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Water Quality and Removal Efficiency of Suspended Solids, Copper, Lead, and Oil/Grease in Malihao River, Negros Occidental, Philippines Using Bivalve Shells

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ABSTRACT

Malihao river was reported to have a decline in water quality over the years due to the increasing human activities surrounding the river. Various pollutants were present in the river such as suspended and dissolved solids, copper, lead, cadmium, and oil/grease; and their concentration levels are beyond the set limit by the national guidelines. The removal of these compounds was studied using waste bivalve shells is a suggested remedy, as they are locally available and abundant in the region. Total suspended solids were removed using chitosan from *Perna viridis* up to 81%; copper and lead were removed using *Polymesoda erosa* in a packed column; and oil/grease was efficiently removed using *Crassostrea* spp. up to 80-100%. Additional monitoring efforts in the locality should be done to properly manage this body of water to prevent from further deterioration.

Keywords: *suspended solids; heavy metals; oil/grease; bivalves; Malihao river*

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INTRODUCTION

The occurrence of pollutants in water can indicate the level of pollution in a certain body of water, such as rivers and lakes. The assessment of the water quality usually requires an examination of water pollution and the factors contributing to it, as well as the areas prone to pollution in the surrounding river sections (Yan, et. al., 2015). The evaluation of parameters involved in the water quality monitoring process is carried out according to relevant national guidelines and with international regulation directives to set the limits (Davies-Colley, 2013; Sasakova et al., 2018).

The decline of water quality in rivers has been observed across the globe (Lintern et al., 2018; Schwarchenbach et al., 2010) and river systems in the Philippines is not an exception. Malihao River has been in constant monitoring by the Department of Environment and Natural Resources – Environmental Management Bureau (DENR – EMB) due to its low water quality standards. The river is generally used for agriculture, transportation especially for sugar industry, recreation, and other domestic purposes within the island. The rapid population growth of the country from 76.52 million in 2000 to 101 million in 2015 (PSA, 2016) has put a huge demand on the natural resources to provide for this growth and anthropogenic activities can significantly contribute to water pollution (Sasakova et al., 2018). The various activities within and surrounding the rivers can lead to environmental deterioration and consequently, will affect human lives.

This study focuses on the determination of the levels of targeted pollutants found in Malihao River such as total suspended solids (TSS), heavy metals copper and lead, and oil/grease. High concentrations of particulate matter in the river can easily decrease photosynthetic activities and increase in bacteria and nutrient load (BFAR-PHILMINAQ, 2007). Suspended solids found in the rivers can also act as

carriers of other potentially harmful pollutants such as heavy metals (Nasrabadi et al., 2018). The presence of oil/grease in water systems of tropical countries is also causing damage to the aquatic environment and this emerging pollutant is recently proposed for inclusion in water quality index parameter for the preservation of marine biota (Eljaiek-Urzola et al., 2019). The removal of these pollutants was also investigated using naturally abundant wasted shells in the region. Chitosan extracted from *Perna viridis* was applied to study the removal of suspended solids and wasted shells from *Polymesoda erosa* and *Crassostrea* spp. focused on the removal of heavy metals and oil/grease, respectively. This investigation can help aid regulatory bodies in the country to properly propose policies to maintain balance in the economic and environmental functions of the rivers.

EXPERIMENTAL

Sample Collection. The location of the study is in Malihao River, Victorias City, Negros Occidental, Philippines. The river is 14.5 km long running from Mount Silay to Guimaras Strait. The sampling stations were located in several sites as illustrated in Figure 1: site 1 is the Malogo River near a pumping station of Victorias Milling Company (VMC), which serves as a control site; site 2 is in Malihao Bridge, where the Malihao River and effluent from VMC pass through; site 3 is in Magnanod River, a tributary of Malihao River located near the households and commercial establishments and offices; site 4 is the mixing zone of Malihao and Magnanod River; and site 5 is located in Daan Banwa Wharf where the Malihao River ends and goes towards the Guimaras Strait. Further details of the sampling sites are described in Table 1.

