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Removal of Cadmium from Water by using Clam Shell-Based Membrane Through Adsorption

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Abstract
Removal of hazardous heavy metals like cadmium is crucial for a clean environment and human health. Clam shells containing high amount of calcium carbonate can be a good candidate for a low-cost adsorbent. It is a natural product that can be incorporated into the polymer for the reactive functional group for adsorption sites of heavy metals. The study aimed to synthesise and characterise membrane derived from clam shell, combined with polyethersulfone (PES) and silica (SiO_2), to evaluate itsefficiency in removing cadmium through adsorption. Two types of flat sheet membranes were fabricated using different ratios of silica to clam shell: one with addition of silica (1:4 ratio) and one without addition of silica (0:4 ratio) using the phase inversion technique. Both membrane surface was determined using SEM, ATR-FTIR confirmed the presence of carbonate minerals and silica in the membranes. Adsorption studies were conducted using different initial concentrations of cadmium, and the data were fitted to Langmuir and Freundlich isotherms. The Langmuir isotherm model was found to be the most suitable for both membranes with R^2 of 0.981 and 0.9757 for membranes without and with silica respectively. The adsorption capacity of the membrane with silica was 0.164 mg/g (97.63% adsorption), while the membrane without silica was 0.159 mg/g (95.77% adsorption). Notably, the membrane with silica demonstrated higher adsorption capacity and percentage. In conclusion, modified clam shell-based membranes, particularly those with silica, showed promising strategy as cost-effective and efficient materials for cadmium removal in wastewater treatment applications.
Keywords: Clam shell; Flat sheet membrane; Langmuir isotherm; Freundlich isotherm

1. Introduction

The rapid growth of industries has contributed to the increase in toxic effluent, including heavy metals through the wastewater streams. The discharge of heavy metals into the water environment produces heavy metal accumulation in aquatic living species, which has a negative impact on both the environment and the organism (Nirmala et al., 2022). It also has a negative influence on water resources since toxins accumulate in the human body and the ecosystem via rivers and oceans (Nakajima et al., 2022).
Cadmium is one of the hazardous heavy metals from industrial activities such as welding, electroplating, mining, smelting, nickel-cadmium (Ni-Cd) rechargeable batteries and alloy manufacturing (Gupta et al., 2021, Abatan et al., 2020). As reported, in the 1990s, the global Cd production was approximately 20,000 metric tons per year; however, its current production is now over 30,000 metric tons per year (Mashhadikhan et al., 2022). Due to their high toxicity and non- biodegradability, even small amounts of discharge can be harmful to humans and the environment (Othmani et al., 2022).
Due to the worrisome prevalence of heavy metal contamination, research into innovative techniques of heavy metals removal should be done. A lot of methods have been developed to remove heavy metals from wastewater contamination such as adsorption, ion exchange, flotation, precipitation, electrochemical coagulation and membrane filtration (Kumar & Dwivedi, 2021). Among all the methods being listed, adsorption has emerged as a preferred technology for efficiently removing heavy metals due to its advantages of simple operation and low cost (Fang et al., 2021).

Clam shells, part of a seashell containing high amounts of calcium carbonate, can be a good candidate for a low-cost adsorbent. According to the study, 10-20 million tonnes of shell waste are discarded annually from seashell processing and the foul odours and eyesores it emits have a negative impact on the environment (Bamigboye et al., 2021). It is a natural product that can be incorporated into the polymer for the reactive functional group as adsorption sites of heavy metals in membrane development for wastewater treatment.

This research is much simpler, less costly and environmentally friendly. This study aims to 1) to synthesise and characterise membranes derived from clam shells as low-cost materials. 2) to determine the efficiency of clam shell-based membrane in removing cadmium from water through adsorption and 3) to determine the adsorption behaviour of the membrane using mathematical calculation of Langmuir and Freundlich isotherm.

2 Literature Review

2.1 Calcium carbonate in clam shell

Moreover, in recent years, as the marine shellfish industry has expanded rapidly, particularly in Asian countries, seashells have been produced as a side product making a challenge for disposal. It is estimated that 1 kg of clam produces 700g of clam shell, which can cause serious odour pollution (Nguyen et al., 2022). Seashells usually contain 89% to 99% of calcium carbonate (Mtavangu et al., 2022). As stated in Souza et al, (2018), clam shells are primarily composed of proteins and high purity calcium carbonate, and their use is not only economically viable but also a long-term solution to the inadequacy of this type of waste disposal (Souza et al., 2018). Calcium carbonate (CaCO_3) is abundant in raw seashells, while burnt seashells contain calcium oxide (CaO) which has various applications, including sewage and wastewater treatment, construction materials, biomaterials for bone and teeth implants, and drugs (Suwannasingha et al., 2022).

