount in light photon form, thus causing a change in the wavelength absorbed by the sample. The “after” wavelength is the wavelength of light transmitted by the sample and is measured by a detector and later compared with the “before” wavelengths, which originally passed through the sample. The changes were absorbed by a signal processor energy absorption peak of distinct wavelengths. The acceptable limits of Ni content as set by Malaysia Environmental Quality (Industrial Effluent) for wastewater discharge upstream and downstream of water supply sources are 0.20 mg/l and 1.0 mg/l, respectively.

3. Results

The characterization of filter media showed that the micrograph for SBC 10 shows uniform pore distribution and no identified agglomeration. The microstructure of SBC 20 and SBC 30 shows the agglomeration. Fig. 3 shows the microstructure of SBC 10, SBC 20 and SBC 30 before filtration.

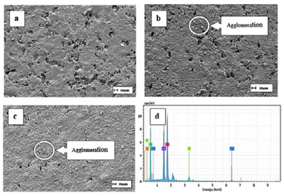

Fig. 3. Microstructure of (a) SBC 10, (b) SBC 20, (c) SBC 30 and (d) EDX of SBC before filtration.

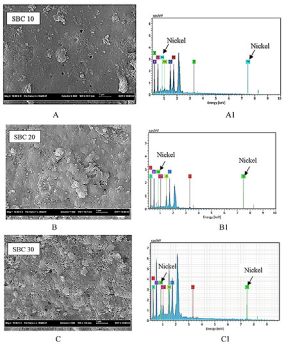

Fig. 4. A—SBC 10 after treatment, A1—EDX of SBC 10 after treatment, B—SBC 20 after treatment, B1—EDX of SBC 20 after treatment, C—SBC 30 after treatment, C1—EDX of SBC 30 after treatment.

Filter media were visualized after the wastewater treatment, which made it possible to observe the deposition of particles (Fig. 4), especially in the pores, in which deposition occurred until some pores are closed completely. FESEM reveals the microstructure of the fabricated SBC membranes for the filtration process of industrial wastewater. The images (Fig. 4) prove that all three types of SBC membranes can filter the wastewater. The chemical content of the SBC membranes after the filtration process was analysed by EDX.

The first membrane was the SBC 30, contrary to the tendency observed at the characterization of the filter media. It showed small pore size and lower permeability in the case of SBC, which indicate an effective filtration. This result reveals that the SBC membranes can filter nickel from industrial wastewater effectively.

3.1. Influence of the particle size

To investigate the effect of the different parameters on the filtration performance, experiments were conducted. According to the classification of pores by the International Union of Pure and Applied Chemistry (IUPAC), the pore size of 2–50 nm can be classified as mesopores. Moreover, SBC 20 had a higher average pore diameter (3.39 nm). SBC 10 and SBC 30 had smaller average pore diameters of 2.44 nm and 2.49 nm, respectively. The

Table 2
Average pore diameter, surface area and pore volume of SBC.

Membrane Type	Average Pore Diameter (nm)	Kaganer Surface Area (m^2/g)	BJH Pore Volume (cm^3/g)
SBC10	2.44	5.41	0.016
SBC 20	3.39	4.27	0.021
SBC 30	2.49	2.95	0.026

Table 3
Nickel content in influent (before treatment) and effluent (after treatment) from real industrial wastewater.

Influent		Effluent			
Sample	Initial Nickel content mg/l	Ion Exchange Treatment mg/l	SBC 10mg/l	SBC 20mg/l	SBC 30mg/l
Waste Water 1	9.84	2.6	2.39	3.58	3.36
Waste Water 2	7.22	0.04	0.34	0.73	0.57
Waste Water 3	5.98	0.46	0.25	0.27	0.14

BET surface area for SBC 10, SBC 20 and SBC 30 is shown in Table 2. It can be seen that the particle powder of SBC 10 is finer compared to SBC 20 and SBC 30. The surface area measured the amount of nitrogen gas required for monolayer absorption of the total surface area. The data also showed an agreement with the microstructure of SBC 10, which has a higher surface area, and the pore is well distributed with no agglomeration detected.