Sampling bottles were acid washed with 10% nitric acid and rinsed with distilled water twice. Around 2 L of water was collected for the various analysis to be conducted. Temperature, pH and turbidity were obtained

from the site during sample collection. Water samples were stored in an ice chest at 4°C until ready to be analysed in the laboratory.

Preparation of bivalve shells and optimization studies. *Perna viridis* shell samples were acquired through waste *P. viridis* shells collected from the local market of Roxas, Capiz. It was scraped free of loose tissue and dried in an oven to constant weight at a temperature of 35 °C. The dried shells were grounded to pass through a 0.15 mm sieve. The extraction of chitin to chitosan was based from the method of (Danarto and Distantina, 2016). The shells were then weighed and soaked in 5% NaOH solution (1:10 w/v) at 70°C for 2 hours. The shells were washed thoroughly with distilled water until neutral pH and was dried at 60°C in oven until weight is constant. The deproteinized shells were weighed and soaked in 2 % HCl (1:10 w/v) at 70°C for 2 hours until no bubbles appear, and the shells were washed until neutral pH and dried. It was then deacetylated in 50% NaOH (1:5 w/v) at 110°C for 10 hours. The chitosan obtained was washed and dried to constant weight. The optimum chitosan dosage for removal of total solids were tested at 50 – 300 ppm chitosan concentration.

Polymesoda erosa shells were collected in local markets of Oton, Iloilo as a waste shell. The shells were washed with water, brushed and

dried thoroughly. The size of the shells was reduced by crushing and grinding using mortar and pestle and homogenized using 0.15 mm and 0.83 mm sieve. The homogenized shell was packed in the column with water until a slurry mixture is achieved. The column was washed several times with distilled water and the water level was kept just above the packing to prevent from drying out. The preparation of the fixed-bed column for heavy metal removal was modified based on the study of (Li and Champagne, 2009). The column was optimized in varying pH (3, 4, 6, and 8) and flow rate (3, 5, 7, and 10 mL min⁻¹). A constant volume of 20 mL mixed standard metal solutions was added in the column and soaked for 1 h before elution. After elution, 30 mL of distilled water was added as washing and the eluate was collected. The eluate collected was then analysed using atomic absorption spectroscopy.

The *Crassostrea* shells used in the study was collected as a fresh waste product from a local supplier and shell retailer at Enrique B. Magalona, Negros Occidental. The collected shells were cleaned and brushed thoroughly to remove organic matter attached and air dried for 48 hours. The dried shells were crushed and reduced to a smaller size using mortar and pestle. The crushed shells were sieved thru different mesh sized in order to remove unwanted particles and separate into different sizes. A two-layer sieve was assembled using

Table 1. Description of Sampling Sites in Malihao River.

Sampling Site	Location	Description	Coordinates
Site 1	Malogo River	Control, near a pumping station; Bathing, and laundry activities are observed	10.8761720, 123.0454320
Site 2	Malihao Bridge	The main course of Malihao River, effluent discharge from VMC	10.896750, 123.0644530
Site 3	Magnanod River	Tributary to Malihao River	10.8975400, 123.0710680
Site 4	Mixing Zone	Mixing Zone of Malogo and Malihao River	10.9061850, 123.0672900
Site 5	Daan Banwa Wharf	The wharf that goes out to Guimaras strait	10.9122740, 123.060509

