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Analysis of River Water Quality in Medan Belawan Regency based on the Diversity Index of Aquatic Insects as an Effort to Improve the Health of River Ecosystems from Heavy Metal Contamination (Ni).

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ABSTRACT

Heavy metals are often found in river water polluted by industrial processes. To separate heavy metals from river water, blood clam shells (*Anadara granosa*) are used as adsorbents. This study aims to analyze the determination of Belawan river water pollution based on the Aquatic Insect Diversity Index and analyze the content of heavy metal (Ni) in waste by utilizing blood clam shell waste as an adsorbent. The method used is solid phase extraction. Based on the diversity index data, the condition of the Belawan River waters in the Control area is not polluted (H' 2.18), Settlement Area 1 is lightly polluted (H' 1.94), Settlement Area 2 is lightly polluted (H' 1.70), Industrial Area 1 is moderately polluted (H' 1.47), and Industrial Area 2 is lightly polluted (H' 1.7). The percentage of heavy metal (Ni) absorption in Residential Area 1, Residential Area 2, Industrial Area 1, and Industrial Area 2 were respectively 28.57%, 33.33%, 31.11%, and 34.38%. This shows that blood cockles (*Anadara granosa*) are able to absorb Ni metal up to 34.38%. Ni levels < 0.05 mg/L so it can still be used (PP No. 22 of 2021).

Keywords: Heavy Metal (Ni), aquatic insects, solid phase extraction, and Diversity Index.

ABSTRAK

Logam berat sering ditemukan pada air sungai yang tercemar akibat proses industri. Untuk memisahkan logam berat dari air sungai, digunakan cangkang kerang darah (Anadara granosa) sebagai adsorben. Penelitian ini bertujuan untuk menganalisis penentuan pencemaran air sungai Belawan berdasarkan Indeks Keanekaragaman Serangga Akuatik dan menganalisis kandungan logam berat (Ni) pada limbah dengan memanfaatkan limbah cangkang kerang darah sebagai adsorben. Metode yang digunakan adalah ekstraksi fasa padat. Berdasarkan data indeks keanekaragaman, kondisi perairan Sungai Belawan pada daerah Kontrol tidak tercemar (H' 2,18), Daerah Pemukiman 1 tercemar ringan (H' 1,94), Daerah Pemukiman 2 tercemar ringan (H' 1,70), Daerah Industri 1 tercemar sedang (H' 1,47), dan Daerah Industri 2 tercemar ringan (H' 1,7). Persentase penyerapan logam berat (Ni) di Kawasan Permukiman 1, Kawasan Pemukiman2, Kawasan Industri 1, dan Kawasan Industri 2 berturut turut sebesar 28,57%, 33,33%, 31,11%, dan 34,38%. Hal ini menunjukkan bahwa kerang darah (*Anadara granosa*) mampu menyerap logam Ni sampai 34,38%. Kadar Ni < 0,05 mg/L sehingga masih bisa digunakan (PP No. 22 Tahun 2021).

Kata kunci: Logam Berat (Ni), serangga air, ekstraksi fase padat, dan Indeks Keanekaragaman.

1. Introduction

Water needs vary and depend on climatic conditions, living standards, and people's habits. Utilization of water for human needs will cause deviations from the normal state of water and this means pollution [1][2]. River as one of the environmental components that has an important function for human life including to support environmental balance [3]. As a result of increased development activities in various fields, both directly and

indirectly, it will have an impact on environmental damage, including river pollution originating from domestic and non-domestic waste such as factories and industries [4][2].

The Belawan area in North Sumatra has a field industrial area and of course the final result of waste is discharged in the river after being treated with special handling. Some things that are out of control such as spilled chemicals or waste whose heavy metals are still above the threshold must certainly be considered for processing [5]. Heavy metal pollution in water is an important environmental problem today [6]. High concentrations of heavy metals when contaminating water can cause adverse effects on the environment and human life. This has become an issue for water pollution forensics which is increasingly concerning [7].

