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FOREWORD

Welcome to the 8th volume and issue number 1 of the ESTEEM Academic Journal UiTM (Pulau Pinang): a peer-refereed academic journal devoted to all engineering disciplines. This issue of journal sees a new Chief Editor and marks the journal's first electronic publication. Using the e-journal inauguration as an occasion, I would like to thank many people who created the opportunity for this e-journal to be born and who made it happen. First and foremost, I would like to extend my sincere appreciation and utmost gratitude to Associate Professor Mohd Zaki Abdullah, Rector of UiTM (Pulau Pinang), Associate Professor Ir. Bahardin Baharom, Deputy Rector of Academic Affairs and Dr. Mohd Subri Tahir, Deputy Rector of Research, Industry Linkages, Community & Alumni for their unstinting support towards the successful publication of this e-journal. Not to be forgotten also are the constructive and invaluable comments given by the eminent panels of external reviewers and language editors who have worked assiduously towards ensuring that all the articles published in this journal are of the highest quality. A special acknowledgement is dedicated to all committees, publication department, and many other relevant parties for making this journal a success. Their affective commitment and close cooperation have facilitated the realization of this journal. Last but not least, my greatest thanks go to all the authors for their interest in publishing with ESTEEM. Their manuscripts are an expression of their commitment towards research and development which, in due course, would benefit the local, national and international communities. Hence, I would like to extend my warm invitation to all researchers who are actively involved in the field of engineering to publish their work in ESTEEM.

Dr. Chang Siu Hua
Chief Editor
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COLOUR REMOVAL FROM INDUSTRIAL WASTEWATER USING BLADDERWORT AS ADSORPTION MEDIA

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ABSTRACT

Adsorption process in wastewater treatment using natural products has become popular due to its low cost and environmentally friendly approach. However, less attention has been focused on the ability of aquatic plant species such as Bladderwort as an adsorption media. This paper discusses the effectiveness of using Bladderwort as a natural adsorbent for the removal of colour from wastewater. Under batch technique, the effect on adsorbent size (75-600 µm), wastewater pH (pH 1-12) and agitation speed (50-250 rpm) was determined. The results indicated that the removal efficiency of colour is in tandem with the size of Bladderwort as higher size particles have more efficiency on removal of colour. Besides, the wastewater pH also plays a major role in the colour removal efficiency where the highest removal was observed in acidic condition compared to alkali. However, the agitation speed is least affected in the removal of colour. The optimum size of Bladderwort and pH to effectively remove the colour was at 600 µm and pH 3.

Keywords: adsorption process; bladderwort; colour removal; natural adsorbent

1. INTRODUCTION

Water is cloudy or gives its colour when visible emission is absorbed from impurities of dissolved materials such as natural metallic ions. Besides, the suspended humus, weeds, plankton, peat materials and industrial waste in water capture the light sources and yield the colour of water. The coloured wastewater is not only aesthetically unpleasant but there are also environmental concerns about the possibilities of harmful materials, which have been exhibited through the colour of water (Lu, Zhang, Zhao, & Wu, 2010). These materials can be toxic and carcinogenic and if this water is discharged without treatment, adverse effects will arouse to the environment.

There are few manufacturing industries that generate significant concentration of colour in their effluent from chemical processes of their products. Such industries that are concerned on the overloading of colour in their wastewater are textile industries, pulp mill industries, paper mill industries, Kraft mill industries and food production industries. The excess of natural and synthetic dye from industries which contributes to the colour of wastewater which are often described as a source of pollution are as shown in Table 1.

