MODELING THE OXIDATION REDUCTION POTENTIAL (ORP) IN URBAN RIVER OF JOHOR BAHRU USING FIELD SPECTRORADIOMETER

Soo Kai Ting (1), Mohd. Rizaludin Mahmud (1)(2)

[1] Department of Geoinformation, Faculty of Built Environment and Surveying, Universiti Teknologi Malaysia, 81310, Skudai, Johor, Malaysia

[2] Geoscience & Digital Earth Centre (INSTEG), Faculty of Built Environment and Surveying, Universiti Teknologi Malaysia, 81310, Skudai, Johor, Malaysia

Email: ktsoo2205@gmail.com; rizaludin@utm.my

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ABSTRACT: Oxidation reduction potential (ORP) is an important indicator used in estimating the biochemical reaction in the water. Urban areas are a known source to produce pollutants, chemical and biological waste to the water drainage and river; therefore, rapid assessment method would be useful for large-scale application. It would be an advantage if there is a low-cost and short-time measurement method instead of using the conventional and physical laboratory measurement of ORP. Hyperspectral remote sensing technique is able to provide information on water contamination and pollutants by observing spectral changes continuously and inexpensively. In this study, the hyperspectral sensing obtained via the field spectroradiometer is used to estimate the ORP values using the water samples taken in urban drainage and river in Johor Bahru district. The spectral region that is sensitive to ORP values changes is identified using the differential techniques. The results showed that the spectral reflectance of water samples peaks frequently at the red and near-infrared region between 648-654nm, while the ORP values ranged from -56.333 to 472.667mV. The biochemical reaction of nitrification and denitrification are both result in significant amounts of nitrates present in the water. It was found that the empirical model predicting ORP using field hyperspectral spectra has a moderate negative correlation of 76%.

1. INTRODUCTION

Oxidation reduction potential (ORP) is one of the water quality parameters that refers to the measurement of potential of a water body in oxidising and reducing another substance (Anderson & Herdan, 2000). It also can be defined as redox which able to act as a mean alternative to indicate types of biochemical reactions sources and pollutant in the water system. When precipitation flows from urban area as runoff and end up to nearby rivers, the rivers would either dissolve the

anthropogenic pollutants through biochemical reaction or otherwise carry the minerals and particles such as nitrate, phosphorus and ammonia to the other stream, rivers, lake, ocean or even being contaminated water. Pollutant contamination not only make drinking water treatment more difficult, extend process time but also deplete the oxygen contents in river water that available for aquatic organisms and in the end causes dead of every single living thing inside the water. ORP allows to define possible water contaminate area also formulate appropriate management plans to decrease or terminate movement of pollutants from watersheds to water bodies in order to reduce impacts from water (Mak Kisevic, 2016).

The traditional method of measuring ORP needed in situ sampling and physical contact to the water molecule. The method leads to a high cost for instruments and materials charges also long time for ORP measurement. As substances that dissolved or appeared to water can significantly change the backscattering characteristics and respond from a water system in whole range of spectral reflectance included visible and non-visible dissolved substances (Jerlov, 1976), remote sensing has become a common and popular technique which correlates the measured changes of spectral characteristic by empirical or analytical models to a water quality parameter (Ritchie, et al., 2003). Field hyperspectral remote sensing is one of the most common remote sensing technologies today that obtain accurate and detail spectral information with no constraints on acquisition time from any reachable study site. Hyperspectral remote sensing is believed as a faster and lowest cost approach to detect and monitor water quality parameter instead of depending on contact or in situ traditional measurement method.

In this research, linear regression analysis was used to create an empirical model for predicting ORP in the studied area.

Biochemical Reactions and Corresponding ORP Values

Biochemical Reaction	ORP, mV
Nitrification	+100 to +350
cBOD degradation with free molecular oxygen	+50 to +250
Biological phosphorus removal	+25 to +250
Denitrification	+50 to -50
Sulfide (H_2S) formation	-50 to -250
Biological phosphorus release	-100 to -250
Acid formation (fermentation)	-100 to -225
Methane production	-175 to -400

Figure 1 Biochemical reactions and it corresponding ORP values (H.Gerardi, 2007)

2. METHODOLOGY

The workflow of the methodology of this research is illustrated as figure 2. A null hypothesis assumes the ORP has relationship with spectral reflectance.