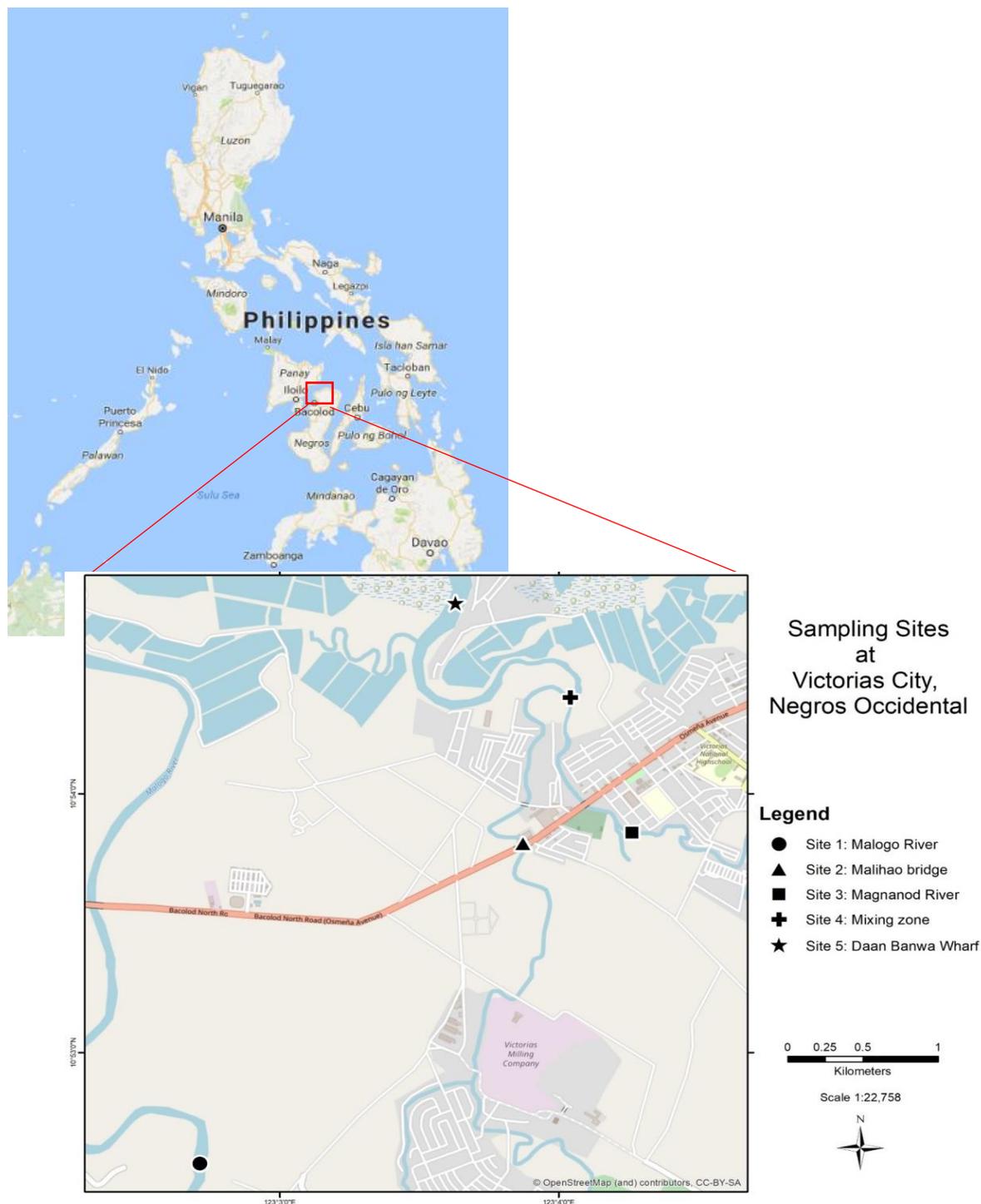


Figure 1. Map of the sampling sites in Malihao River, Victorias City.

aluminum screen with mesh size of 1 mm for one layer referred as coarse powder and 0.15 mm mesh size standard sieved for the other layer which was referred as fine powder. The shell powder was washed thoroughly with

distilled water and dried. The column was packed with an alternating layer of coarse and fine shell powders. The packed column is connected to a tubing and submersible pump modified from (Abd El-Gawad, 2014). The

optimum contact time (30, 60, 75, 90, 150, and 240 min) and varying concentrations (10-90 ppm) were studied for adsorption experiments.

Analysis of Total Suspended Solids. The filtering apparatus was assembled, and the pre-weighed filter paper was moistened with distilled water. The water sample was mixed vigorously, and 100 mL was transferred to the filtering apparatus under vacuum. The filter paper was removed in the filter support and dried to constant weight at 103-105 °C (APHA, 2017). Another volume of water sample was also stirred for 30 min with 50 mL chitosan extracted from *P. viridis* solution with a dosage of 15 mg per 100 mL, then was filtered and dried. The total suspended solids were reported in mg L⁻¹.