2.2 Polyethersulfone (PES)

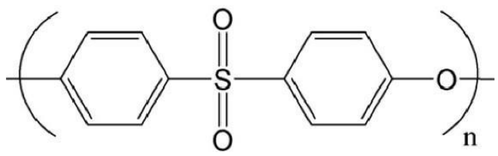


Figure 1. Structure of polyethersulfone (Abdul et al., 2021)

PES in Figure 1 is the second widely used of Membrane bioreactor (MBr) after polyvinylidene difluoride (PVDF) (Mohammad et al., 2019). It is always chosen as the membrane-forming polymer because it is chemically resistant to (aliphatic hydrocarbons, alcohols and acids), good chlorine resistance (sometimes for cleaning approaches), easy to fabricate and has high pH and temperature tolerances, besides able to produce membranes with a wide range of pore sizes (Giwa et al., 2017). The native PES has a number of disadvantages, including the lack of functional groups, which limits its use in water treatment (Mustafa et al., 2022).

2.3 N-Methyl-Pyrrolidone (NMP)

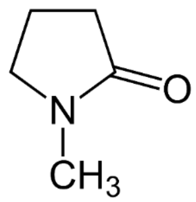


Figure 2. Structure of n-methyl-pyrrolidone (Abdul et al., 2021)

NMP in Figure 2 is reported as a useful solvent for many chemical reactions that desire non- reactive mediums, because of its properties of non-toxic, mild odour, high polarity, low melting (-23°C), and high boiling point (202°C), making it have good tolerance with high temperature and low viscosity (Abdul et al., 2021). Many previous studies used NMP as a casting solvent for membranes fabrication. For example, it acts as a casting solution of membrane production of Graphene Oxide (GO) blended with polysulfone (PSF) membrane (Mohammad et al., 2018).

2.4 Adsorption

Adsorption technology is widely used in wastewater treatment due to its low cost, efficiency, simplicity, versatility, and environmental friendliness. It involves the accumulation of a gas or liquid solute on the surface of a solid or liquid, forming a molecule or film. The process takes place on a porous solid medium, where a mixture of multi-component fluid is attracted to the solid surface through chemical or physical bonds (Al-Ghouti & Da'ana, 2020). There are three main types of adsorption mechanisms: chemical adsorption, which involves the formation of chemical bonds; physical adsorption, which involves van der Waals forces; and ion exchange (Wang & Guo, 2020). Two common isotherm which is Langmuir and Freundlich can be in adsorption assumption process. The Langmuir isotherm is based on the following assumptions which are monolayer adsorption while Freundlich model use to describe multilayer adsorption and monolayer adsorption (Nirmala et al., 2022).

2.5 Cadmium (Cd)

Cadmium (Cd) is a toxic, non-essential, and non-biodegradable heavy metal found in divalent form in stable compounds(Khan et al., 2022). It is discharged into the environment through various industrial activities like welding, electroplating, mining, and battery production, posing risks to both soil and aquatic bodies. The permissible limit of Cd for drinking water is 0.003mg/L based on the World Health Organization (Nakajima et al., 2022). Cd exposure occurs through inhalation, diet, and smoking, with detrimental effects on the kidneys, blood pressure, anemia, bone diseases like Itai-Itai disease, and cancer (Sasamoto et al., 2022).

2.6 Silica (SiO_2)

Silica has been intensively researched in recent decades due to its unique qualities such as low cost, formability (easy to form spherical particles ranging in size from nanometers to micrometres), chemical stability, and optical transparency (Liang et al., 2012).

3 Methodology

3.1 Materials

1000mg/L Cadmium (Cd) Standard Solution was purchased from Merck KClark (Germany), N-methyl- 2-pyrrolidone (NMP) was purchased from sigmaaldrich.com (Germany), Polyethersulfone (PES) was purchased from Solvay Veradel, clam shell were obtained from Pengkalan Nelayan Ayer Baloi, Pontian (Johor, Malaysia), silica powder, 20nm was purchased from Shanghai Xinglu Chemical Technology Co, Ltd and laboratory sieve, 140 um was purchased from Endecotts LTD (London, England).

3.2 Preparation of clam shell powder

The species of clam *Tegillarca granosa* was obtained from Pengkalan Nelayan Ayer Baloi, Pontian. The collected clam shells have already undergone species identification by Institute of Oceanography and Environment (INOS), Universiti Malaysia Terengganu (UMT). Clam shells were washed with tap water before being boiled at 100°C for 1 hour to remove physical impurities such as mud, sand and clay. This method is followed by rinsing the clams with water before drying at 50°C in the furnace for 7 days. Then, the clam shells were crushed into powder form with pestle and mortar and later mashed by a grinder and sieved to further obtain finer powder of shells.