Heavy metal pollution of river water can have detrimental effects on the environment and human health, including human health, where heavy metals can accumulate in living organisms including humans [8] [9]. Long-term exposure to heavy metals such as Nickel (Ni) can cause various health problems such as neurological disorders, damage to organs, damage to the immune system, and even cancer. Heavy metal pollution can reduce the availability of natural resources that depend on river water, such as clean water for human consumption, agriculture, and industry [10].

The level of contamination of aquatic ecosystems can be measured by utilizing bioindicators [11]. Bioindicators are living organisms such as plants, plankton, animals, and microbes, which are used as a sign of changes in the health of natural ecosystems in the environment or organisms that have sensitivity to environmental conditions so that they can be used as a sign of changes in the environment [12]. One important group of organisms in aquatic ecosystems is aquatic insects. Aquatic insects are good indicators of water quality. Some aquatic insects are sensitive to pollution while some can live and breed in the presence of pollution [3].

In this work, we will develop an analysis of the determination of Belawan river water contamination based on the Diversity Index of aquatic insects in forensic entomology and analyse the heavy metal content before and after the heavy metal waste extraction process using blood clam shell adsorbents.

2. Materials and Methods

2.1 Materials and Instrumentation

River water samples were procured from the Belawan River. Next, Formalin 4%, Distilled Water$_{(l)}$, Methanol$_{(l)}$, Chloroform$_{(l)}$, Dichloromethane$_{(l)}$, Ethyl Acetate$_{(l)}$, Ammonia $_{(l)}$, $H_2SO_{4(p)}$, HCl $_{(p)}$, $NaOH_{(l)}$, $HNO_{3(P)}$, Ni Standard Solution 100 mg/L. The Instrumentation was used an atomic absorption spectrophotometer (AAS), FTIR, X-Ray Diffraction.

Procedure

2.1.1Placement of Research Stations

The research station was determined through purposive sampling, resulting in the selection of five stations. Two stations were located in residential areas adjacent to the river, two in industrial areas, and one in an area that was neither residential nor industrial (control).

1. Residential 1 (3°37'13.74″N, 98°37'45.84″E)
2. Resident Settlement 2 (3°42'47.18 "N, 98°38'15.03 "E)
3. Industrial Area 1 (3°46'29.02 "N, 98°40'18.14 "E)
4. Industrial Area 2 (3°47'16.73 "N, 98°41'11.16 "E)
5. Control / Area Not Residential and Not Industrial Area (3°30'32.10 "N, 98°35'55.46" E)

The determination of sampling points at the research station is based on the condition of the research location, which allows for the collection of water insects with predetermined tools.

2.1.2 Sampling of Aquatic Insects

All species of aquatic insects were sampled from the larval, nymph/naiad, and imago stages on the substrate or streambed. Sampling was done when the water was low. Aquatic insects were collected using the hand-picking method, in which aquatic insects were directly picked up or caught with hands and other tools such as tweezers and placed on a tray. Then they are brushed and rinsed with water, the rinse water is checked for larvae, then the collected insects are placed in sample bottles and given 4% formalin to preserve them, then the sample bottle is labelled with the name of the station [13-14].

2.1.3Water Insect Analysis

Following the collection of the insects, their identification was conducted using taxonomic guides in order to ascertain the species or family to which they belonged. The ability to recognise the morphology of larvae, pupae, or adults is of great importance when attempting to identify specific species, as this can assist in determining diversity indices and serve as bioindicators.

2.1.4 River Water Sampling

The sampling of water from the Belawan river was conducted at the designated sampling point. The water samples were placed into containers that had been previously rinsed with local river water, and the sample bottles were then labelled with the name of the station.