Analysis of Total Dissolved Solids. The total dissolved solids of the water sample were determined using Hanna Instrument HI5522. Sufficient amount of sample was transferred to a 50-mL conical tube and the conductivity probe was inserted to the tube until the upper vent holes were covered with solution (APHA, 2017). The TDS value were recorded and reported in mg L⁻¹.

Heavy Metal Analysis. A 50 mL sample was transferred to a 100-mL beaker and were added with 1 mL conc. HNO₃ and 2.5 mL conc. HCl. It was evaporated until the volume reduced to around 10 mL, the solution was allowed to cool, and the beaker walls was washed down with distilled water and filtered. The final volume was adjusted to 100 mL with distilled water (APHA, 2017). The initial concentration of the heavy metals (lead and copper) in the sample was first determined using Varian SpectraAA 55B AAS. The standard solutions for lead, copper, and cadmium (II) nitrate (Scharlau, AR grade) were prepared ranging from 2 – 10 ppm in 100 mL volumetric flasks. A plot of the calibration curves were prepared and used to determine the concentration of the sample solutions.

Another sample of water was passed on the column containing *P. erosa* shells with 150 µm particle size, several times with a flow rate of 7 mL min⁻¹ at pH 6. The eluate was collected, and the concentration of the heavy metals was determined. The concentration of the heavy metal was measured by difference between the initial values and final values which were derived before and after passing through the column, respectively.

Oil/Grease Analysis. An aliquot of the water sample was acidified to pH < 2 and extracted thrice with 30 mL hexane using a separatory funnel. The extract was dried with anhydrous sodium sulfate before concentration using Heidolph VV2000 rotary evaporator. It was then transferred into a crucible for drying at 70°C until constant weight (US EPA, 2010). The initial amount of oil/grease was first determined and then, the water sample treated using *Crassostrea* spp. shells with alternating coarse and fine particles in a fixed bed column was analysed for adsorption experiment for 90 min.

Analysis for the removal of suspended solids, heavy metals and oil/grease using different bivalve shells was calculated using this formula:

$$\% \text{ Removal Efficiency} = \frac{(C_i - C_f)}{C_i} \times 100$$

Where C_i and C_f represent the initial and final concentration, respectively.

RESULTS AND DISCUSSION

Occurrence of pollutants in Malihao River.

The pollutants found in Malihao river was based on the water quality parameters for freshwater source. The primary parameters measured were temperature, pH, turbidity, salinity, total suspended solids, and total dissolved solids. The secondary parameters determined for water quality are heavy metals copper, lead and cadmium together with oil/grease. The water quality of Malihao river

is mainly classified under class C, which is used as fishery and recreational water for boating, fishing, agriculture, livestock watering, and similar other activities (DENR, 2016). The collected water from five sampling sites were used to obtain different parameters of the pollutants found in the river. The parameter values were based on the guidelines set by DENR Administrative Order 2016-08 and other international standards. Table 2 shows the water quality parameters found in Malihao River under class C standards.

The control site from Malogo River near the pumping station of VMC, site 1, gave results in TSS and TDS under the allowable limits while the concentration of copper, lead, and oil/grease did not pass the set standards. Site 2 had the values exceeding the set limit of standards in almost all water quality parameters. It has the highest turbidity among all sampling sites at 48 NTU. This sampling site

is mainly coming from the effluent discharge of the sugar company, Victorias Milling Company, and some nearby residential households. Site 5 also significantly exceeded the standard limits, especially the high amount of total dissolved solids and the total suspended solids in water. This site is located at the end of the river and serves as a wharf with various activities that leads to high concentrations of these particulate matter.

Each sampling location has different water usage from the river. Site 1 is near the VMC pumping station, which served as the control site and the results showed that the primary parameters are within the allowable limit. This site is mainly surrounded by sugarcane and rice plantation and other agricultural areas. There are few residential houses but there is an ongoing construction of a relocation houses just beside the river. Site 2 is located at the vicinity of Victorias Milling Company, the

Table 2. Water quality parameters in Malihao River, Negros Occidental, Philippines.