3.3 Preparation of clam shell-based membrane

Table 1 Composition for preparation of dope suspension

Ratio Silica: Clam (Shell)	PES (wt%)	NMP (wt%)	Arlacel (wt%)	Clam Shell (wt%)
1:4	9	50	1	40 (32 g clam shell+ 8g silica)
0:4	9	50	1	40

A flat sheet membrane was fabricated using the phase inversion method. The procedure started with grinding the clam shells into powder. Next, silica powder was added and mixed with clam shell powder at ratios of (0:4) and (1:4), which is the ratio of silica powder to clam shell powder.

Meanwhile, NMP and Arlacel were mixed and completely dissolved with gentle stirring. Then, the silica-clam shell mixture was added to the solution and ball-milled for 48 hours at 192 rpm. PES was then added and continued in the ball mill for another 48 hours to produce a homogenous dope suspension. Air bubbles were removed from the mixture by a degassing process at ambient temperature for 3 hours under vacuum conditions with gentle stirring. All weight percentages are stated in **Table 1**.

3.3 Characterization

3.4.1 Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR)

Clam shell powder and clam shell-based membrane with and without silica was characterised with Perkin Elmer Model 1600 Infrared-Attenuated Total Reflection in Faculty of Science, UTM to define the type of functional group present. IR spectrum obtained e to determine the membrane materials and its functional group present was set at (650-3500) cm^{-1}.

3.4.2 Scanning Electron Microscope (SEM)

JSM-5510LV, JEOL scanning electron microscopy was used to determine the surface of clam shell- based membrane.

3.4.3 Experimental

An adsorption test was performed in a set of Erlenmeyer flask (100mL) where 50 mL of cadmium solution with initial concentration (3-20) ppm. 1.0 g of clam shell-based membrane without silica (0:4) ratio was added to each flask. The experiment was conducted under room temperature. Adsorption process carried out at orbital shaker at 150 rpm for 2 hours. After that, the solutions were taken out. All adsorption experiments were carried out in triplicate. The concentration of cadmium after adsorption process was determined by AAS. The experiment was repeated by using 1.0 g of clam shell-based membrane with silica (1:4) ratio.

4 Results and discussion

4.1 ATR-RTIR analysis

Figure 3 shows the spectrum of clam shells powder that shows that C=O peak at 1785.17cm^{-1}. Three strongest absorption bands at broad peak at (1467.03, 858.65, 712.00) cm^{-1} are assigned to the group of CO_3^{2-}in calcium carbonate as described by (Li et al., 2020). For both membranes, (a) and (b), both shows carbonate bands and the presence of peak at 1786.93 and 1786.66 cm^{-1}indicate the presence of C=O. However, (b) shows the addition of silica functional group at the peaks of at 1080.60 cm^{-1} indicated the presence of Si–O-Si bond (Liang et al., 2012). This showed the successful fabrication of membrane. ATR-FTIR spectrum is changing after adsorption, it is proven that adsorption process has occurred. After adsorption, both membrane (b) and (d) in Table 2 shows the new broad peak at peak 3371.64 and 3383.49 cm^{-1} which is indicate OH stretching comes from the aqueous cadmium solution.

This phenomenon confirms the hydrophilicity of the membrane and its capacity as good adsorbent. There were significant changes on the FTIR spectrum carbonyl vibration of both membranes following the interaction with Cd (II). For (a) the absorption bands of carbonate shifted from (1467.40, 857.14 and 713.71) cm^{-1} to (1448.58, 854.53, and 711.64) cm^{-1} after adsorption in (b). Meanwhile, for (c) the absorption bands of carbonate shifted from (1470.26, 857.62 and 713.57) cm^{-1} to (1448.59, 856.64, and 711.69) cm^{-1} after the interaction with cadmium (II) in (d). The interaction of positively charged metal ions with negatively charged adsorption sites of membrane via electrostatic attraction could explain the shift in peak position, change in peak strength, and introduction of novel vibrational characteristics (Ahmed Eljiedi et al., 2019).