2.1.5 Preparation of Blood Clam Shell Adsorbent

The preparation of the adsorbent utilizing blood clam shells (*Anadara granosa*) entailed a three-stage washing process with water, followed by a washing and rinsing stage with 0.5 M NaOH. The material was then dried under bright sunlight for seven hours, after which it was mashed using a mortar and pestle. It was subsequently placed in an oven at 105°C for three hours and then sieved using a 100-mesh sieve. The material was subjected to a four-hour activation process at 500°C via the application of heat in a furnace. The material was then cooled in a desiccator for 30 minutes and chemically activated by soaking in H_2SO_4 for 24 hours. The resulting solution was washed with distilled water until the pH was neutral, after which the material was calcined in a furnace at 900°C for 2 hours. It was then stored and cooled in a desiccator, and subsequently characterized by XRD.

2.1.6 XRD Characterization

X-ray diffraction (XRD) is employed to assess the characteristics of clam shell materials, utilising research-grade XRD devices. The key to success is to press the ON button on the XRD, then place a nano meter-sized sample of clam shell grains in the sample holder in order to prevent the escape of X-ray radiation. It is essential to ensure that the XRD is securely closed after the sample is placed in order to prevent any unwanted contamination. Subsequently, the angle of the goniometer or x-ray intensity detector is calibrated using a personal computer (PC). This enables the generation of a graph of the relationship between the angle 2θ and the x-ray intensity**.**

2.1.7 Solid Phase Extraction

The adsorbent was introduced to the membrane at the base of the column, which was filled to a height of 100 mg. Subsequently, the column was conditioned with 4 mL of methanol and neutralized with 4 mL of phosphate buffer. Moreover, the sample is inserted into the column and 4 ml of dichloromethane: isopropanol is added, which serves to remove impurities from the sample. Subsequently, the sample is eluted with ethyl acetate and ammonium hydroxide, and the resulting extract is collected and subjected to analysis.

2.1.8 FTIR Analysis

Infrared spectrophotometric (FTIR) characterization is employed to ascertain the functional groups present in the solid phase extraction results. It is essential that the sample be anhydrous. The sample should be placed in the NaCl window and the two windows should be pressed together to ensure the absence of air bubbles. For quantitative analysis, the sample should be placed in the removable cuvette. The sample is now ready for analysis.

2.1.9 Analysis used SSA

2.1.9.1 Preparation of Nickel Calibration Curve

1. Operate the device and optimize the SSA device
2. Aspirate the blank solution into the SSA then set the absorption to zero
3. Aspirate the working solution one by one into the SSA, then measure the absorption at a wavelength of 232.0 nm
4. Perform flushing on the aspirator hose with dilution solution
5. Do the same with standard solutions 0.01; 0.025; 0.05; 0.075; 0.1 mg/L
6. Determine the equation of the straight line until you get a linear regression correlation coefficient (r) > 0.995.
7. If the linear regression correlation coefficient (r) < 0.995, check the condition of the device and

repeat the above steps[15].

2.1.9.2 Preparation of dissolved metal test samples (deconstruction with HNO_3)

Measurement of metal content in river water samples using SSA is done through the following steps:

1. The sample is homogenized, then the sample is filtered using a filter media with a pore size of 0.45 µm.
2. The sample was taken as much as 100 mL quantitatively and then the sample was put into a 250 ml beaker glass, then the sample was added to concentrated HNO3 solution as much as 5 mL and then closed the beaker glass using a watch glass.
3. After that the sample is heated (extruded) slowly until the volume ranges from 10 mL - 20 ml.
4. The watch glass is rinsed with distilled water and put the rinse water into a beaker glass.
5. The sample was transferred into a 100 mL volumetric flask and added distilled water until exactly the mark, then homogenized.

2.1.9.3 Testing of Samples

Aspirate the sample into the SSA and measure the absorption and record the measurement results.

3. Results and Discussion

3.1. Index of Diversity

Forensic entomology is the process of identifying samples using insects. In this study, the parameter utilized is the diversity index, which provides insight into the environmental conditions present by indicating the diversity of insect species present [6]. The complete list of all organisms identified at each research station is provided in Table 1.