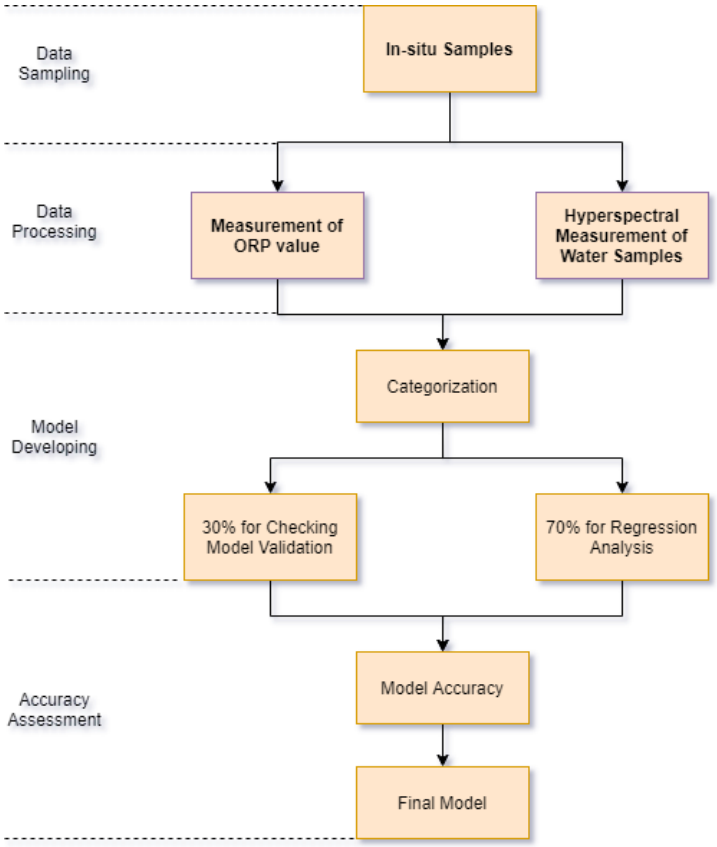

Figure 2 Flow chart that describing methodology

2.1 Study Area

This study covers rivers that located at urban area of the south of the Johor. The selected study points are the rivers that situated in urban area which receiving direct and indirect wastewater from nearby housing, industrial and agriculture area. Besides that, the selected study stations also near to the water treatment plants of Ranhill SAJ.

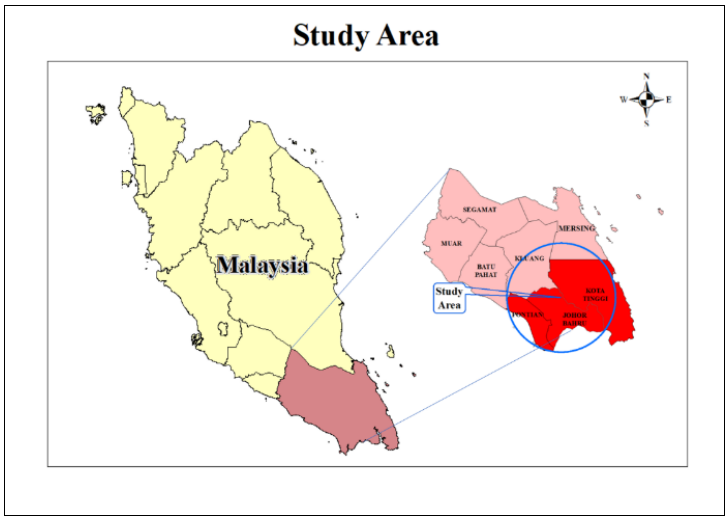

Figure 3 Study area

2.2 In Situ Sampling and data collection

Water samples collected at the study area – urban river and drainage of Johor Bahru. A total of forty-four samples were taken from the study area in urban region of Johor such as Sungai Semengar, Sungai Tiram, Sungai Sayong and Taman Aman Senai.The GPS location of each sampled site recorded. The water samples collected at each site were then be stored in transparent polyethene bottles until returned to the laboratory and stored in room temperature for further analysis.