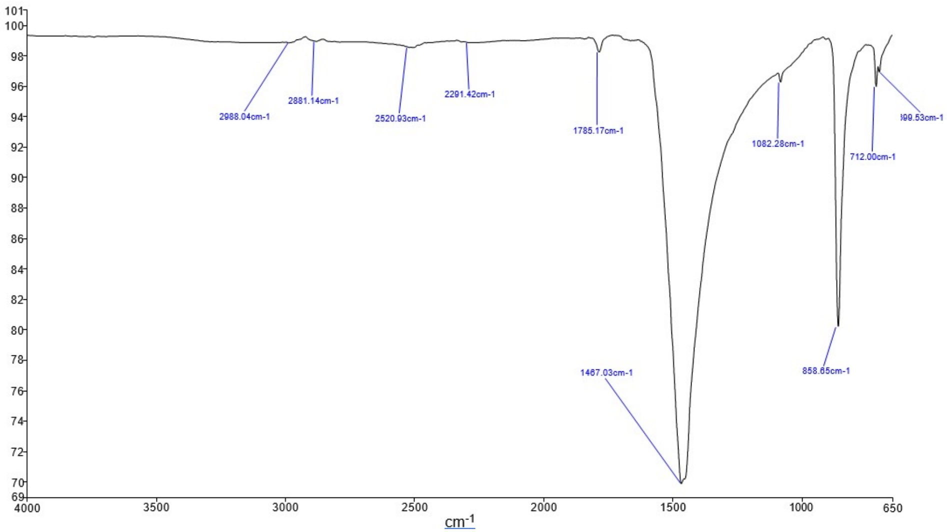
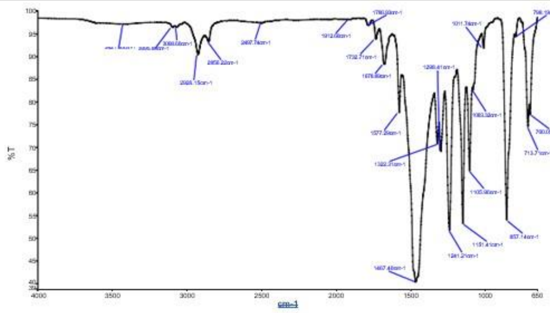
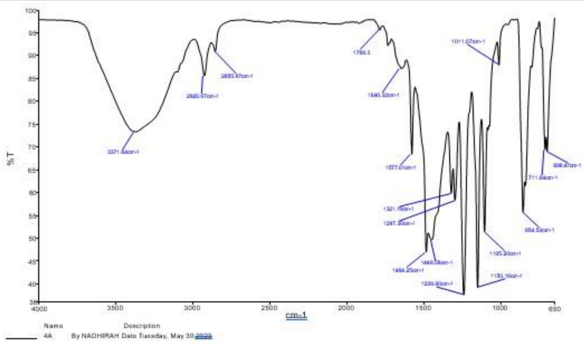
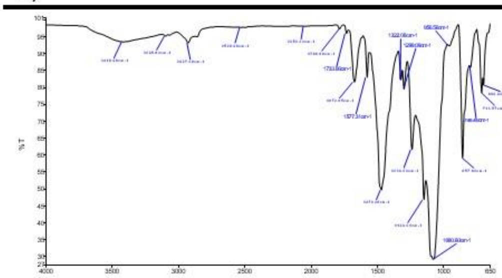
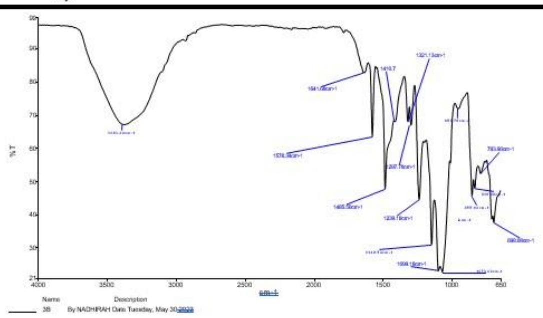


Figure 3. ATR-FTIR analysis of clam shell powder

Table 2. Comparison spectra for membrane ratio a) (0:4) before b) (0:4) after c) (1:4) before and d) (1:4) after adsorption

Before adsorption	After adsorption
 a)	 b)
 c)	 d)

4.2 SEM analysis

SEM analysis was done to provide the surface morphology of the membranes. Figure 4 shows the membrane with and without addition of silica. From the comparison of both, the 0:4 ratio membrane has a rougher surface due to the clam shell particle that dominating the surface compared to 1:4 ratio membrane with addition of silica in nanometre size particle. The inclusion of silica in the membrane assisted in smoothing the membrane's surface by creating a smaller pore size (Mansur et al., 2021).