Table 1. List of organisms found in Belawan River

	Taxa	Identity of test sample				
		Control	Settlement 1	Settlement 2	Industry 1	Industry 2
I	Class: Insecta					
	Fam: Naucoridac					
1	*Pelocoris sp*	-	55.5	200	177.7	66.6
	Fam: Elmidac					
2	*Stenelmis sp*	133.3	-	-	-	-
	Fam: Gyrinidac					
3	*Gyrinus sp*	22.2	-	-	-	-
	Fam: Perlidac					
4	*Neoperla sp*	66.6	-	-	-	-
	Fam: Simulidae					
5	*Simulium sp*	55.5	-	-	-	-
	Fam: Gerridae					
6	*Gerris sp*	88.8	22.2	44.4	--	
	Fam: Bactidae					
7	*Baetis sp*	55.5	-	-	-	-
	Fam: Calopterygidac					
8	*Calopteryx sp*	188.8	144.4	122.2	144.4	100
	Fam: Gomphidae					
9	*Progomphus sp*	55.5	-	-	-	-
10	*Ophigomphus sp*	88.8	33.3	88.8	77.7	100
	Fam: Petaluridac					
11	*Tachopteryx sp*	66.6	100	-	-	-
	Fam: Chironomidae					
12	*Chironomus sp*	244.4	-	-	-	-
	Fam: Macromiidac					
13	*Macromia sp*	-	55.5	133.3	155.5	122.2
	Fam: Heptagenidae					
14	*Leucrocuta sp*	-	77.7	100	144.4	33.3
	Fam: Psephenidae					
15	*Psephenus sp*	-	66.6	-	-	133.3

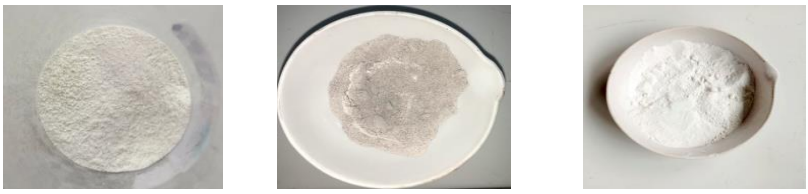
Taxa	Identity of test sample				
	Control	Settlement 1	Settlement 2	Industry 1	Industry 2
Total number of taxa	11	8	6	5	6
Total Density (Idn/m^2)	1066.6	555.5	688.8	700	555.5
Index of Diversity (H')	2.18	1.94	1.70	1.47	1.71
Index of Uniformity (e)	0.91	0.93	0.95	0.91	0.95
Domination (C)	0.01	0.02	0.01	0.01	0.02

Table 1 shows that aquatic insects in Belawan River are in class I, consisting of 14 families. The diversity index found in the Belawan River in 5 research stations, namely the control area is not polluted because it has H' 2.18, residential area 1 is slightly polluted because it has H' 1.94, residential area 2 is slightly polluted because it has H' 1.70, industrial area 1 is moderately polluted because it has H' 1.47, and industrial area 2 is slightly polluted because it has H' 1.71. According to Nuraini [5], the condition of a water body can also be seen from the diversity index (H'), in heavily polluted waters the value of H' <1, moderately polluted H' values between 1.0-1.5, lightly polluted H' values between 1.6-2.0, and unpolluted H' >2.0.

3.2. Preparation of Blood Clam Shell Adsorbent (Anadara granosa)

Activation was carried out by heating 105ºC, 500ºC, 900ºC, and H_2SO_4 acid immersion, after which washing the clam shell powder is carried out until the water from the washing of blood clams reaches pH 7 using distilled water to maintain the pH of the clam shell when used as an adsorbent so that in the implementation of adsorption the pH of the solution does not change.

The blood clam shells are activated, namely first heating at 105ºC aims to remove the remaining water content contained in the blood clam shells. Then, heating the blood clam shells at 500ºC aims to remove organic substances contained in the blood clam shells and can increase the surface area of the adsorbent with the aim of increasing the adsorption ability [3]. The results of the treatment by heating at 500ºC caused the colour of the blood clam shell adsorbent to change from white-brown to grey. Then activation by soaking the adsorbent using H_2SO_4 and heating at 900ºC aims to increase the surface area of the adsorbent by removing impurities contained in the adsorbent. This event is because the acid used can dissolve the constituent elements of the shell so that it becomes more organized and cleaner. Blood clam shells after heating can be seen in Figure 1 below.