An adsorption isotherm was obtained by measuring the N2 gas adsorbed across a wide range of relative pressures at a temperature of 77 K. Conversely, a desorption isotherm was achieved by measuring the gas removed as pressure was reduced. The isotherms of SBC 10, 20 and 30 by BET nitrogen adsorption are shown in Fig. 4.9. All SBC membranes show a type IV isotherm pattern. The type IV isotherm pattern occurs on porous adsorbents with pores in the range of 1.5–100 nm. At higher pressures, the slope shows increased uptake of adsorbate as pores become filled. The inflection point typically occurs near the completion of the first monolayer. The results of BET analysis (Figure 7), the monolayer volume of nitrogen uptake was higher in SBC 10 with 1.24 cm^3/g, followed by SBC 20 (0.98 cm^3/g) and SBC 30 (0.68 cm^3/g).

3.2. *Performance and efficiency of treatment systems*

The industrial wastewater quality was expressed by the rejection of nickel content. The standard deviation of the parameters was considered throughout the study period (28 weeks). It was observed that the initial nickel content in the real industrial wastewater before treatment was very significant in all influent samples, where the lowest content was 5.98 mg/l. The nickel content in influent is very high and beyond the permissible limit allowed by Malaysia's Environmental Quality Act (EQA) 1974, which must be lower than 1.0 mg/l.

Since the experiment was performed using three membranes, the responses of the filtration for the three membranes were analysed to determine if there was a significant difference. The ion exchange treatment from the industry reduced the nickel content up to 73.57%, while SBC 10, 20 and 30 reduced the nickel content by 75.63%, 63.62% and 65.83%, respectively. Table 3 shows the initial content of influent and the effluent in wastewater.

4. Conclusion

Sayong Ball Clay (SBC) membranes were prepared to determine the optimal milling parameters of SBC powder at three different milling times (10, 20 and 30 h). The SBC powders were then mixed with 25% weight of cassava starch, pressed at 50 MPa and fired at 1100 °C for 2 h. The SBC membranes obtained had adequate physical and mechanical properties in terms of density and porosity for use as a wastewater filtration medium. It has been found that when the milling time increases, it will cause the fine particles of SBC to become agglomerated and affect the quality of the fabricated SBC membrane because of their larger pore size. The effectiveness of SBC membranes was proved by performing a filtration experiment of wastewater containing various concentrations of nickel by using all three types of fabricates.

The obtained results confirmed that the rejection of nickel can be successfully filtered by using SBC membranes. From the filtration results, the average nickel rejection rates for SBC 10, SBC 20 and SBC 30 were

88.87%, 82.96% and 85.13%, respectively. SBC 10 is the best membrane to filter wastewater containing nickel from real industrial wastewater. SBC membranes are therefore a very promising and green medium to filter wastewater containing heavy metal. Due to the positive results, SBC membranes should find applications for wastewater treatment in industrial or other suitable application in developing countries.

References

[1] I.K. Kalavrouziotis, C.A. Apostolopoulos, An integrated environmental plan for the reuse of treated wastewater effluents from WWTP in urban areas, Building and Environment 42 (2007) 1862–1868.

[2] S. Shrestha, F. Kazama, Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan Environmental Modelling & Software 22 (2007) 464–475.

[3] M. Anbia, N. Mohammadi, K. Mohammadi, Fast and efficient mesoporous adsorbents for the separation of toxic compounds from aqueous media, Journal of hazardous materials 176 (2010) 965–972.

[4] I. Heidmann, W. Calmano, Removal of Zn (II), Cu (II), Ni (II), Ag (I) and Cr (VI) present in aqueous solutions by aluminium electrocoagulation, Journal of Hazardous Materials 152 (2008) 934–941.