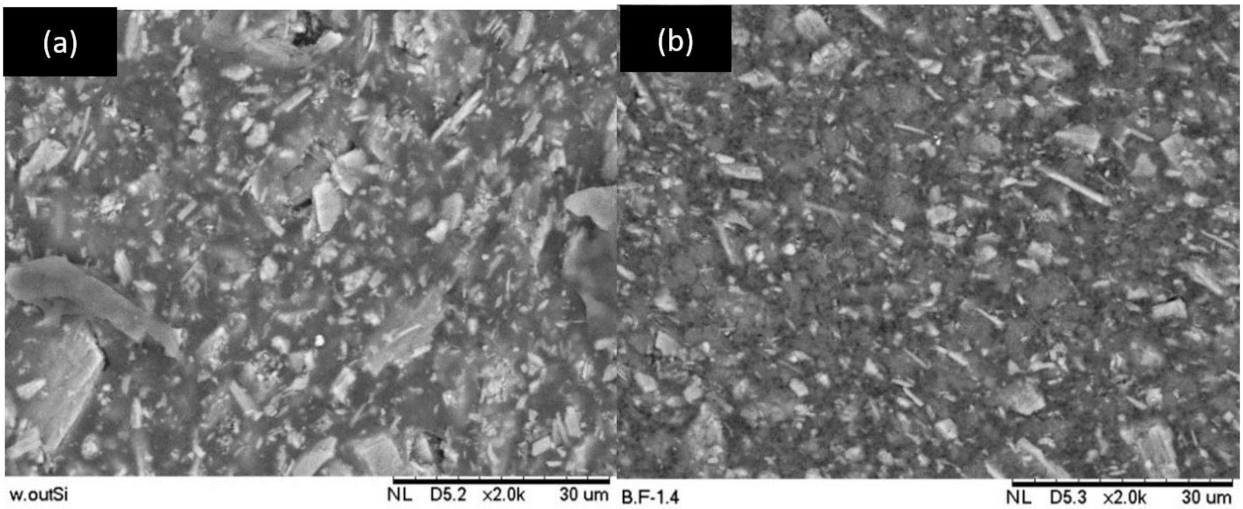


Figure 4. SEM pattern of (a) (0:4) ratio membrane (b) (1:4) ratio with 2.0k magnification

4.3 Atomic Absorption Spectroscopy (AAS)

The results of the concentration in Table 3 were taken before and after adsorption experiment using AAS for both membranes. Experiment using both (0:4) ratio and (1:4) ratio membrane shows the reduction of cadmium concentration in the solution after the adsorption process which confirmed the adsorption phenomena of cadmium ions onto the membrane surface. The adsorption performance is very important with the removal percentage that was achieved more than 90% using membrane with silica for all different concentrations of contaminant solution ranging from 3 to 20 ppm. Meanwhile, membrane without silica shows great removal percentage too with more than 90% for concentration ranging from 3 to 6 ppm and more than 70% and 80% removal percentage with concentration 12 ppm to 15 ppm. This shows the great capacity of the membrane in adsorbing the cadmium ions from contaminated solution at high concentration in membrane especially with addition of silica.

Table 3 The results of adsorption experiment

Membrane without Silica (0:4)			Membrane with silica (1:4)		
Initial concentration (ppm)	Absorbance	Final concentration (ppm)	Initial concentration (ppm)	Absorbance	Final concentration (ppm)
15.375	1.009±0.274	3.703±1.443	20	0.284±0.082	1.033±0.301
12.6	0.347±0.108	1.267±0.224	12.5	0.186±0.033	0.671±0.125
9.5	0.176±0.011	0.638±0.003	9.68	0.164±0.016	0.594±0.061
5.82	0.105±0.010	0.375±0.002	6.16	0.054±0.010	0.187±0.036
3.33	0.042±0.005	0.141±0.000	3.37	0.025±0.002	0.08±0.008

4.4 Isotherm calculation

With concentration of initial concentration of cadmium 3ppm, it resulted the adsorption capacity, q_e of the membrane with silica was 0.164 mg/g (97.63% adsorption), while the membrane without silica was 0.159 mg/g (95.77% adsorption). This shows membrane with silica is provide better adsorption process for cadmium ion in contaminated water. The results of (0:4) ratio membrane and (1:4) membrane more fitted in Langmuir isotherm as the R^2 of both of them were higher compared to Freundlich isotherm. This suggests that both type of membrane adsorb cadmium
is more consistent with monolayer adsorption and uniform adsorption force on the homogenous adsorbent's surface rather than multilayer adsorption phase. This implies that the composite membrane has a restricted number of specific adsorption sites at which cadmium ions can build a monolayer on the surface.

Where, adsorption% is adsorption efficiency of cadmium, Ci is the initial concentration of cadmium solution (ppm), Ce is the concentration of cadmium at equilibrium (ppm), V is the volume of solution (L), w is the mass adsorbent (g), q_e is the adsorption capacity at equilibrium (mg/g), q_t, is the adsorption capacity at any time, t. C_t is the concentration of cadmium at any time (ppm)

4.4.1 Langmuir Isotherm

By using the linearised form of Langmuir, R^2 values can be obtained by plotting the graph $1/q_e$ versus $1/C_e$ in Figure 5. The R^2 recorded for (0:4) ratio membrane is 0.9809 while (1:4) ratio membrane is 0.9757. Results R^2 from the isotherm plot will be compared to Freundlich isotherm.