Parameter	Site 1	Site 2	Site 3	Site 4	Site 5	Standard range
Temperature (°C)	27.3	29.8	28.2	29.7	30.2	25-31 ¹
pH	6	6	7	6	7	6.5-9.0 ¹
Salinity (%)	0.20	2.9	0.20	6.8	9.3	N.A.
Turbidity (NTU)	N.D.	48	12	24	12	29 ²
TSS (mg L ⁻¹)	22.0	125.5	39.5	66.5	232.0	80 ¹
TDS (mg L ⁻¹)	91.0	743.6	61.2	1726.2	23947	N.A.
Copper (mg L ⁻¹)	0.08	0.09	0.14	0.19	0.16	0.02 ¹
Lead (mg L ⁻¹)	0.09	0.14	0.15	0.18	0.51	0.05 ¹
Cadmium (mg L ⁻¹)	N.D.	N.D.	N.D.	N.D.	0.094	0.005 ¹
Oil/grease (mg L ⁻¹)	8.4	9.6	12	7.0	8.2	2.0 ¹

N.D. – not detectable; N.A. – not available; ¹DAO 2016-08; ²US EPA (Florida)

largest sugar industry in the region, where their effluent discharge is released after being treated. The DENR gave a cease and desist order in 2013 for non-compliance of the air and water standards; and in 2015, the company have acquired air and water pollution control devices (Sarito, 2017). This site showed high concentrations of measured parameters in the river such as turbidity, TSS, and oil/grease. The large amount of suspended solids, and oil/grease, correlate with the high concentrations of copper and lead, which also exceeded their allowable concentration. There is a linear relationship between TSS and turbidity where TSS is usually 1-3 times more than the measured turbidity and can aid in the transport of other pollutants (Rügner, et al., 2013). In addition, the linear relationship between TSS and total metal concentrations in rivers is also observed independent of season and events (Nasrabadi et al., 2018). Site 3 is surrounded by residential and commercial areas and it has the highest concentration of oil/grease. Oil/grease are usually found in municipal wastewater ranging from 50-150 mg L⁻¹; sources of which include domestic activities such as cooking or cleaning and leached hydrocarbons from gas stations and parking lots of automobile vehicles (Pintor et al., 2016). The concentration of TDS in site 4 is very high (1726.2 mg L⁻¹) as well as heavy metals Cu and Pb, and oil/grease. Site 4 is the mixing zone of the two rivers, where concentrations of inputs have salts and reactive inorganic and organic constituents that can transport materials by dilution or forming other type of pollutant. This mixing zone behaves as a source of resuspension process of particulate matter and dissolved inorganic nutrients to be released from surface sediments (Rodrigues, et al., 2009). The location of site 5 is in Daan Banwa Wharf, an old town of Victorias City where most residents are involved in fishing and houses the port for sugar milling products and other services which are transported. The high concentrations of TDS and TSS at the outlet of the river are highly influenced by port activities and tidal levels – higher values

during low tides compared to high tides (Jahan and Strezov, 2017).

The three metals tested (Cd, Cu and Pb) in the river were also present in this site, all values exceeding the standard limit. Extensive and diverse activities in the port such as shipping, tourism, and fisheries have significant impacts on the water quality of the river (Jahan and Strezov, 2017). The heavy metal concentrations of copper and lead towards the end of the river showed the highest reported values of 0.19 mg L⁻¹ for copper at site 4 and 0.51 mg L⁻¹ for lead at site 5. Site 4 is referred as the mixing zone of the two rivers, the Malihao River and Magnanod River while site 5 is a busy location for boats and vessels transporting goods and services to and from the island. Additionally, the concentration of cadmium at 0.094 mg L⁻¹ in site 5 was found to be beyond the set limit of DAO 2016-08.

