Synthesis and Characterization of Chitosan-clay Hydrogels for Lead removal

Matthew Kyle Ang[1], James Daniel Cudo[1], Loise Kassandra Tizon[1], Angela Terese Yu[1],
and David Peñaloza Jr.[2]*
[1] *De La Salle University – Integrated School Manila*
[2] *Department of Chemistry, College of Science, De La Salle University Manila*
**Corresponding Author: david.penaloza.jr@dlsu.edu.ph*

Abstract: Given the rising global concern on water pollution, wastewater treatment procedures have changed drastically over the past decade to maximize efficiency. For this reason, biodegradable polymers are being investigated as potential materials for metal absorption. Hydrogels are three-dimensional structures attained by crosslinking polymer chains either physically or chemically. They have gained significant interest for their potential industrial applications because they are highly stable and able to imbibe large amounts of fluid which are desirable traits for wastewater purification. This study reports the fabrication and properties of chitosan-clay hybrids, and their potential in heavy metal removal. Chitosan with different concentrations of Kaolin clay (1%, 3%, 5%, and 10% w/w) were prepared by solution casting method. The hydrogel composites were subjected to mechanical strength and swelling behavior assessments. To determine entrapment efficiency, the composites were submerged in a 10ppm lead solution for 24 hours. Lead (Pb) uptake was measured by atomic absorption spectroscopy (AAS). Surface morphology and elemental analysis (EDX) was also performed with the use of a JEOL JSM-5310 scanning electron microscope.

Key Words: hydrogel; clay; heavy metal removal

1. INTRODUCTION

It has been observed that the use of heavy metals has led to serious environmental consequences, especially water pollution in the Philippines. According to the World Bank (2003), the effects of water pollution costs approximately Php 67 billion annually.

Lead (Pb) is used in materials such as weights, batteries, and in storage. Due to its high density and absorbance, it is used as protection against radiation and coating for wires. Despite these, lead-containing materials carry heavy metal ions that are toxic to the human body in amounts exceeding 0.6 ppm.

Water moves through plumbing systems, which often include lead pipes. This may contaminate its potability and result in lead poisoning (Tirtom, Dinçer, Becerik, Aydemir, & Çelik, 2012).

Previous studies have shown that the industrial use of heavy metals is partially responsible for the widespread problem of water pollution. In the study of Marges, Su, and Ragragio (2014), high amounts of total copper, total lead, and total zinc were found in the waters and soils of Calancan Bay. This may be due to the mining operations done in the study area whose mine wastes still affect the environment and health of the people that depend on these waterways. Similarly, Su et al. (2009) conducted an assessment on the presence of heavy metals, specifically total cadmium, total lead, and total chromium, in the waters and species found in Manila Bay. The fish species obtained include the Halfbeaks

(Hyporhamphus dussumieri), Mullet (Liza sp.), Greenback mullet (Liza subviridis), Otomebora mullet (Mugil melinopterus), Deep body sardinella (Sardinella brachysoma), Barred queenfish (Scomberoides tala), Yellowstripe scad (Selaroides leptolepis), Barracuda (Sphyraena qenie), Anchovies (Stolephorus comersonii), and Tigerperches (Terapon jarbua). The macroinvertebrate species caught were the Mollusk Hard clam (Mercenaria sp.), Shrimp (Penaeus sp.), Blue crab (Portunus pelagicus), and the Mud crab (Scylla serrata). This study revealed that significant amounts of these heavy metals have contaminated the coastal waters and marine life.

Another study conducted by Solidum, J. and Solidum, G. (2014) identified the amounts of lead and cadmium in the community tap water in Manila. Lead and cadmium concentrations in the water samples were found to exceed the limit set by the United States Environmental Protection Agency of 0.015ppm and 0.005ppm respectively. From these findings, the researchers also learned that chitin may be a good candidate for lead (37.131% to 60.511%) and cadmium (42.982% to 62.411%) absorption.

Kaolinite is a common clay mineral with the chemical formula $Al_2Si_2O_5(OH)_4$. Igneous, metamorphic, or sedimentary rocks with an abundance of kaolinite are referred to as kaolinite clay. It is a major component in the production of paper, porcelain, cosmetics, and is often used as adsorbents in water treatment. Kaolinite particles exposed to temperatures of at least 500°C decompose and form water, free silica, and aluminum. The morphology of these minerals under high temperatures can be observed through an electron microscope (Chakraborty, 2013).