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Table 1: Colour of Wastewaters Released from Industries

Effluent/ Industry	Colour of Wastewater	Physical/ Chemical Method	References
Aqueous solution	Methylene Blue (MB)	Adsorption (Pineapple leaf powder)	Weng, Lin, and Tzeng (2009)
Synthetic waste solution	Drimarene Red CL-3B	Ozonation	Konsowa, Ossman, Chen, and Crittenden (2010)
Aqueous solution	Malachite Green (MG)	Adsorption (Coffee bean)	Baek, Ijagbemi, and Kim (2010)
Textile Industry	Blue Bezaktius-GLD150 Black NovacronR	Nano-filtration	Khouni, Marrot, Moulin, and Amar (2011)
Pulp and Paper Mill Industry	Brownish Colour	Ozonation	Kreetachat, Damrongsri, Punsuwon, Vaithanomsat, Chiemchaisri, and Chomsurin (2007)
Natural wastewater contains of humic acid	Yellow or brown Colour	Coagulation	Edwards and Amirtharajah (1985)

Generally, the treatment of wastewater contains high concentrations of colour and requires advanced technology which is costly. The advance oxidation process using ozonation (Konsowa et al., 2010), photo fenton process (Kang, Liao, & Po, 2000), electrochemical technique (Malpass, Miwa, Machado, & Motheo, 2008) and membrance process (You, Tseng, & Deng, 2008) are norm use to treat wastewater due to colour.

Adsorption process has gained momentum in recent years for removal of colour from wastewater as its low cost approach. Besides, adsorption process has widely been used for separation and purification in industrial processes due to its efficiency removal of pollutants and operative in most natural physical and chemical systems. In wastewater treatment, commercially limestone (Sdiri, Higashi, Jamoussi, & Bouaziz., 2012), zeolite (Salem & Sene, 2011) and activated carbon (El-Sikaily, Nemr, Khaled, & Abdelwehab, 2007) have long been used as common adsorbent. The activated carbon remains expensive because of its widespread use in various purification procedures. The high demand of commercial adsorbent has lead to the development of alternative low-cost adsorbents (Viraraghavan & Ramakrishna, 1999). The use of low cost natural adsorbents derived from waste products such as chitosan (Wu, Tseng, & Juang, 2010; Ngah, Teong, & Hanafiah, 2011) and activated carbon which can be derived from oil-palm shell (Guo & Lua, 2003; Sumathi, Bhatia, Lee, & Mohamed, 2010) have been studied extensively. Besides the potential of varies floating aquatic plants as an adsorbent such as Lemna Minor (Horvat, Vidaković-Cifrek, Orescanin, Tkalec, & Kozlina, 2007), seaweeds (Senthilkumar, Vijayaraghavan, Thilakavathi, Iyer, &

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Velan, 2006; Park, Yun & Lee, 2006) and marine algae (Kumar, King, & Prasad, 2006; El-Sikaily et al., 2007), waterweed (Eichhornia crassipes) (Susarla, Medina, & McCutcheon, 2002) were also investigated. However to date, there is a very scarce research on the Bladderwort (Ulticularia vulgaris), another species of floating aquatic plant as an adsorbent. Figure 1 and Figure 2 show the picture of common Bladderwort and its distribution at all over the world.

Figure 1: Structure of the Common Bladderwort (*Ulticularia vulgaris*)

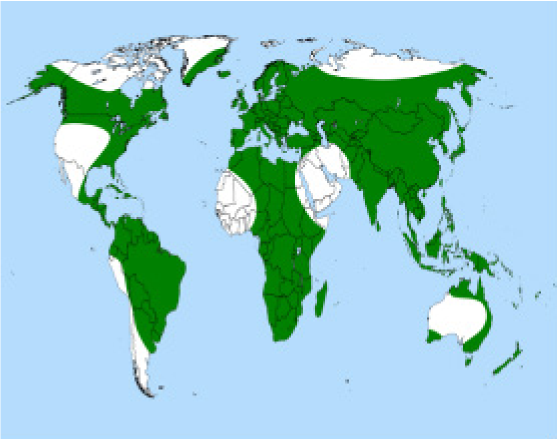

Figure 2: Bladderwort Distribution in the World (Juniper, Robins, & Joel, 1989)

Generally, in adsorption process, the pollutants (adsorbate) will accumulate at the surface of an adsorbent and creates a thin layer on the adsorbent's surface. The attachment of adsorbate to the surface of adsorbent can be due to Van der Waals interaction, covalent bonding or electrostatic forces (Hammer, 2008). Aquatic plants species are more beneficial as it can absorb pollutants from the surrounding water via two processes, biosorption and bioaccumulation (Keskinkan, Goksu, Yuceer, Basibuyuk, & Forster, 2003). The unique structure of aquatic plant such as Bladderwort offer sophisticated entrapment and adsorption surface as its bladders can entrap and digest small particles. Besides, this bladder-like trap which can exceed 5 mm diameter size can promote larger surface area for adsorption.