(a) (b) (c)

Figure 1. Blood Clam Shells Heating 105oC (a) Blood Clam Shells Heating 500°C (b) Blood Clam Shells After Immersion with H_2SO_4 and Heating 900ºC (c)

3.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Blood Clam Shells (Anadara granosa)

The objective of adsorbent characterization is to ascertain the nature and attributes of adsorbents derived from blood clam shells. In this study, the functional groups present in blood clam shell adsorbents were identified using a Fourier Transform Infra-Red (FTIR) Spectrophotometer. The shape of the spectrum was examined to identify specific peaks that indicated the type of functional group present. The FTIR results for both activated and non-activated blood clam shell adsorbents are presented in Figure 2.

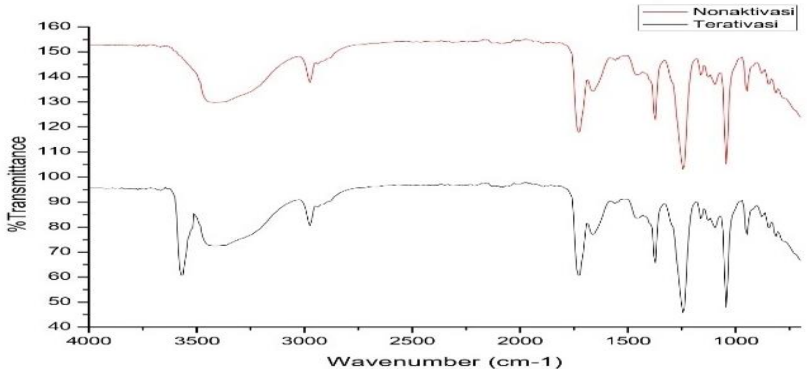


Figure 2. FTIR spectrum of the blood clam shell adsorbent, both in its original state and following the activation process.

Figure 2 displays the FTIR spectrum of the blood clam shell adsorbent prior to activation. It reveals an absorption band at wave number 3442.5 cm^{-1}, which is attributed to the amine group ($-NH_2$) and overlaps with the O-H group and the C=O group at absorption number 1786.5 cm^{-1}. This latter group functions as a metal binder. Following the activation process, there is an observable enhancement in the adsorbent's capacity to absorb at wave number 3452.5 cm^{-1}, specifically the amine group ($-NH_2$), and the emergence of a novel group at wave number 3643.7 cm^{-1}, namely the -OH group, which serves to attract positive ions. The negatively charged -OH group attracts positively charged metal ions, facilitating their absorption. Following activation at 900°C, the functional groups present in the clam shell adsorbent undergo a process of breakdown and shift, thereby increasing the adsorbent's capacity for adsorption. This is evidenced by the opening of pores on the surface of the adsorbent. The FTIR results demonstrate that the blood clam shell powder (*Anadara granosa)* possesses the requisite functional groups to support its ability to adsorb heavy metals, thereby making it a suitable adsorbent.

3.5. XRD Analysis of Blood Clam Shells (Anadara granosa)

The blood clam shell adsorbent was further characterized using the XRD method to determine the crystallinity of the activated blood clam shell adsorbent before adsorption and after adsorption through the intensity peaks that appeared. In this study, characterization using XRD with 2θ angle used is 20°-100°, as shown in Figure 3 below. After the clam shell powder was tested using x-ray diffraction, the results showed that the peaks with high intensity were found at an angle of 2θ of 25°, indicating the presence of $CaSO_4$ and also the presence of $CaCO_3$.