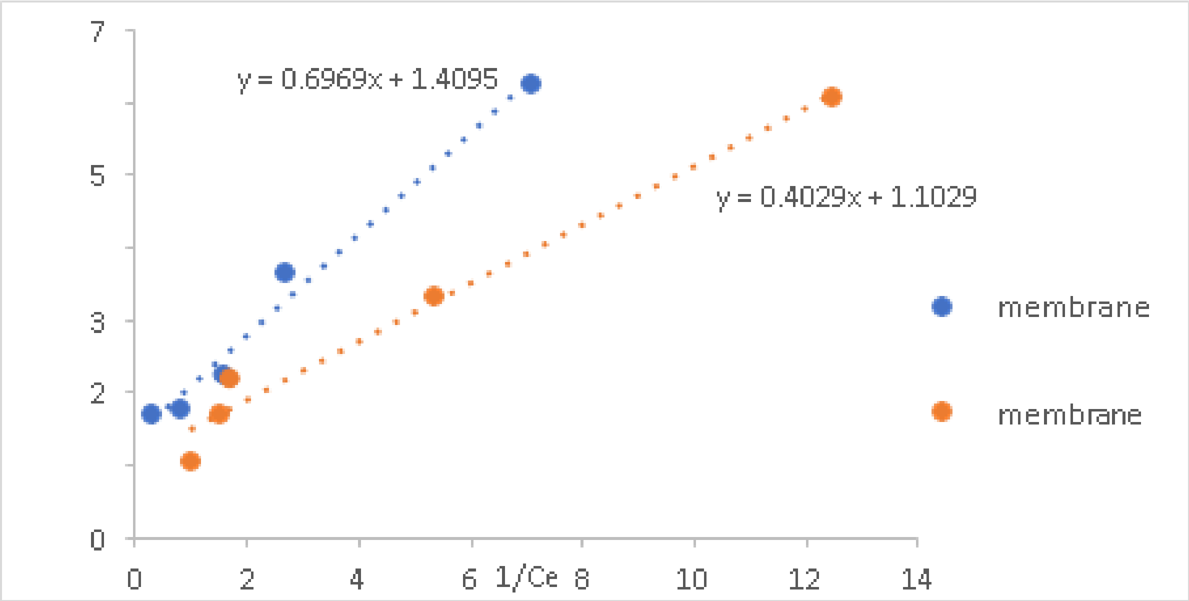


Figure 5 Graph $1/q_e$ versus $1/C_e$

4.4.2 Freundlich Isotherm

By using the linearised form of Freundlich, R^2 values can be obtained by plotting the graph log q_e versus log C_e in Figure 6. The R^2 recorded for (0:4) ratio membrane is 0.8622 while (1:4) ratio membrane is 0.9521.

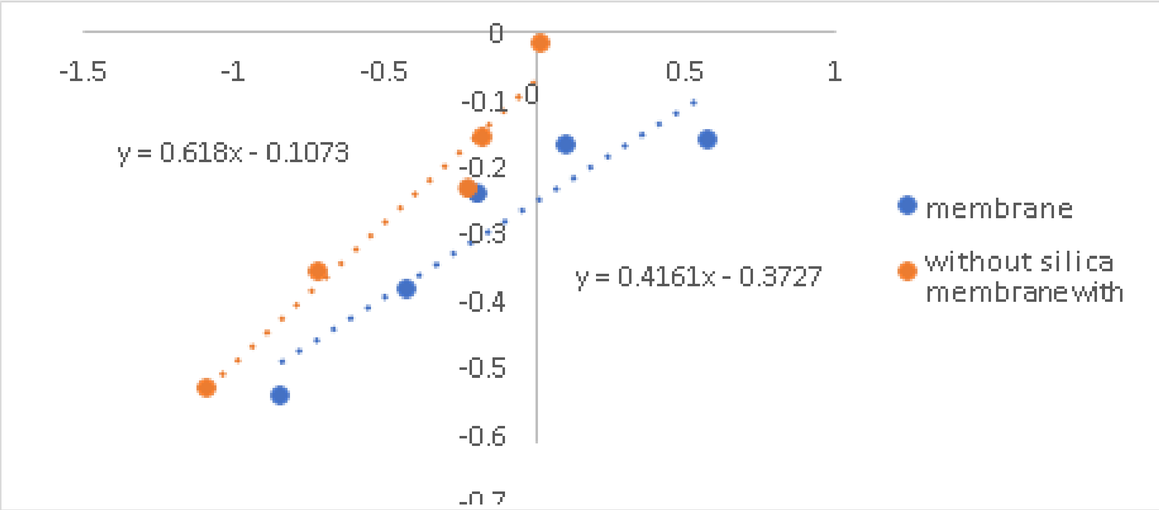


Figure 6 Graph log q_e versus log C_e

From Langmuir and Freundlich plotting data, it can be concluded that both membrane with and without addition of silica favoured Langmuir isotherm as they better fit to experimental data by providing higher R^2 of Langmuir isotherm than Freundlich isotherm. This suggests that both type of membrane adsorb cadmium is more consistent with monolayer adsorption and uniform adsorption force on the homogenous adsorbent's surface rather than multilayer adsorption phase (Chen *et al.*, 2022). This implies that the composite membrane has a restricted number of specific adsorption sites at which cadmium ions can build a monolayer on the surface.