Besides the size of adsorbent, the performance of adsorption process also depends on the pH and agitation speed (Inglezakis, Stylianou, Gkantzou, & Loizidou, 2006; Senthilkumar et al.,

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2006). Thus the aim of this study is to investigate the ability of Bladderwort as an adsorbent for the removal of colour in water. It was tested using different sizes of Bladderwort, pH of wastewater and agitation speed. Colour occupies an important role in characterizing the treatability and the degree of contaminant removal in wastewater as it can physically been observed via the naked eyes.

2. METHODOLOGY

In this study, all the water quality analysis was tested in accordance to the Standard Methods for the Examination of Water and Wastewater, (American Public Health Association, American Water Works Association, Water Environment Federation, 2006). The framework as illustrates in Figure 3 was adopted in this study.

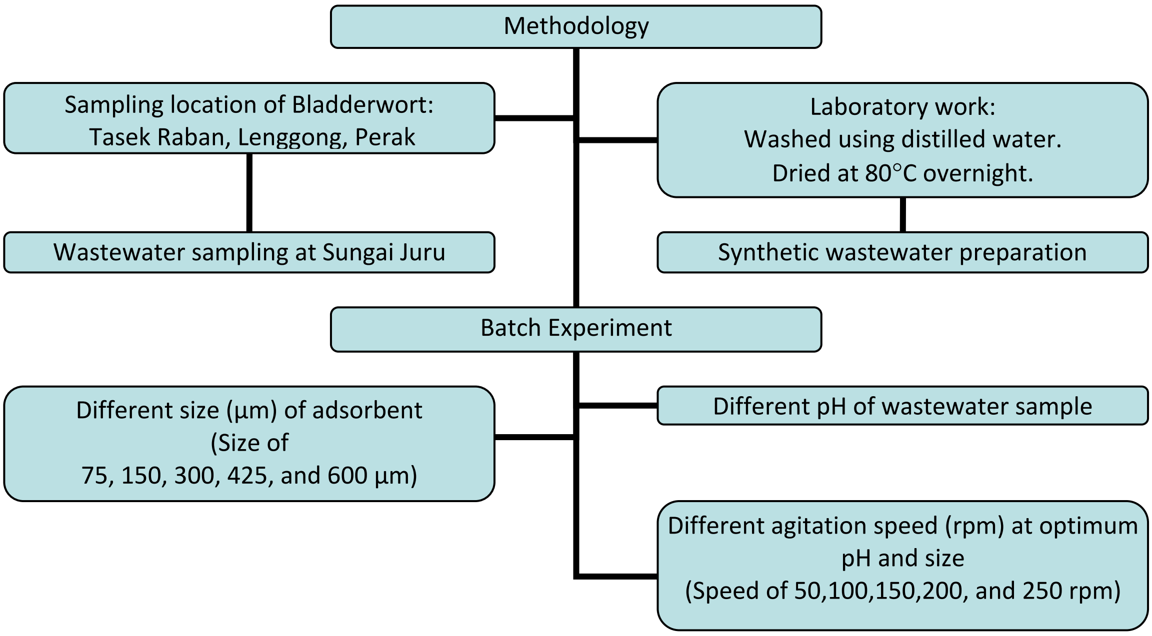

Figure 3: Methodology Framework

2.1 Collection and Preparation of Bladderwort

Bladderwort was collected from Tasik Raban, Lenggong Perak. It was washed four times using tap water and rinsed two times using distilled water before subjected to oven dried at 80 ^{o}C. About 150 g of dried Bladderwort was obtained and blended. It was sieved using Sieve Shaker to get range of size between 75 – 600 µm.