The addition of high amounts of kaolinite clay to hydrogels induces the formation of nanocomposites. This impacts the structural properties of hydrogels as it increases mechanical resistance and speeds up the rate of water absorption (Thakur, V., & Thakur, M., 2018).

Through swelling and dehydration tests conducted with mineral kaolinite clay and nanocomposite hydrogels, Bahramian et al. (2012) found that as the amount of clay is increased, both the swelling ratio and dehydration rate decreased. In this study, the surface morphology of the hydrogels was observed through the use of a scanning electron microscope.

Hydrogels are long, crosslinked chains of chemical compounds that attract water. Due to their composition, they have the ability to hold significant volumes of water while retaining its structure. One of its more notable uses are in wastewater treatment (Shah, & Khan, 2019).

Polysaccharides are naturally occurring carbohydrate-based biopolymers that make up hydrogels due to their presence in living organisms (Kalia & Sabaa, 2013). Compared to synthetic polymers, polysaccharides are also more suitable since they are both biocompatible and non-toxic. They also hold an economical advantage over the former, since its sources are renewable (Coviello, Matricardi, Marianecci, & Alhaique, 2007).

Biopolymers are produced by living organisms and are often found in plant material. These are composed of monomeric units that are synthesized, an example of which is chitosan (Reddy, N., Reddy, R., & Jiang, 2015).

Among the different polymers, hydrogels have drawn increased attention to wastewater treatment. This is mainly because of its self-healing, water-retention and adsorptive ability, appropriate elasticity, and network structures (Shah, & Khan, 2019).

The hydrophilic structure of hydrogels allows them to hold large volumes of water at given periods of time. Aside from this, their crosslinked structure holds the polymers together, creating a strong bond between the material (Kumar et al., 2017).

In this work, the researchers utilized kaolin clay to serve as an additive to chitosan (CS) hydrogel films. This study investigates the effect of clay concentration on swelling capacity, mechanical stability, and lead uptake.

2.METHODS

2.1 Conceptual Framework

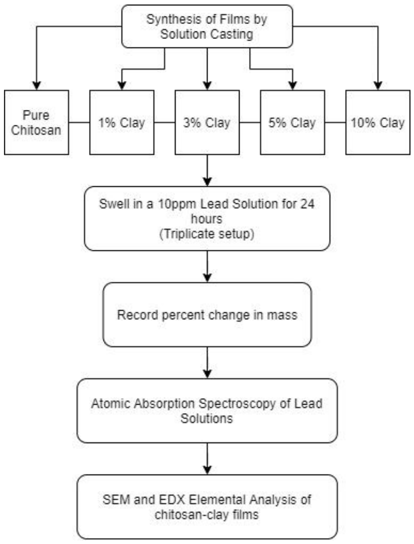


Fig. 1. Experimental flow

2.2 Materials and Apparatus

Chitosan in high molecular weight (310 - >375 kDa) was obtained from Sigma-Aldrich, Inc. and was used as received. Glacial acetic acid and a 1000 mg/L Pb standard for AAS were readily available at the DLSU Chemistry laboratory stockroom. Atomic Absorption Spectroscopy (AAS) was performed at the DLSU Chemistry Laboratory Instrumentation Room.

2.3 Fabrication of the films

The preparation of the chitosan-clay films was adopted from the methods of Salazar, Sanoh, and Peñaloza (2019). The clay-based films synthesized had 1%, 3%, 5%, and 10% clay concentrations (w/w). The chitosan solutions were mixed at 80°C stirred at 100rpm for 20 minutes with the addition of a clay dispersion in distilled water. The solutions were air dried for 48 hours.

2.4 Mechanical strength and swelling ratio determination

The hydrogel films were weighed and swelled in 10ml of a 10ppm Lead solution for 24 hours. Thereafter, the films were retrieved and weighed. The formula used to determine the swelling ratios of the hydrogels is

$$\text{swelling ratio} = \frac{\left(W_s - W_d\right)}{W_d} \times 100$$

where Ws is the mass of the hydrogel film after 24 hours in 10ml of the solution, while Wd is its mass prior to submersion. The ability of the films to retain their shape and refrain from disintegrating was used as an indicator of their mechanical strength.

2.5 Lead uptake

The same set of films were submerged in a 10ml 10ppm lead solution for 24 hours. For reference, the FDA deems 0.015ppm and above of lead in drinking water as toxic for human life. The solutions from which the CS-Clay membranes were immersed were analyzed by Atomic Absorption Spectroscopy (AAS). Standard solutions of 1.0, 3.0, 5.0, and 10.0ppm of Lead solution were used to form the calibration curve for the samples placed in 10.0 ppm Lead solution. The formula used to determine lead uptake was

$$Q_e = \frac{V(C_i - C_f)}{M}$$

where V is the volume of the lead solution before immersion, Ci and Cf are the initial and final concentrations (ppm) of the lead solution, and M is the final mass (g) of the film after being placed in the lead solution for 24 hours.