[5] T.A. Kurniawan, G.Y. Chan, W.-H. Lo, S. Babel, Physico–chemical treatment techniques for wastewater laden with heavy metals, Chemical engineering journal 118 (2006) 83–98.

[6] J. Duruibe, M. Ogwuegbu, J. Egwurugwu, Heavy metal pollution and human biotoxic effects, International Journal of Physical Sciences 2 (2007) 112–118.

[7] R.A. Goyer, T.W. Clarkson, in: C.D. Klaassen (Ed.), Toxic effects of metals Casarett & Doull's Toxicology. The Basic Science of Poisons, Fifth Edition, McGraw-Hill Health Professions Division, ISBN, 1996, p. 71054766.

[8] J.R. Peralta-Videa, M.L. Lopez, M. Narayan, G. Saupe, J. Gardea-Torresdey, The biochemistry of environmental heavy metal uptake by plants: implications for the food chain, The international journal of biochemistry & cell biology 41 (2009) 1665–1677.

[9] J. Huang, S. Cunningham, Lead phytoextraction: species variation in lead uptake and translocation, New phytologist 134 (1996) 75–84.

[10] L. Järup, Hazards of heavy metal contamination, British medical bulletin 68 (2003) 167–182.

[11] B.S. Levy, W.J. Nassetta, Neurologic effects of manganese in humans: a review, International journal of occupational and environmental health 9 (2003) 153–163.

[12] G.S. Shukla, R.L. Singhal, The present status of biological effects of toxic metals in the environment: lead, cadmium, and manganese, Canadian Journal of Physiology and Pharmacology 62 (1984) 1015–1031.

[13] E. Nemeth, E.V. Valore, M. Territo, G. Schiller, A. Lichtenstein, T. Ganz, Hepcidin, a putative mediator of anemia of inflammation, is a type II acute-phase protein, Blood 101 (2003) 2461–2463.

[14] P.B. Belibi, M. Nguemtchouin, M. Rivallin, J.N. Nsami, J. Sieliechi, S. Cerneaux, M. Ngassoum, M. Cretin, Microfiltration ceramic membranes from local Cameroonian clay applicable to water treatment, Ceramics International 41 (2015) 2752–2759.

[15] C.A. Basha, N. Bhadrinarayana, N. Anantharaman, K.M.S. Begum, Heavy metal removal from copper smelting effluent using electrochemical cylindrical flow reactor, Journal of Hazardous Materials 152 (2008) 71–78.

[16] N. Adhoum, L. Monser, N. Bellakhal, J.-E. Belgaied, Treatment of electroplating wastewater containing Cu 2+, Zn 2+ and Cr (VI) by electrocoagulation, Journal of hazardous materials 112 (2004) 207–213.

[17] M. Pudukudy, Z. Yaakob, M. Mohammad, B. Narayanan, K. Sopian, Renewable hydrogen economy in Asia–Opportunities and challenges: An overview, Renewable and Sustainable Energy Reviews 30 (2014) 743–757.

[18] Changlun Chen, Xiangke Wang, Adsorption of Ni (II) from aqueous solution using oxidized multiwall carbon nanotubes, Industrial & Engineering Chemistry Research 45.26 (2006) 9144–9149.

[19] Shitong Yang, et al., Competitive sorption and selective sequence of Cu (II) and Ni (II) on montmorillonite: Batch, modeling, EPR and XAS studies, Geochimica et Cosmochimica Acta 166 (2015) 129–145.

[20] Yuantao Chen, et al., Understanding the adsorption mechanism of Ni (II) on graphene oxides by batch experiments and density functional theory studies, Science China Chemistry 59.4 (2016) 412–419.

[21] L. Kong, W. Zhu, O. Tan, Preparation and characterization of Pb (Zr 0. 52 Ti 0. 48) O 3 ceramics from high-energy ball milling powders, Materials letters 42 (2000) 232–239.