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Figure 4: Bladderwort Was Rinsed Thoroughly with Distilled Water

Figure 5: Bladderwort Was Dried in an Oven at 80 ^{o}C

Figure 6: Blending Process

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Figure 7: Bladderwort in the Form of Powder

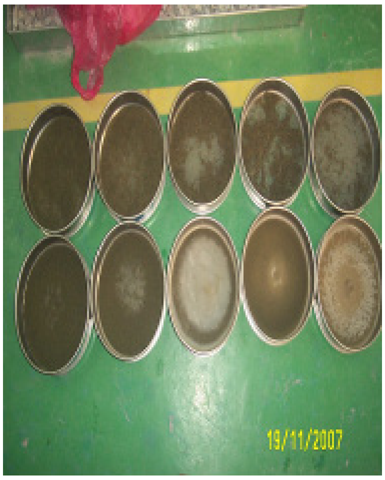

Figure 8: Bladderwort was Sieved at Various Sizes

Figure 9: Different Size of Bladderwort Range from 75 to 600 µm

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2.2 Wastewater Sampling and Preservation

In this study, an artificial wastewater was prepared to simulate the condition of brown colour produced from the wastewater which contains organic matter. This preparation involved the mixed clay soil of Sg. Juru at the ratio of 0.005 (w/v). The water was taken at the downstream of the Bukit Minyak area, Seberang Perai, Pulau Pinang by grab sampling. Few industries and residential areas are found at the upper stream of Sg. Juru are as shown in Figure 10. The polypropylene containers were filled with Sg. Juru water, preserved in an ice-box and immediately transported to the Environmental laboratory, Faculty of Civil Engineering, Universiti Teknologi MARA Pulau Pinang. The colour of Sg. Juru water and artificial wastewater reported as apparent colour and measured using DR 2400 HACH Spectrophotometer in the unit of Platinum-Cobalt (PtCo). The water quality parameters of Sg. Juru and the prepared artificial wastewater are as tabulated in Table 2.

Table 2: Sg. Juru and Artificial Wastewater Quality Parameter Used in this Study (*Standard B of the Environment Quality [Sewage and Industrial Effluents] Regulation 1979, Under Environment Quality Act of Malaysia 1974)

Water Quality Parameter	Sg. Juru	Artificial Wastewater	Standard B*
pH	7.4	7.0	5.5 - 9
Suspended Solid (mg/L)	50	5175	100