2.6 Surface Morphology and Elemental Analysis

SEM micrographs of the chitosan-clay film before and after submersion were taken on a JEOL JSM-5310 Scanning Electron Microscope at the DLSU Surface Physics Laboratory. Elemental analysis by Energy Dispersive X-ray Spectroscopy (EDX) was also performed to show the presence of Lead in the film after submersion.

3. RESULTS AND DISCUSSION

3.1 Mechanical strength and swelling assay

Chitosan films filled with clay exhibited twice as much swelling capacity as compared to chitosan films without clay loading. As shown in table 1, CS:clay at 3% configuration yielded the highest swelling capacity among the films at 1,331% while unmodified chitosan (CS) had the lowest at only 583%. Swelling capability, however, begins to decrease between 3% and 5% clay concentration (Fig. 3). It would be difficult to say, however, if increasing clay content would result in higher swelling capacity due to limited films. All films prepared had good swelling behavior and remained intact during retrieval, and therefore mechanically stable even after immersion (Fig. 2). It is also shown that clay-filled hydrogels are more swollen (i.e. larger film) visually than the unmodified chitosan film.

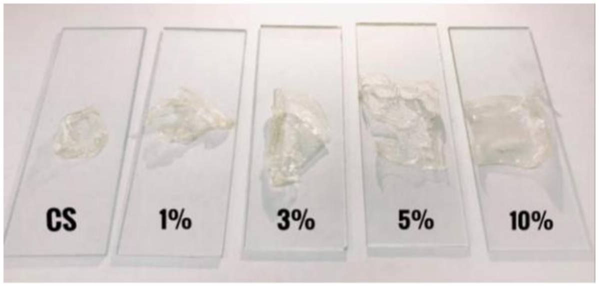


Fig. 2. Swollen films placed on glass slides (L-R: CS, 1%, 3%, 5%, 10%)

Table 1. Percent swelling of CS and CS-clay films

0% (CS)	1%	3%	5%	10%
583%	1,162%	1,331%	1,126%	1,132%

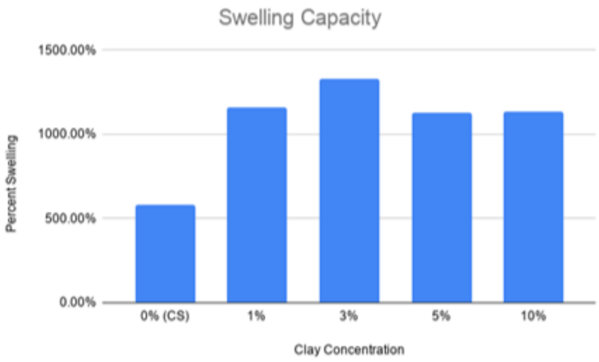


Fig. 3. Percent swelling of prepared hydrogels with various clay loadings

3.2 Lead uptake

Among the hydrogel films tested for Pb uptake, the CS-clay film containing 10% kaolin clay by weight recovered the highest amount of Pb (Table 2) from the simulated heavy metal-contaminated water sample at 21.23 mg Pb/g of hydrogel as shown in table 3. This is 42% better in terms of Pb recovery than that of the bare CS film, at only 14.99 mg Pb/g of hydrogel. At 5% by mass clay loading, the CS-clay sample recovered more Pb, at 17.13 mg Pb/g of hydrogel (14% better than CS only).

Table 2. Final concentration in ppm of solution after 24 hours

Film	Mean	Standard deviation
CS	4.00ppm	0.205
3%	6.83ppm	1.205
5%	3.14ppm	1.311
10%	1.51ppm	0.674

Table 3. Adsorptive capacity of films in 10ppm Pb Solution (expressed in mg Pb/g of hydrogel)

Film	Mean	Standard deviation	%CV
CS	14.99	0.525	3.502%
3%	7.94	3.015	36.97%
5%	17.13	2.932	17.11%
10%	21.23	1.692	7.97%

It can also be deduced that the addition of kaolin clay to the CS hydrogel film increases its ability to recover Pb, hence higher Pb uptake values for the nanocomposite materials. The enhanced Pb uptake capacity of the clay-filled CS films can be related to their increased swelling ratios – more trapped water, the greater the possibility of retaining Pb in their network structures of the CS-clay hydrogel films.