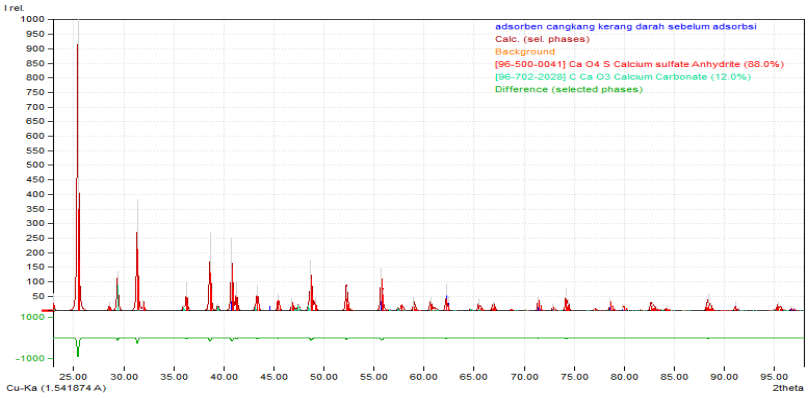


Figure 3. XRD Characterization Results of blood clam shell adsorbent before adsorption

3.6. SSA Analysis

Heavy metal concentrations were determined using a Perkin Elmer-400 AAS on Belawan river water samples. The quality standard limits or concentration levels of heavy metals in this study are based on Appendix VI of the Government Regulation of the Republic of Indonesia No. 22 of 2021 concerning the implementation of environmental protection and management. The results of measuring heavy metal levels before adsorption can be seen in Table 2.

Table 2 the results of heavy metal level measurements conducted before and after the adsorption process.

Location	Ni			
	Before (mg/L)	After (mg/L)	% adsorption	Quality Standard (mg/L)
Settlement 1	0.021	0.015	28.57	0.05
Settlement 2	0.015	0.010	33.33	0.05
Industry 1	0.045	0.031	31.11	0.05
Industry 2	0.032	0.021	34.38	0.05
Control	0.010	0.007	30.00	0.05

Table 2 known that the analysis of Ni heavy metal levels in Belawan River water samples revealed a notable decline following the adsorption process. These findings align with the quality standards outlined in Appendix VI of the Government of the Republic of Indonesia Regulation No. 22 of 2021 concerning the Implementation of Environmental Protection and Management. In Residential Area 1, a decrease in metal concentration was observed, with a percentage of Ni metal adsorption of 28.57%. The percentage of adsorption for Residential Area 2 is 33.33%. The percentage of adsorption for Industrial Area 1 is 31.11%. The percentage of adsorption of Industrial Area 2 is 34.38%. The adsorption percentage of the Control Area is 30.00%. Therefore, the utilization of blood clam shell waste as an adsorbent can effectively adsorb heavy metal levels in Belawan river water samples, thereby reducing metal levels in samples and improving the health of river ecosystems by adsorbing heavy metals in water polluted with heavy metals. The permissible limit of Ni metal as stipulated in Appendix VI of Government Regulation of the Republic of Indonesia No. 22 of 2021 concerning the implementation of environmental protection and management is 0.05 mg/L. Long-term exposure to heavy metals such as nickel (Ni) has been linked to a range of adverse health outcomes, including neurological disorders, organ damage, immune system dysfunction, and even cancer. The findings indicated that Ni levels were below the quality standard in five sampling locations, as outlined in Appendix VI of the Government Regulation of the Republic of Indonesia No. 22 of 2021 concerning the Implementation of Environmental Protection and Management, with a percentage of Ni metal adsorption of 28.57%. The percentage of adsorption for Residential Area 2 is 33.33%. The percentage of adsorption for Industrial Area 1 is 31.11%. The percentage of adsorption of Industrial Area 2 is 34.38%. The adsorption percentage of the Control Area is 30.00%.