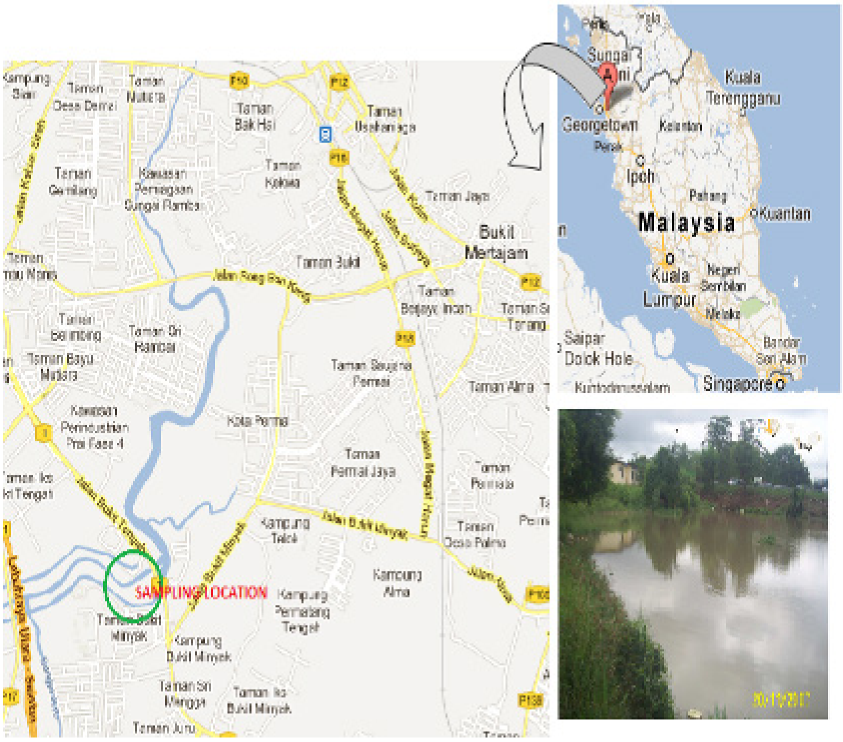

Figure 10: Sampling Location of Sg. Juru at Bukit Minyak, Seberang Perai, Pulau Pinang

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2.3 Batch Experiment

Batch adsorption experiments were conducted by shaking 150 ml wastewater containing 1 g of Bladderwort in 250 ml Erlenmeyer flask at room temperature (Orbital Shaker model 719). The experiment was conducted in one hour shaking time followed by one hour settling time. For each shaking operation, five (5) different sizes of Bladderwort which were 75, 150, 300, 425 and 600 µm were used at wastewater pH of 1. The experiment was repeated at different pH that were 3, 5, 7, 9 and 12. The pH of wastewater was adjusted by 0.1 M H_2SO_4 or NaOH at the beginning of the experiment and not controlled afterwards and it was measured by using Benchtop pH / Mv / Temperature. The colours of wastewater after the pH adjustment are as depicted in Table 3. The effect of agitation speed on the removal of colour was investigated at the rate of 50, 100, 150, 200, and 250 rpm. Each treatment was repeated for 3 times and the average value was used in the results. The apparent colour of wastewater was determined before and after of each experiment. The percentage removal of each parameter was calculated as following equation:

$$\%\,\mathrm{Re}\,moval = \left[\left(C_i - C_f\right)/\,C_i\right] \times 100\% \quad (1)$$

Where, C_i = initial colour concentration of sample, C_f = final colour concentration of sample.

Table 3: Initial Colour of Wastewater at Predetermined pH

pH	Initial colour (PtCo)
pH 1	450
pH 3	700
pH 5	810
pH 7	925
pH 9	525
pH 12	650

3. RESULT AND ANALYSIS

3.1 Introduction

The effectiveness performance of Bladderwort as an adsorbent was evaluated for the percentage removal of colour. It can be determined by comparing the colour contains in the wastewater before and after the treatment process.

3.2 Effects on Different Sizes of Bladderwort on the Removal of Colour

Surface area of the adsorbent is an important parameter for the efficiency of adsorption process. Figure 11 shows the percentage removal of colour at different sizes of Bladderwort. It obviously shows that on increase in size, significantly affect on the removal efficiency of colour. The colour removal was drastically reduced from 925 PtCo to less than 540 PtCo when Bladderwort sizes of 75-600 µm were introduced (pH 7). These changes showed 42% - 63% of colour removal. At pH 9, Bladderwort size of 75 µm absorbed 40 PtCo of colour from the initial colour measured of 560 PtCo which lead to 7.1% of removal. When Bladderwort

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size of 600 µm was applied, the removal % of 29.5 was calculated with the colour remained in wastewater at 395 PtCo. The colour adsorbed efficiently to the surface of Bladderwort when the larger size of this adsorbent was applied. The adsorption capacity was reduced when the smaller size of Bladderwort was introduced. This finding deviates from what normally is found from the previous studies (Inglezakis & Poulopoulos, 2006; McGhee & Steel, 1991). It is hypothesized that the smaller size will offer larger surface area that resulted in the greater removal of pollutants. Inglezakis and Poulopoulos (2006) found that dust particles was more efficient than granular form of mineral as the attribute increased the mineral surface area, which helps the phenomenon of ion exchange.