Rohindra, Nand, and Khurma (2004) state that the degree of crosslinking, swelling, and the absorptive capabilities of a film are inversely proportional. The more crosslinked a film is, the lesser its swelling capacity since it restricts the access of ions into the film. The 10% configuration was second best in swelling compared to the other configurations. By this, the 3% configuration which exhibited the best swelling capacity should have attracted the highest amount of lead, but the results from AAS have shown a significant difference in adsorptive capacity with the 10% configuration performing better than the 3% configuration as shown in figure 4.

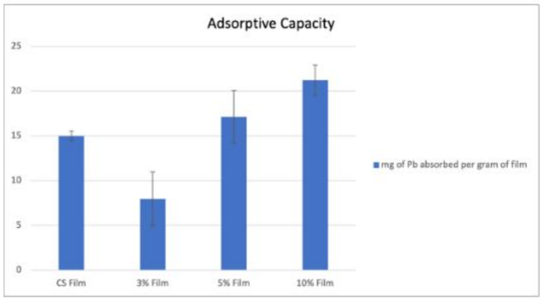


Fig. 4. Average adsorptive capacity of films expressed in mg Pb/g of hydrogel

3.3 Surface morphology and EDX

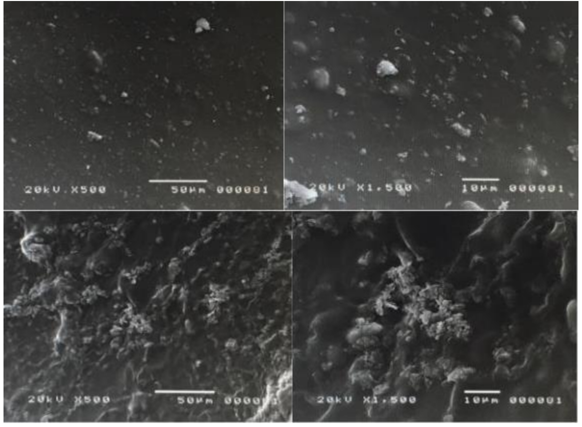
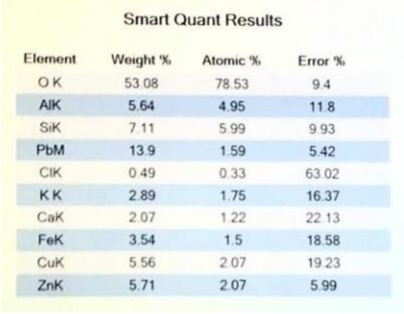


Fig. 5. SEM micrographs of chitosan-clay film prior to submersion (Top left: 500x, Top right: 1,500x) and chitosan-clay film after submersion in a 10-ppm Pb solution (Bottom left: 500x, Bottom right: 1,500x)

As shown in figure 5, the SEM micrographs of the chitosan-clay film prior to submersion showed a more uniform surface compared to the film subjected to the lead uptake test. The lack of uniformity in the morphology of the film swelled in a lead solution indicates attraction of particulate matter. The swelled film showed a globular, heterogeneous structure. SEM micrographs of CS reported in other studies show similar morphologies (Neji, Jridi, Kchaou, Nasri, & Dhouib Sahnoun, 2020; Ordikhani, Dehghani, Simchi, 2015).



Smart Quant Results

Element	Weight %	Atomic %	Error %
O K	53.08	78.53	9.4
AlK	5.64	4.95	11.8
SiK	7.11	5.99	9.93
PbM	13.9	1.59	5.42
ClK	0.49	0.33	63.02
K K	2.89	1.75	16.37
CaK	2.07	1.22	22.13
FeK	3.54	1.5	18.58
CuK	5.56	2.07	19.23
ZnK	5.71	2.07	5.99

Fig. 6. EDX elemental analysis of CS-clay film after immersion

Further energy dispersive x-ray analysis carried on the CS-clay film sample confirmed the incorporation of the clay as evidenced by the presence of Al, Si, and O. The chemical composition of kaolin clay is $Al_2(OH)_4Si_2O_5$ (Chakraborty, 2013). EDX also showed a 13.9% weight content of lead with 5.4% error (Fig. 6), verifying its presence in the films. analyzed. This supported the results of Pb uptake measurements discussed in an earlier section.