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4 Conclusion

To be summarized, membrane with addition of silica (1:4) is more effective in removal of cadmium than membrane (0:4) based on calculation of percentage of cadmium adsorption. From the characterization of the membrane using FTIR and determination of removal percentage using AAS, it was confirmed that membrane that made of clam shell with additives could be a great adsorbent. Both membranes had been characterized using SEM and ATR-FTIR, and it shows successful fabrication.

It has also been proved that adsorption process by both membranes followed Langmuir isotherm by calculating and plotting the graph. The absorbance was obtained from the products that have been conducted in the constant temperature of 25°C and time 2 hours R^2 value that has been recorded from linearized form of Langmuir is 0.981 for (0:4) ratio membrane, and 0.9757 for (1:4) ratio membrane. Meanwhile, the R^2 value that has been obtained from linearized form of Freundlich is 0.8622 for (0:4) ratio membrane and 0.9521 for (1:4) ratio membrane. Hence, the most effective adsorbent is (1:4) ratio membrane that experiencing monolayer adsorption in which followed Langmuir isotherm.

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References

Abatan, O. G., Alaba, P. A., Oni, B. A., Akpojevwe, K., Efeovbokhan, V., & Abnisa, F. (2020). Performance of eggshells powder as an adsorbent for adsorption of hexavalent chromium and cadmium from wastewater. *SN Applied Sciences*, *2*(12), 1–13. https://doi.org/10.1007/s42452- 020-03866-w

Abdul, F., Juber, H., Abbas, Z., Bridgid, J., Fui, L., Swee, C., Yeap, P., & Leng, T. (2021). The prospect of synthesis of PES / PEG blend membranes using blend NMP / DMF for CO2 / N2 separation. *Journal of Polymer Research*. https://doi.org/10.1007/s10965-021-02500-6

Ahmed Eljiedi, A. A., Kamari, A., Sunardi, & Fatimah, I. (2019). Lala clam (Orbicularia orbiculata) shell as an eco-friendly adsorbent for Cd(II), Cu(II) and Pb(II) ions. *Arab Journal of Basic and Applied Sciences*, *26*(1), 462–475. https://doi.org/10.1080/25765299.2019.1674046

Al-Ghouti, M. A., & Da'ana, D. A. (2020). Guidelines for the use and interpretation of adsorption isotherm models: A review. *Journal of Hazardous Materials*, *393*(November 2019), 122383. https://doi.org/10.1016/j.jhazmat.2020.122383

Bamigboye, G. O., Nworgu, A. T., Odetoyan, A. O., Kareem, M., Enabulele, D. O., & Bassey, D. E. (2021).

Sustainable use of seashells as binder in concrete production: Prospect and challenges. *Journal of Building Engineering*, *34*(October 2020), 101864. https://doi.org/10.1016/j.jobe.2020.101864

Fang, L., Ding, L., Ren, W., Hu, H., Huang, Y., Shao, P., Yang, L., Shi, H., Ren, Z., Han, K., & Luo, X. (2021). High exposure effect of the adsorption site significantly enhanced the adsorption capacity and removal rate: A case of adsorption of hexavalent chromium by quaternary ammonium polymers (QAPs). *Journal of Hazardous Materials*, *416*(April), 125829. https://doi.org/10.1016/j.jhazmat.2021.125829

Giwa, A., Chakraborty, S., Mavukkandy, M. O., Arafat, H. A., & Hasan, S. W. (2017). Nanoporous hollow fiber polyethersulfone membranes for the removal of residual contaminants from treated wastewater effluent: Functional and molecular implications. *Separation and Purification Technology*, *189*(April), 20–31. https://doi.org/10.1016/j.seppur.2017.07.058

Gupta, K., Joshi, P., Gusain, R., & Khatri, O. P. (2021). Recent advances in adsorptive removal of heavy metal and metalloid ions by metal oxide-based nanomaterials. *Coordination Chemistry Reviews*, *445*, 214100. https://doi.org/10.1016/j.ccr.2021.214100

Khan, Z., Elahi, A., Bukhari, D. A., & Rehman, A. (2022). Cadmium sources, toxicity, resistance and removal by microorganisms-A potential strategy for cadmium eradication. *Journal of Saudi Chemical Society*, *26*(6), 101569. https://doi.org/10.1016/j.jscs.2022.101569

Kumar, V., & Dwivedi, S. K. (2021). A review on accessible techniques for removal of hexavalent Chromium and divalent Nickel from industrial wastewater: Recent research and future outlook. *Journal of Cleaner Production*, *295*, 126229. https://doi.org/10.1016/j.jclepro.2021.126229

Li, Y., Feng, Y., Xu, Z., Yan, L., Xie, X., & Wang, Z. (2020). Synergistic effect of clam shell bio-filler on the fire-resistance and char formation of intumescent fire-retardant coatings. *Journal of Materials Research and Technology*, *9*(6), 14718–14728. https://doi.org/10.1016/j.jmrt.2020.10.055