The reason to the finding of the current study might due to the dissolution of smaller particle of Bladderwort into the water especially at the size of lower than 200 µm which contribute to the increase in the colour of water. Moreover, another reason that makes the removal of colour being less competent in smaller size of adsorbent because this adsorbent will generate organic debris which in turn increases the organic loading in the wastewater. This organic matter will contribute to the increase of colour appearance of wastewater. Besides, the intra-particle diffusion of pollutants into the adsorbent is time dependent (Mondal, Majumder, & Mohanty, 2007). When the larger size of adsorbent was introduced, it will enhance the ion exchange mechanism at the outer level of adsorbed.

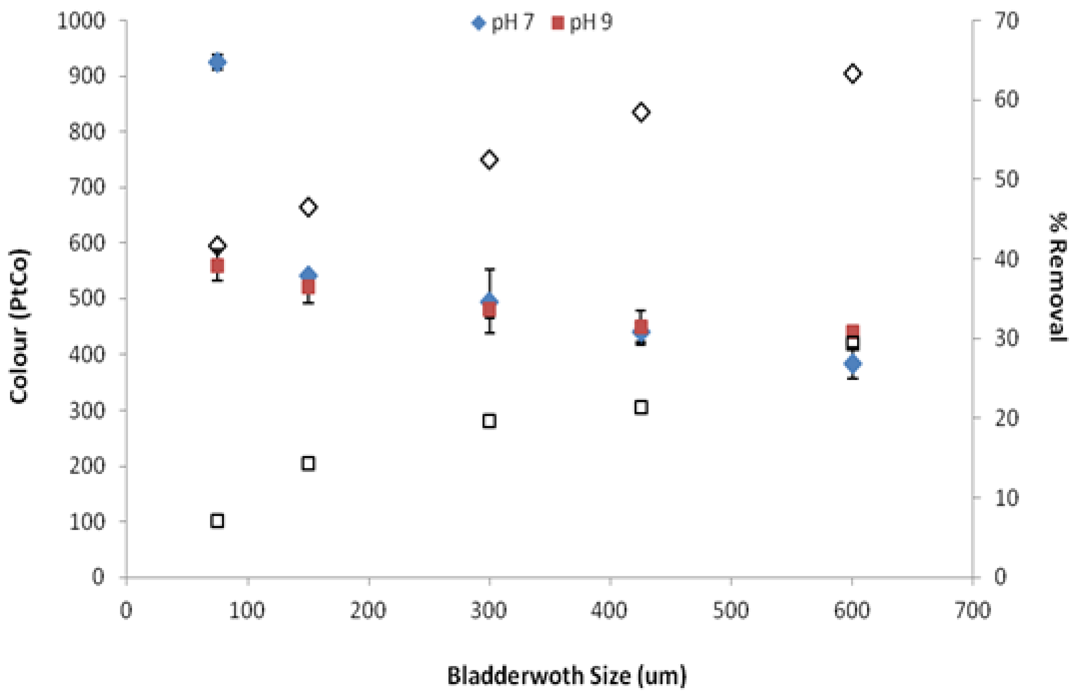

Figure 11: Colour Removal Against Bladderwort Size. Solid Symbols Indicate the Colour Measured in the Unit of PtCo While Hollow Symbols Indicate the % Removal of Colour. Error Bars Indicate Standard Deviation of Triplicate Samples.

3.3 Effects on Different pH of wastewater on the Removal of Colour

The pH of solution plays important role over the size of adsorbent in the removal of colour through adsorption process as extensively discussed in many studies. Figure 12 clearly

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demonstrates that the removal of colour were pH dependent. The smooth increase in the removal of colour was observed when the pH of wastewater is acidic. Under high alkali condition, almost no removal of colour was determined probably due to weak chemical interaction between colour and Bladderwort surface. Adsorbed molecules in solution are attracted to, and may be held by, a surface in contact with the solution. The forces holding adsorbed molecules to the surface may results from either chemical bonding or Van der Waals attraction (McGhee & Steel, 1991).