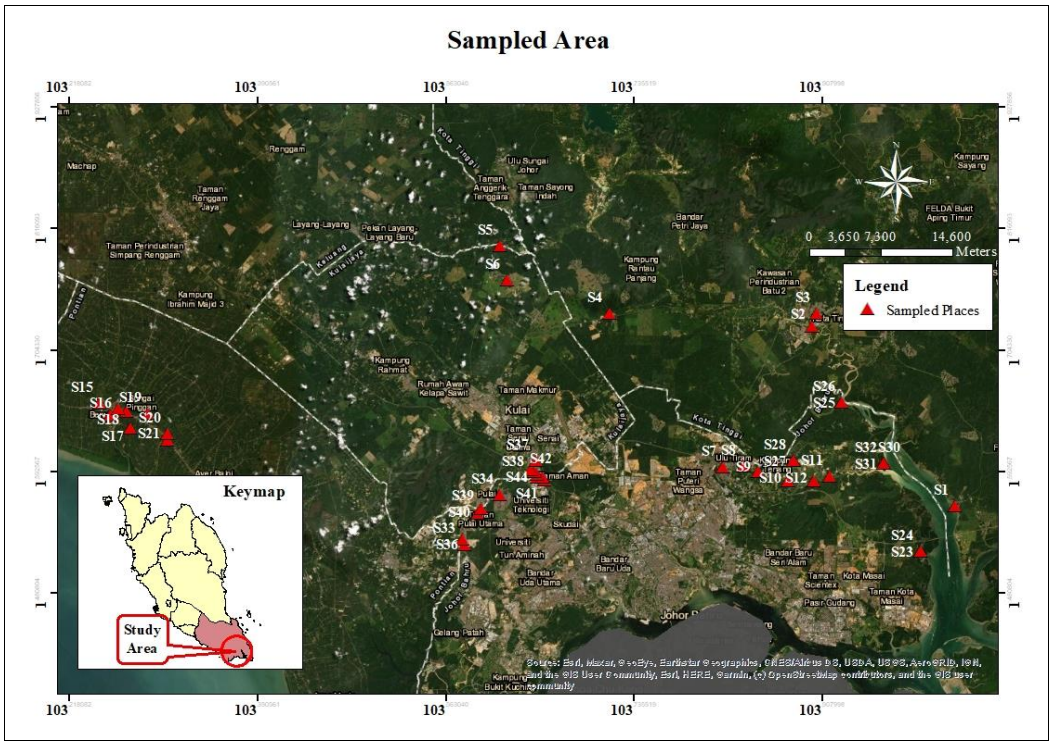

Figure 4 Sampled area

Measurement of ORP: Horiba Multiparameter Water Quality Checker U-50 device used in this study to obtain ORP in shorter time. The device can measure and indicate nearly 11 water quality parameters simultaneously. However, only the ORP value used to achieve the research's objectives. As to increase understanding and exploring the possible biochemical reaction inside the water samples and how the effect of the chemical substance on the ORP values, a chemical test on the appearance of nitrate, ammonia and phosphate was performed. The higher concentration of nitrate, ammonia and phosphate can be explained there is a high possibility that excess fertilizers entered the river stream system from nearby vegetation land.

Hyperspectral Measurement of Samples: The water samples that brought to the laboratory for measurement of spectral reflectance. Spectral Evolution RS-3500 Spectroradiometer is an optical device that uses detectors to measure the distribution of radiation in a specific wavelength

region other than uses of photographic film. It measures the spectral behaviour and characteristic of the region of visible, near-infrared (VNIR) and short-wave infrared (SWIR) spectra with a precision of 1nm within 350 – 2500nm. In this research, Spectral Evolution RS-3500 Spectroradiometer used to break down light intensity that reflected or scattered from the water samples that collected from rives in urban area of Johor into spectral components, digitized the signal as a function of wavelength and displayed it through a computer. The obtained spectra then be inspected to determine the region that might consists of useful information with a constant rising or decreasing to the peak.

As the chemical substances causes various peaks in raw data, the data is needed to be normalized (Zeef, 2004). Minimum normalization, maximum normalization and standard normal variate normalization were tried to the samples spectra, peak normalization with maximum value of the intensity was chosen in the end as it showed best fit for data (Julian, et al., 2019). After normalization, a Savitzky-Golay second spectral derivative with 21 smoothing points and 2nd order polynomial were computed (Mancini, et al., 2019). Savitzky-Golay derivative was used as it can be a good noise filter by removing background due to scattering (Indrajit , 2019). The derivatives of spectra help to reveal information in a spectrum.