The concentration of oil/grease is notably high in site 3 at 12 mg L⁻¹ as compared to the set limit of 2.0 mg L⁻¹. This site is located nearby the commercial and residential areas and the water is mainly coming from its tributary, the Magnanod River. This pollutant can be mainly attributed to domestic waste discharges. The occurrence of pollutants in Malihao river are mainly anthropogenic in origin and the activities surrounding each sampling site represent the type of pollutant present. These pollutants have concentrations beyond the set limit of the standard guidelines. It should be noted that most of the domestic discharge of wastewater goes directly to the river system without any treatment done. The continuous growth of the municipality can also lead to higher stress to our natural resources, producing more water pollutants that can cause the destruction of water systems.

Adsorption studies of the bivalve shells.

Flocculation and adsorption mechanism were applied in the removal of total suspended solids from the water samples. Chitosan was added to the water sample and after 10 minutes, a noticeable formation of suspended

particles was observed. Chitosan has abundant free amino groups along its backbone which can be protonated in which chitosan can behave as a cationic polyelectrolyte. Since most pollutants are have negative surface charges, chitosan as a cation has charge neutralization effect. This destabilizes the colloidal or suspended particles mainly by interparticle bridging (Teh, et. al., 2016). The optimum concentration of 15 mg chitosan per 100 mL water efficiently removed 83% of suspended solids.

The effects of pH and flow rate on the removal efficiency of the copper, lead, and cadmium was also studied and maximum adsorptions for the metals is at pH 6 with flow rate of 7 mL min⁻¹. Copper follows Langmuir adsorption model ($R^2 = 0.9182$) while lead observes the Freundlich model ($R^2 = 0.9359$). Table 3 shows the figures of merit determined from the heavy metal analysis.

The oil/grease maximum adsorption was observed at 90 mins contact time and follows the Freundlich model ($R^2 = 0.8532$). The alternating layer of coarse and fine powder shells enhanced the adsorption of oil/grease in the adsorbent. Oil and grease favors adsorption by chemisorption as describe by Freundlich isotherm for heterogenous multilayer adsorption (Pintor, et. al., 2016).

Removal of pollutants in Malihao River using bivalve shells. Inexpensive adsorbents from various agro-industrial and municipal wastes are emerging nowadays. The use of waste shells as an adsorbent for pollutants are considered as a possible alternative to most water treatment processes because they are

low-cost, naturally abundant and available materials. This can help eliminate disposal problems in the environment and avoid purchases of expensive conventional media (Liu et al., 2010; Yao et al., 2014). Oyster shells have been studied as adsorption and filtration media and shown to effectively remove up to 90% of influents BOD₅, P, N, and TSS in a constructed wetland unit (Park and Polprasert, 2008).

Waste oyster shells showed a great potential in removing combined wastewater in tidal rivers at the estuary. This treatment method is a suitable material for combined wastewater degradation as active filler to improve water quality (Luo et al., 2013). The removal of the targeted pollutants using locally available shells was performed in the study. *Perna viridis* (green mussel), *Crassostrea* spp. (talaba) and *Polymesoda erosa* (tuway) were selected as the adsorbents for the removal of total suspended solids, oil/grease, and heavy metals copper and lead, respectively.

The removal efficiency of total suspended solids ranges from 34-81% using chitosan extracted from *P. viridis* shells. The heavy metals copper and lead have a % removal efficiency from 8-65% at sites 3 to 5, while at site 1 and 2, it was observed that the *P. erosa* shell used was not able to remove the target metals due to negative percent removal (*). It may be attributed to several factors to include location and the adsorption mechanism that caused the insignificant removal on copper and lead. On the other hand, it is the *Crassostrea* shells that has a high removal efficiency at 80-100% in removing oil/grease from the river waters.

Table 3. Figures of merit for copper, lead and cadmium.