At high pH (pH 12), there was slight removal of colour determined for all Bladderwort size. However, when the wastewater pH reduced gradually from pH 9 to 5, considerable increase on the removal of colour was observed. The smooth increase in the removal of colour was observed when the pH of wastewater in acidic condition. The removal of colour varied with the size of Bladderwort if only the wastewater pH in the range of 1 to 9. At all pH condition, the highest removal of colour was observed at pH 3.

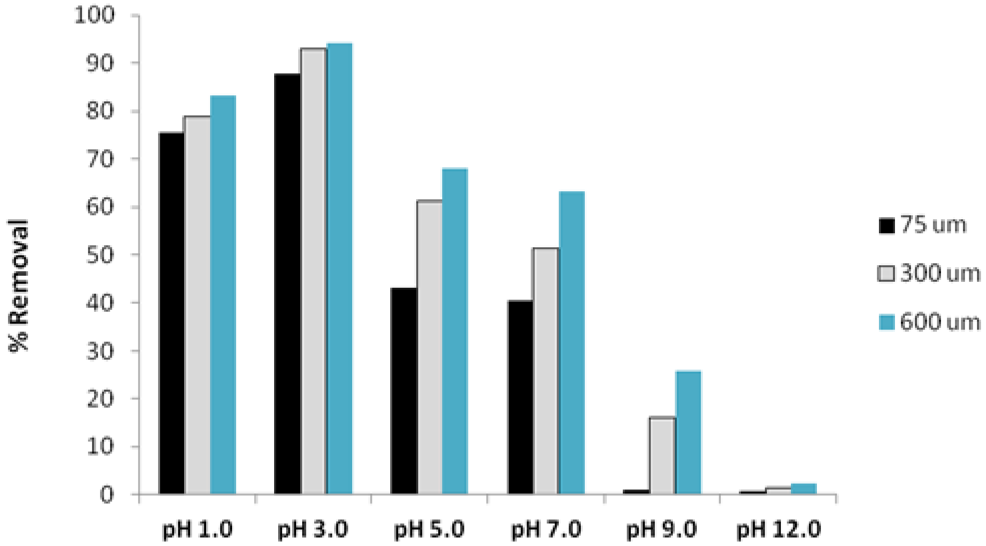

Figure 12: Trend of Colour Removal in Percentage Against pH of Wastewater

From physical observation after treatment process, the colour of the wastewater turned from reddish yellow (from the colour of clay used) to very light yellow at lower pH value as depicted in Figure 13. The percentage of removal starts to have very crucial decrease from pH 7 to 12. The degree of protonation of the surface reduces gradually with increase in pH value which will decrease the adsorption rate. Adsorption rate is efficient at a lower pH because the adsorbent is positively charged by adsorption of hydrogen ions and most of the colloidal materials and all ionized polar group on organic molecules are negatively charged (McGhee & Steel, 1991).

The previous study mentioned that the optimum removal of colour in natural water is excellent in acidic conditions (Duan & Gregory, 2003). The hydrogen ion concentration primarily affects the degree of ionization of the colour and the surface properties of the adsorbents (Iqbal & Ashiq, 2007). From Figure 12, low pH value results in lowering the negative charge on the surface of the Bladderwort and increasing the positive charge on the surface, thus enhancing the adsorption of the negatively charged adsorbate. With the increase

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in pH value, the hydroxyl ion concentration increases and the negative charge on the surface of the Bladderwort increased, thus the adsorption capacity of the adsorbent is decreased.

The current study showed that percentage removal in pH 1 was lower than in pH 3 (Figure 12). With occurring of higher positive ion in the wastewater, the solution become unstable and affects the ability of adsorption of the adsorbent. Therefore, the highest percentage removal of colour occurred at lower pH which is at acidic condition, thus will increase the effectiveness to remove colour appearance of wastewater.