Savitzky-Golay (SG) filter is a digital filter for smoothing and differentiation which introduced by Abraham Savitzky and Marcel. J. E. Golay in 1964. The process of SG filter is derived from mathematical method of simplified least squares known as convolution. The concept of convolution generated by using simple moving average. The procedure is to multiply the integer of convolution coefficients with the number opposite it and dividing the product to normalizing factor (Savitzky & Golay, 1964). According to the concept, the expression 2.1 as below applied to the normalized spectra in the 21-moving window.

$$Y_j = \frac{1}{33649}\left(190_{y_j-10} + 133_{y_j-9} + 82_{y_j-8} + 37_{y_j-7} + -2_{y_j-6} + -35_{y_j-5} + -62_{y_j-4} + -83_{y_j-3} + -98_{y_j-2} + -107_{y_j-1} + -110_{y_j} + -107_{y_j+1} + -98_{y_j+2} + -83_{y_j+3} + -62_{y_j+4} + -35_{y_j+5} + -2_{y_j+6} + 37_{y_j+7} + 82_{y_j+8} + 133_{y_j+9} + 190_{y_j+10}\right) \quad (3.1)$$

where yj is the value of normalised spectra and 190, 133, 82….. are convolution coefficients based on the convolution coefficient table published by Savitzky and Golay in the article of establishing the Savitzky Golay smoothing and differentiation method.

Modelling the Oxidation Reduction Potential

The water samples were categorised randomly into 30% (13 samples) for validation and 70% (31 samples) for model development. A regression model with linear assumption has been chosen for the research to show the relationships between the data from spectroradiometer and ORP value as it is procedural simple (Amiya, 2020). ORP value measurement and hyperspectral data were statistically analysed using Minitab software. ORP as dependent variable and highly significant wavelength of hyperspectral spectra as independent variable.

2.3 Accuracy Assessment

To validate the regression model, the data of the test set or validation dataset were used to find how well the model works by seeking mean squared error from the test set (Diego , et al., 2012). The correlation coefficient of training set with appropriate p-value also used in supporting the relation and accuracy of the model. The prediction of the test set is used to calculate the error, which is the difference between the predicted response and the observed actual response the results were used to compare to the model created.

3.0 RESULT AND DISCUSSION

The oxidation reduction potential measures the ability of the rivers to break down pollutants and contaminants through biochemical reaction by exchanging electrons. Electrons can be lost and gained from any substance; the most common example is the dissolved oxygen required for bacterial biochemical reactions. The results of the measured ORP values for the water samples ranged from -56.333 to 472.667mV with an average value of 171.826mV. Sample 29 recorded the highest value of positive ORP within the water samples indicating the water sample is a strong oxidizing agent (Zulhafizal, et al., 2015). Normally, a healthy water system has the ORP value in the range of 300mV to 500mV (Wetzel, 1983).