Metal	LOD (ppm)	LOQ (ppm)	R ²
Copper	0.002	0.006	0.9998
Lead	0.030	0.090	0.9996
Cadmium	0.001	0.003	0.9991

The chitosan obtained from *P. viridis* (dosage=15mg/100 mL) was used to determine the % removal efficiency against total suspended solids. Chitosan is a natural polymeric flocculant that is obtained from chitin by deacetylation. The structure and conformation of polymer determines the performance of the flocculant; and their coagulation and flocculation properties can remove particulate organic or inorganic suspensions and dissolved organic substances (Renault, et al., 2009; Yang, et al., 2016). The removal of sugar industry effluent using chitosan used a dosage of 7.41 mg L⁻¹ for resin effluents and this removed 68% of total suspended solids and it was observed to significantly decrease the cloudiness of the effluents (Pambi and Musonge, 2015). Chitosan from *P. viridis* was able to decrease the values of TSS in all sampling sites ranging from 34-81% removal efficiency. Based on the initial TSS values, site 2 and site 5 have the highest values. And with the same dosage used per treatment, the amount of chitosan might not be enough to increase the percentage removal of TSS at site 5; while at site 2, 73% removal efficiency of the suspended solids in the sample was obtained.

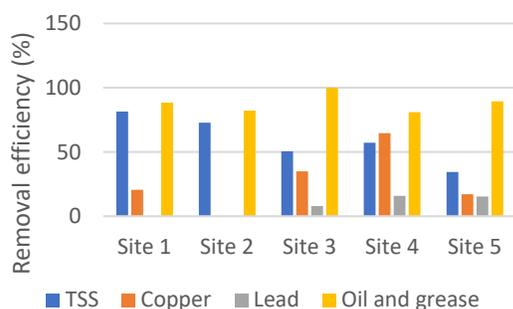


Figure 2. Removal efficiency of different adsorbents on selected pollutants in Malihao River.

The removal of copper and lead used a waste material from locally available bivalve shell *P. erosa* and the adsorption of metals was done in a column packing of the ground shells. A study in India on waste material from marine environment such as crab and arca shells showed to be a good sorption material for both

copper and lead with percentage removal of 88-91% (Dahiya et al., 2008). The removal efficiency from *P. erosa* shells for copper ranges from 17-65% and 7-16% for lead. The highest removal of copper and lead in site 4 is still above the allowable limit based on the set standards. This result needs further investigation on the various factors on the adsorption mechanism of the metals such as biomass particle size, elution time and sorbent packing.

Furthermore, the presence of oil/grease in Malihao River was effectively removed using another waste bivalve shell, *Crassostrea* spp. An effective way for removal of this pollutant was studied using adsorption method by agricultural residues such as banana pith and sugarcane bagasse and results showed that for banana pith, 5g of the biomass for 1 hour contact time can remove 97% of oil/grease (Abdul Hamid, et al., 2016). Other method such as electro-coagulation was used to remove oily emulsions and heavy metals in bilge water discharges and it showed that carbon steel and aluminium electrodes can efficiently remove oil/grease at a rate of 1 L/min and 0.6 A/cm² of current density (Rincon and La Motta, 2014). Oil/grease are challenging to remove and often need a combination of treatment technologies (Pintor et al., 2016). This has a disadvantage of causing suffocation to animals and plants by oxygen depletion, produce rancid odours and clog waterways (US EPA, 2018). In this study, *Crassostrea* spp. shells was able to remove oil/grease 80-100% from the river samples. The site with the highest concentration is located at the residential and commercial areas, thus, the oil/grease are mostly anthropogenic in origin.

The removal of suspended solids, copper, lead, and oil/grease using locally available and abundant bivalve shells is one of the steps to minimize water pollution and waste disposal to achieve a better water quality for Malihao river and surrounding water bodies in the Philippines. This preliminary evaluation of removal of pollutants using a waste material is moving towards a sustainable management of

the bodies of water through proper treatment of waste and sustainable usage of the rivers.

CONCLUSIONS

The high concentrations of suspended solids, copper, lead, and oil/grease showed that Malihao river is not compliant based on the guidelines set by the DENR. The location and anthropogenic activities surrounding the river is significantly affecting the levels of the measured parameters. The improvement of the values for the parameters mainly used waste bivalve shells that are locally available in the region. It showed a potential for a better water quality for municipal rivers and help eliminate disposal problems for the bivalve shells.

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