In sum of Figure 11 and 12, the size of Bladderwort and solution pH play significant role on the removal of colour from wastewater. The higher size promotes significant removal compared to lower size as it's provide larger surface active site. However, the strong adsorption between the Bladderwort and colour is still subjected to the pH of wastewater.

Figure 13a: Colour of Wastewater Before the Experiment

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Figure 13b: Colour of Wastewater After the Experiment

3.4 Effects on Agitation Speed in Colour Removal

The effect of agitation speed on the removal of colour was conducted at the optimum size of Bladderwort (600 µm) and pH of wastewater (pH 3). Figure 14 obviously shows that agitation speed was found to be less appropriate for maximum adsorption of colour from the wastewater. The agitation speed has no crucial effect on the ability to remove the colour. Only at the speed of 100 rpm, it clearly depicted significant decrease on the colour. Meanwhile, at the speed of 150 rpm to 250 rpm, there was no obvious effect on the efficiency removal of colour.

This finding contradicted with the results found by Inglezakis et al. (2006) and Alias, Marajan and Jamain (2009). The studies found that the greater the shaking time, the greater will be the adsorption and consequently, the greater will be the percentage removal of metal. Agitation of suspensions during experiments has led to a decrease of the boundary layer and a decrease to the resistance of transportation of ions. This increases the transfer rate of the ions and the adsorption of the minerals (Inglezakis et al., 2006).

For economical cost purposes, it was suggested to use lower speeds in order to save electrical power. However, for proper application, higher speed was suggested in order to distribute properly the adjusted pH of wastewater and uphold the contact between Bladderwort and contaminants.

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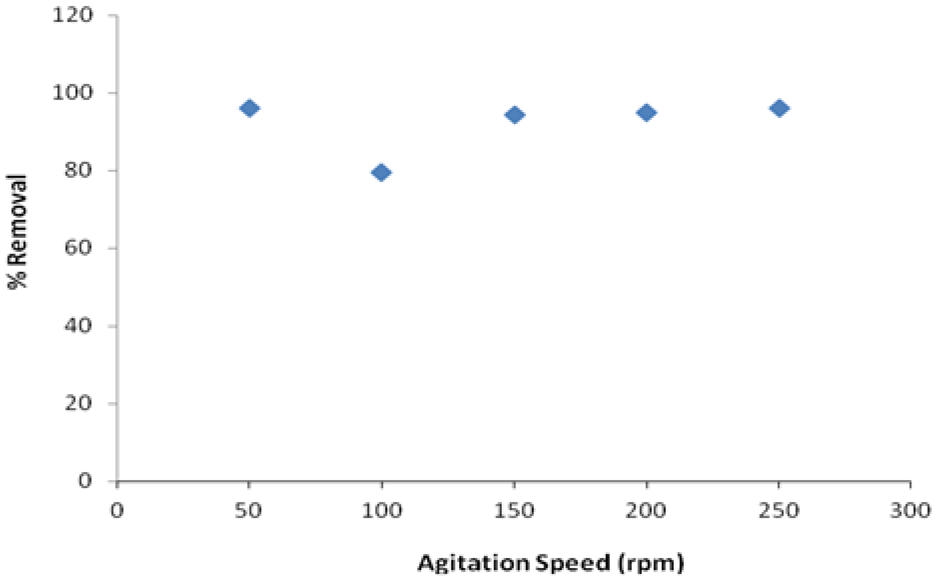

Figure 14: Removal Percentage of Colour Against Agitation Speed (rpm)

4. CONCLUSION

The study shows that Bladderwort was found as a suitable adsorbent to remove colour in wastewater. The performance of Bladderwort is dependent on its properties. The best performance of colour removal was in acidic conditions compared to in alkali. Adsorbent with higher size particle has more efficiency to absorb colour. Thus, the most appropriate size of Bladderwort to remove colour is 600 µm at optimum pH condition of 3. For economical purposes, it was suggested to agitate the wastewater at the speed of 50 rpm, but for proper application, agitation speed of 150 rpm was more efficient and recommended.

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