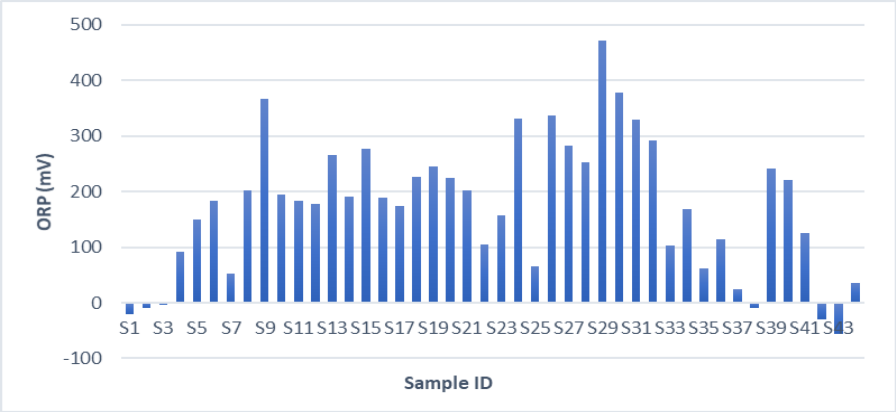

Figure 5 ORP values in millivolts (mV) for all samples

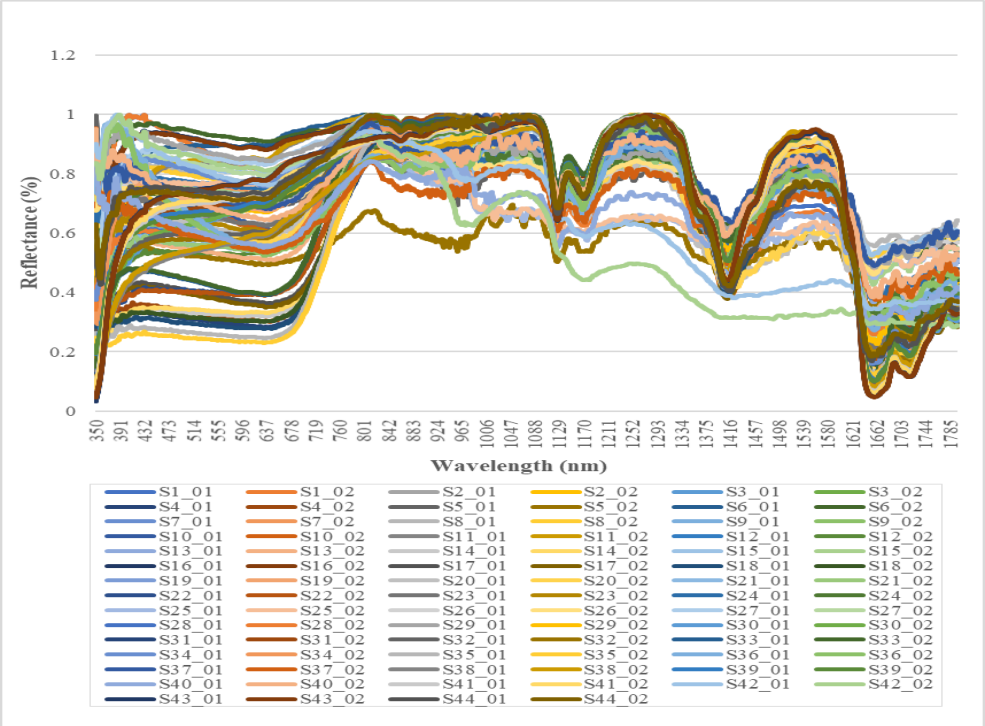

Figure 6 Normalized spectra

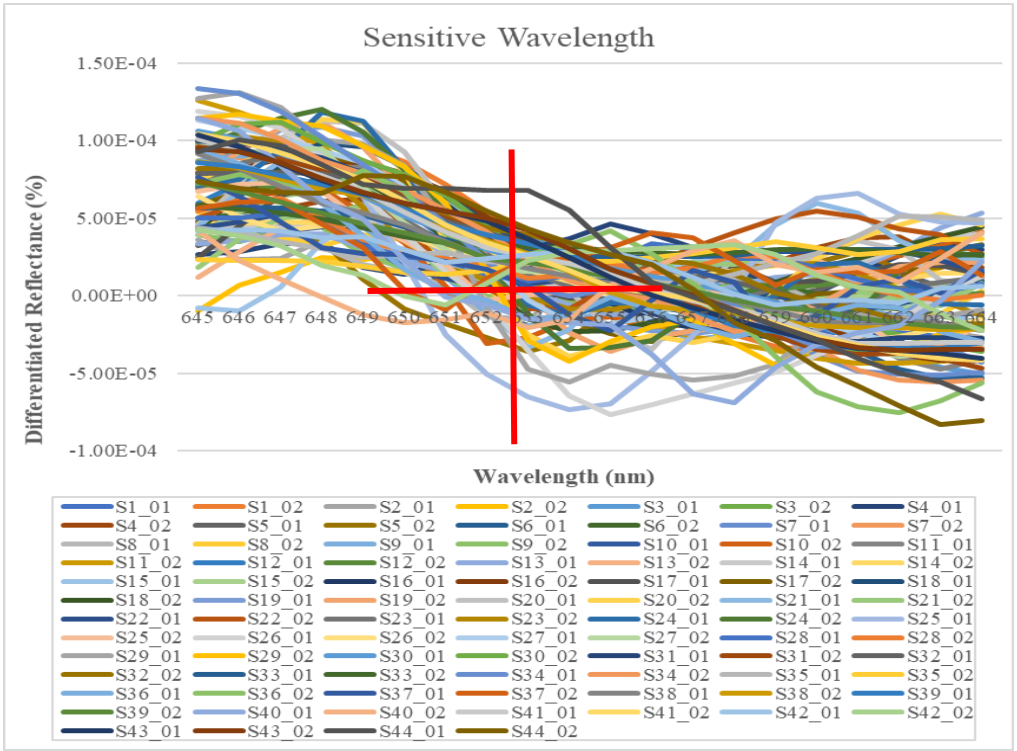

Figure 7 Most appropriate and correlated wavelength (654nm)

The result of normalized spectra showed the spectral characteristics of all water samples are basically the same within each other. The result of normalized spectra showed the trend in visible region still showed a dramatic rise at blue light region and a steady drop in the red-light region.

Meantime, the spectral reflectance of water samples peaks frequently at the red and near-infrared region. Commonly, wavelength that presents the peaks and troughs in reflectance selected as the slope of the reflection spectrum curve changes (Shafique, et al., 2003). Hence, the sensitive regions were distinguished based on the plausible peaks and reasonable falls of all hyperspectral reflectance.