4. CONCLUSIONS

The researchers have successfully prepared stable, physically crosslinked chitosan (CS)-clay hydrogel films that exhibited remarkable swelling capacity (doubled that of the unmodified chitosan hydrogel) and exhibited increased Pb uptake characteristic. At 10% by weight loading, CS-clay hydrogel film was able to recover 21.23 mg Pb per gram of hydrogel, this is 42% better than that of the CS hydrogel film only. SEM analysis further supports the results of the Pb uptake measurements – when Pb is confirmed through EDX measurement to be present in the CS- clay film after immersion.

5. ACKNOWLEDGMENTS

The researchers thank the DLSU Chemistry Department and their laboratory technicians for generously letting them use their equipment. The researchers also thank Mr. Emmanuel Punzalan for overseeing them in the laboratory and Dr. Marissa Noel, Dr. Joel Garcia, Dr. Vincent Ng, and Mr. Vince Mesias of the Department of Chemistry for sharing their knowledge in general chemistry and sparking the interest of the researchers in the field.

6. REFERENCES

Bahramian, A. R., Hassan, Z. M., Kokabi, M., & Sirousazar, M. (2011). Mineral kaolinite clay for preparation of nanocomposite hydrogels. Journal of Applied Polymer Science, 125(S1). doi: 10.1002/app.35095

Chakraborty, A. K. (2013). Phase Transformation of Kaolinite Clay. Springer.

Coviello, T., Matricardi, P., Marianecci, C., & Alhaique, F. (2007). Polysaccharide hydrogels for modified release formulations. Journal of controlled release, 119(1), 5-24.

Kalia, S., & Sabaa, M. (2013). Polysaccharide based graft copolymers. Berlin: Springer.

Kumar, A., Wang, X., Nune, K., & Misra, R. (2017). Biodegradable hydrogel-based biomaterials with high absorbent properties for non-adherent wound dressing. International Wound Journal, 14(6), pp.1076-1087.

Marges, M., Su, G. S., & Ragragio, E. (2011). Assessing heavy metals in the water and soils of Calancan Bay, Marinduque Islands, Philippines. Journal of Applied Sciences in Environmental Sanitation, 6(1), 45-49.

Neji, A. B., Jridi, M., Kchaou, H., Nasri, M., & Dhouib Sahnoun, R. (2020). Preparation, characterization, mechanical and barrier properties investigation of chitosan-kaolinite nanocomposite. Polymer Testing, 84 doi:10.1016/j.polymertesting.2020.106380

Ordikhani, F., Dehghani, M., & Simchi, A. (2015). Antibiotic-loaded chitosan–laponite films for local drug delivery by titanium implants: cell proliferation and drug release studies. Journal of Materials Science: Materials in Medicine, 26(12), 269.

Reddy, N., Reddy, R. and Jiang, Q. (2015). Crosslinking biopolymers for biomedical applications. Trends in Biotechnology, 33(6), pp.362-369.

Salazar, G. M., Sanoh, N. C., & Penaloza, D. D., Jr. (2018). Self-Healing Materials: Novel Biocompatible Polysaccharide-Based Self-Healing Hydrogel (Adv. Funct. Mater. 9/2015). Kimika,29(2), 44-48. doi:10.26534/kimika.v29i2.44-48\

Shah, L. A., & Khan, S. A. (2019). Polymer hydrogels for wastewater treatment. Environmental Chemistry and Recent Pollution Control Approaches. doi: 10.5772/intechopen.89000

Solidum, J. N., & Solidum, G. G. (2012). Assessment and remediation of heavy metals in community tap water from Manila, Philippines. International Proceedings of Chemical, Biological and Environmental Engineering, 32, 1-6.

Su, G. S., Martillano, K. J., Alcantara, T. P., De Jesus, J., Hallare, A., & Ramos, G. (2009). Assessing heavy metal in the waters, fish and macroinvertebrates in Manila Bay, Philippines. Journal of Applied Sciences in Environmental Sanitation, 4(3), 187-195.

Thakur, V. K., & Thakur, M. K. (Eds.). (2018). Polymer Gels: Science and Fundamentals. Springer.

Tirtom, V. N., Dinçer, A., Becerik, S., Aydemir, T., & Çelik, A. (2012). Removal of lead (II) ions from aqueous solution by using crosslinked chitosan-clay beads. Desalination And Water Treatment, 39, 76–82. doi: 10.5004/dwt.2012.2547

World Bank (2003). Philippines Environment Monitor. Retrieved from http://documents.worldbank.org/curated/en/144581468776089600/pdf/282970PH0Environment0monitor.pdf