Liang, Y., Ouyang, J., Wang, H., Wang, W., Chui, P., & Sun, K. (2012). Synthesis and characterization of core-shell structured SiO 2 @YVO 4 :Yb 3+ ,Er 3+ microspheres. *Applied Surface Science*, *258*(8), 3689–3694. https://doi.org/10.1016/j.apsusc.2011.12.006

Mansur, S., Othman, M. H. D., Abidin, M. N. Z., Ismail, A. F., Abdul Kadir, S. H. S., Goh, P. S., Hasbullah, H., Ng, B. C., Abdullah, M. S., & Mustafar, R. (2021). Enhanced adsorption and biocompatibility of polysulfone hollow fibre membrane via the addition of silica/alpha-mangostin hybrid nanoparticle for uremic toxins removal. *Journal of Environmental Chemical Engineering*, *9*(5). https://doi.org/10.1016/j.jece.2021.106141

Mashhadikhan, S., Ebadi Amooghin, A., Sanaeepur, H., & Shirazi, M. M. A. (2022). A critical review on cadmium recovery from wastewater towards environmental sustainability. *Desalination*, *535*(March). https://doi.org/10.1016/j.desal.2022.115815

Mohammad, A. W., Teow, Y. H., Chong, W. C., & Ho, K. C. (2018). Hybrid processes: Membrane bioreactor. In *Membrane Separation Principles and Applications: From Material Selection to Mechanisms and Industrial Uses*. Elsevier Inc. https://doi.org/10.1016/B978-0-12-812815- 2.00013-2

Mtavangu, S. G., Mahene, W., Machunda, R. L., van der Bruggen, B., & Njau, K. N. (2022). Cockle (Anadara granosa) shells-based hydroxyapatite and its potential for defluoridation of drinking water. *Results in Engineering*, *13*(February). https://doi.org/10.1016/j.rineng.2022.100379

Mustafa, F. H. A., Attia, H. A. E. A., Yahya, R., Elshaarawy, R. F. M., & Hassan, N. (2022). Cellulose microfibrils-embedded sulfonated polyethersulfone for efficient Zn2+ ions removal from aqueous effluents. *Chemical Engineering Research and Design*, *186*, 374–386. https://doi.org/10.1016/j.cherd.2022.08.007

Nakajima, S., Araki, S., Sasamoto, R., Kanda, Y., & Yamanaka, S. (2022). Key particle properties of shells for cadmium chemisorption. *Chemosphere*, *287*(P3), 132257. https://doi.org/10.1016/j.chemosphere.2021.132257

Nguyen, T. T., Huang, H., Nguyen, T. A. H., & Soda, S. (2022). Recycling clamshell as substrate in lab-scale constructed wetlands for heavy metal removal from simulated acid mine drainage. *Process Safety and Environmental Protection*, *165*, 950–958. https://doi.org/10.1016/j.psep.2022.04.026

Nirmala, N., Shriniti, V., Aasresha, K., Arun, J., Gopinath, K. P., Dawn, S. S., Sheeladevi, A., Priyadharsini, P., Birindhadevi, K., Chi, N. T. L., & Pugazhendhi, A. (2022). Removal of toxic metals from wastewater environment by graphene-based composites: A review on isotherm and kinetic models, recent trends, challenges and future directions. *Science of the Total Environment*, *840*(June), 156564. https://doi.org/10.1016/j.scitotenv.2022.156564

Othmani, A., Magdouli, S., Senthil Kumar, P., Kapoor, A., Chellam, P. V., & Gökkuş, Ö. (2022). Tayeh et al., 2019. *Environmental Research*, *204*(August 2021). https://doi.org/10.1016/j.envres.2021.111916

Sasamoto, R., Kanda, Y., & Yamanaka, S. (2022). Difference in cadmium chemisorption on calcite and vaterite porous particles. *Chemosphere*, *297*(January), 134057. https://doi.org/10.1016/j.chemosphere.2022.134057

Souza, T. A., Mascarenhas, A. J. S., Andrade, H. M. C., & Santos, T. S. M. (2018). Combining Sewage Sludge and Clam Shell Waste to Prepare Adsorbents for Efficient Phosphorous Removal. *Water, Air,* *and Soil Pollution*, *229*(12), 1–13. https://doi.org/10.1007/s11270-018- 4029-1

Suwannasingha, N., Kantavong, A., Tunkijjanukij, S., Aenglong, C., Liu, H. B., & Klaypradit, W. (2022). Effect of calcination temperature on structure and characteristics of calcium oxide powder derived from marine shell waste. *Journal of Saudi Chemical Society*, *26*(2), 101441. https://doi.org/10.1016/j.jscs.2022.101441

Wang, J., & Guo, X. (2020). Adsorption isotherm models: Classification, physical meaning, application and solving method. *Chemosphere*, *258*, 127279. https://doi.org/10.1016/j.chemosphere.2020.127279