After differentiated the normalized spectra by Savitzky Golay method, all possible frequency wavelength (plausible and logically peak and trough) of Savitzky-Golay second derivatives at the identified sensitive regions were tested for the relationship with ORP values until it was found wavelength 654nm and ORP correlated with the highest certainly.

The ORP and spectral data were statistically analyzed and an empirical model was established. The empirical model describing ORP by a regression equation or algorithm as ORP = 176.1-4005935 Wvl 654.

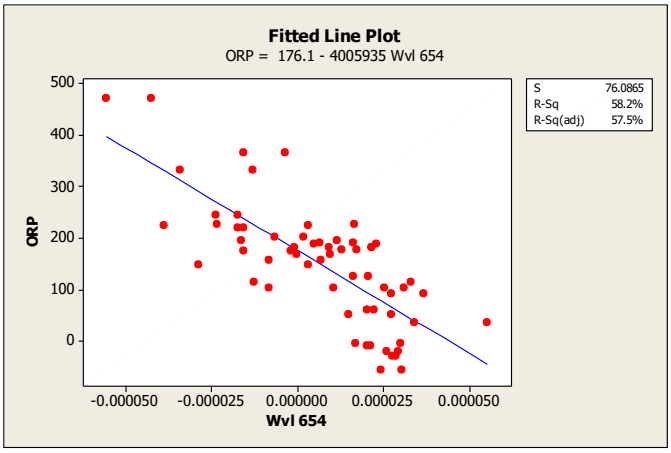

Figure 8 Regression model between ORP and wavelength 654nm

The R-squared (R^2) of the empirical model is 0.582, and adjusted R-squared is 0.575 and the p-value is 0.00. Consequently, the correlation coefficient of the generated model is -0.76. As correlation coefficient measure the strength of the relationship between two variables, the wavelength 654nm shows the highest effective and correlated wavelength in this set of data with a moderate negative correlation 0.76. R^2 is the coefficient of determination which represents the proportion of the response variable, ORP that is accounted by the predictor variable, wavelength 654nm (Chatterjee, et al., 2000). In this study, it can be concluded that the algorithm provides a moderate fit to the data set. The null hypothesis accepted as the result proved there is a relationship between ORP and hyperspectral spectra.

In terms of accuracy evaluation, the model was found to be difficult to distinguish between nitrification and denitrification wells. This may because of the spectroradiometer detects the

chemical substances (suspended or dissolved) in water (Raúl , 2014). In short, the presence of nitrate may be related to nitrification or denitrification. The ORP value can be in the range of positive or negative values. In other words, if there is a large amount of nitrate in the water system without other necessary conditions, such as bacterial enzymes, suitable temperature and pH, the biochemical reaction of denitrification cannot be carried out. Moreover, certain biochemical reactions can proceed forward and backward in response to certain conditions until the water system reaches equilibrium (Geoffrey , 2000). When the forward and reverse reaction happens in same rate, it led to the equilibrium state. To solve this problem, the predicted biochemical reaction was compared with the observed biochemical reaction to determine the accuracy level. In short, the model has moderate accuracy of 53.85%.

4.0 CONCLUSION

The urbanization of Johor has caused countless wastewater runoff in nearby rivers, resulting in excessive nutrient enrichment and eutrophication, and indirectly affected the biochemical reactions in the rivers and eventually caused river pollution (Zazali, 2020). The common value of ORP in the urban rivers and drainage of Johor Bahru is about 171.826 mV, which indicates the nitrification reaction in the presence of dissolved oxygen. The chemical tests results revealed excess nitrates discharged to the nearby rivers in urban setting of Johor especially sample 8. Spectral Evolution RS-3500 provides reflectance at 350nm to 2500nm for all water samples, which peaks in the red and infrared region. The region most sensitive to ORP was found at the wavelength of 648 to 654 nm. An empirical model of predicting ORP has been developed with moderate negative correlation of 0.76 and R^2 of 0.582 for the uncontrolled research ($p = 0.000$), the null hypothesis accepted.

The results of this study are useful to be a guide for further studied in modeling ORP using different method of remote sensing techniques. It can't be denied that ORP is useful in water treatment and water supply as it easier prediction on practical materials and substances that needed for treating polluted water into drinking water and usable water supply for daily life. An ORP model can beneficial many people in different fields.

5.0 REFERENCE

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