Heavy metal pollution (Ni) has become a major concern for areas with industrial, mining, and poorly managed waste disposal activities, including in North Sumatra. Nickel is one of the heavy metals that can pollute rivers and have significant impacts on both aquatic ecosystems and human health. Ni pollution on river biota and human health has a very large impact[6]. Nickel pollution in rivers can damage the balance of aquatic ecosystems and threaten the survival of various types of aquatic biota. Nickel in high concentrations can cause poisoning in various aquatic organisms, such as fish, invertebrates, and aquatic plants. Nickel is toxic to fish by disrupting the function of the respiratory system and metabolism[16]. Accumulation of nickel in fish tissue can affect their nervous system, kidneys, and liver, even causing death in severe pollution conditions. Nickel pollution can inhibit the reproductive process of several species of fish and other aquatic organisms. Nickel can interfere with the development of eggs and larvae, and cause a decrease in the survival rate of young individuals. In addition, disruption of the growth of aquatic organisms can cause a decrease in the population of certain species that play an important role in the aquatic food chain. Nickel pollution can reduce biodiversity in river ecosystems. Species that are less tolerant of these heavy metals tend to disappear, while species that are more tolerant of contamination may reproduce more rapidly, but often at an unbalanced rate. This can cause disruption to the structure and function of aquatic ecosystems. Microorganisms that play an important role in nutrient cycling and the breakdown of organic matter in rivers can also be affected by nickel. Nickel pollution can affect the survival of decomposing bacteria and affect biological processes such as the decomposition of organic matter, which can change river water quality[8][3].

Nickel pollution is not only a risk to river ecosystems, but can also pose a serious threat to human health, especially for communities that depend on rivers as a source of clean water or a source of livelihood. Nickel can enter the human body through consumption of contaminated water or through direct contact with the skin. Exposure to high amounts of nickel can cause acute poisoning with symptoms such as nausea, vomiting, diarrhoea, and respiratory problems. In the long term, chronic nickel exposure can cause more serious health problems, such as damage to the kidneys, liver, and nervous system. Long-term exposure to nickel can increase the risk of cardiovascular disease and respiratory disorders, especially for workers in industries that use nickel

or for people who live close to polluted areas. Nickel can cause inflammation of the respiratory tract, asthma, and even increase the risk of lung cancer in individuals who are exposed for a long time. Nickel has been classified by the International Agency for Research on Cancer (IARC) as a group 1 carcinogen[17][18], which means it can cause cancer in humans. Long-term exposure to nickel dust or vapor in the air or water can increase the risk of cancer, especially lung cancer and nasal cancer. Nickel exposure can affect the human reproductive system. Nickel has the potential to cause damage to reproductive cells, interfere with development of the fetus, and increase the risk of genetic abnormalities or premature birth. Accumulation of nickel in the body can also cause dangerous genetic mutations. Ni can cause skin allergies, especially in individuals exposed to nickel for a long period of time. Allergic contact dermatitis due to nickel can occur when the skin comes into contact with jewellery or items containing nickel, and symptoms can include redness, itching, and irritation. However, in this work, Water Quality analysis is very important in Routine monitoring of water quality in rivers that are potentially contaminated by nickel is very important to detect and control contamination levels.

4. Conclusion

The contamination of the Belawan River has been investigated through the application of forensic entomology, utilising the diversity index parameter. The diversity index data indicate that the Belawan River waters in Residential Area 1 are lightly polluted (H' 1.94), while those in Residential Area 2 are also lightly polluted (H' 1.70). The waters in Industrial Area 1 are moderately polluted (H' 1.47), and those in Industrial Area 2 are likewise lightly polluted (H' 1.71). In contrast, the control area is not polluted (H' 2.18). Heavy metal analysis was conducted using solid-phase extraction and SSA analysis. The concentration of heavy metals in the samples was found to have decreased. The percentage of adsorption of Ni metals in Residential Area 1 is 28.57%. In Residential Area 2, 31.11%. In Industrial Area 2, 34.38%, while in the Control Area, they were 30.00%. The findings indicated that the metal concentrations at the four sample locations exceeded the quality standards set forth in PP No. 22 of 2021.

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6. Conflict of Interest

The author declares no conflict of interest

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