

PRELIMINARY STUDY ON HEAVY METAL REMOVAL AND TURBIDITY REDUCTION FROM GROUNDWATER BY USING APPLE PECTIN (BIOFLOCCULANT)

Anis Nabilah Muhamad Tarmizi, Norli Ismail*, and Harlina Ahmad

Environmental Technology Division, School of Industrial Technology
Universiti Sains Malaysia, 11800, Minden, Penang, Malaysia.

*Email: norlii@usm.my

ABSTRACT

This study is based on the use of bioflocculant as an alternative flocculant in the treatment of groundwater. Bioflocculant is used due to their environmental friendly characteristics and to prevent the addition of heavy metal from the flocculant itself into the water during the treatment process. The availability of heavy metal in groundwater, exceeding the permissible limit may cause damage to human health and high turbidity of water may cause the unpleasant effect to the consumer. In this study, bioflocculant (apple pectin) has been used as a flocculant to treat groundwater by using Jar Test method for the removal of heavy metal (As, Cd, Cr, Fe, Pb) and turbidity reduction. Based on Jar Test experiment, there is 97.71% turbidity reduction achieved by using apple pectin with the optimum dosage of magnesium chloride 15 mg/L and 5 mg/L of apple pectin at pH 10. From the heavy metal analysis, the results have shown that before treated with pectin, it has been found that all elements of As, Cd, Cr, Fe and Pb with concentration of 0.136 mg/L, 0.076 mg/L, 0.089 mg/L, 1.374 mg/L and 0.099 mg/L respectively exceed the standard. After the treatment conducted with apple pectin, only the concentration of Fe is accepted within the standard limit with the concentration of 0.107 mg/L.

Keywords: Bioflocculant, groundwater, heavy metal, pectin, turbidity.

INTRODUCTION

In a few states of Malaysia such as Kelantan, Terengganu, Pahang, Perlis, Kedah, Sabah, and Sarawak, groundwater is one of the water supplies that are used as drinking water [1]. In Kelantan, as a supplier of water, Air Kelantan Sdn Bhd, state that 40% of groundwater as water sources is used for public needs [2]. Suspended matters or impurities, interfering with the clarity of the water is called turbidity [3]. The clarity of water plays an important role in household use whereby high turbidity of water can cause unpleasant effect to consumer.

Health issues regarding the consumption of groundwater has become one of major concern because some groundwater is directly extracted from the aquifers without treating it with any form of filtration or chlorine disinfection. For water supply, the contamination by heavy metal is one of the main concerns to public health either naturally from natural soil or from other anthropogenic sources. The characteristics of the media through which the water passes to the ground water zone of saturation will affect the quality of groundwater sources and their extensiveness of heavy metal pollution in groundwater [4]. In addition, activities such as heavy metal discharged by industries, use of fertilizers for agricultural purposes and oil spillage also can affect the concentration of heavy metal in groundwater [5]. Heavy metals are known as it cannot be chemically degraded and need to be physically removed or be transformed into nontoxic compounds [6].

The metals with ionic species which comes from the most stable oxidation states such as Cd^{2+} , Pb^{2+} , Hg^{2+} , Ag^+ and As^{3+} , they react with the body's bio – molecules to form very stable biotoxic compounds which are difficult to dissociate [7]. Various diseases and disorders cause from accumulation of heavy metal in body tissue due to its non-biodegradable characteristics [8]. Allergies, hyperpigmentation, skin lesions, skin cancer, neurological effect, hypertension, cardiovascular disease and pulmonary disease are one of the adverse impact of drinking water with heavy metal contamination, such as Pb, Cd, Cu, Zn, Ni, Cr, and especially As which known as metalloid. It's targeting the liver, kidneys, lungs, brain and bones once absorbed through diverse pathways [9].

There are various types of water treatment available in this era of high technology. Coagulation – flocculation is one of the types of water treatment which use coagulant and flocculant agent in their treatment process. Coagulation is the process that used coagulant to destabilized colloidal matter in water by rapid mixing [10]. The destabilised particles are brought into contact with one another to form larger “floc” particles in the flocculation process and then readily be removed from the water in subsequent processes [11]. In the fields of water and wastewater treatment, a variety of flocculants such as inorganic flocculants, manufactured organic high polymer flocculants and naturally occurring flocculants have been used. However, some of them will bring a risk to the environment through which some of them are not readily biodegradable and intermediate products of their degradation are harmful to humans. Utilization of the naturally occurring flocculants extracted from microorganisms and biomass has been recommended due to their biodegradability and the harmlessness to the environment of their degradation intermediates to solve these environmental problems [12].

Furthermore, there is also a new possible source of bioflocculant which is pectin. A single extracellular matrix which is a complex structure that is formed constantly through the body of the plant is called as pectin. Different types of polysaccharides, protein and lignin forms the cell matrix [13]. Moreover, pectin can be categorized as one of the anionic polysaccharides in the cell wall that consists of “smooth” α -D-galacturonic acid with 1–4 linkages region monomer. It also can be extracted from outer

cell layer of oranges, apples, grapes, peaches, etc. Pectin has been acclaimed to have flocculating activity in inorganic and organic suspensions, and is applicable as a biodegradable, edible and harmless biopolymer flocculant like chitin [12].

METHODOLOGY

A sample of well water was taken at a private well, Bayan Lepas, Pulau Pinang. Apple pectin, purchased from Fluka, with 70 – 75% degree of esterification, was used throughout this experiment as the bioflocculant. On the other hand, the coagulant, magnesium chloride ($MgCl_2$) was purchased from Sigma Aldrich. A standard Jar Test apparatus (Velp Scientifica type FC6S), manufactured in Italy, was used in the coagulation – flocculation test to perform an experiment which comprised of a six-spindle multiple stirrer unit with stainless-steel paddles. The working volume for each sample was 1000 mL. Desired pH was adjusted using 1.0 M HCl or 1.0 M NaOH solutions. After the pH adjustment, coagulant ($MgCl_2$) was added followed by rapid mixing at 150 rpm for 3 min to homogenize the ions. Next, bioflocculant (apple pectin) was added to the mixture and it then underwent slow mixing at 30 rpm for 20 min. The mixture was then allowed to stand for 5 min, to settle. 10 mL of supernatant was withdrawn with a syringe at 1 cm from the surface. This experiment was carried out in triplicates at ambient temperature. Turbidity was measured by a Hach 2100P Turbidimeter (USA). The pH value was determined and calibrated daily using pH buffer solutions. Heavy metal analysis was conducted by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis.

RESULTS

Jar Test Analysis

Table 1 shows the results obtained from the jar test analysis by treating well water by using $MgCl_2$ and apple pectin as bioflocculant.

Table 1. Turbidity reduction by $MgCl_2$ and pectin (Apple)

pH	Dosage of $MgCl_2$ (mg/L)	Dosage of pectin (mg/L)	Final turbidity (NTU)	Turbidity reduction (%)
6	10.00	5.00	95.30	47.92
6	15.00	5.00	143.00	21.86
6	20.00	5.00	125.00	31.69
8	10.00	5.00	58.20	68.20
8	15.00	5.00	113.00	38.25
8	20.00	5.00	99.80	45.46
10	10.00	5.00	13.60	92.57
10	15.00	5.00	4.18	97.71
10	20.00	5.00	10.60	94.20

*Initial turbidity = 183 NTU

From the Tables 1 above, plot of turbidity reduction against different dosage of $MgCl_2$ at different pH values is given in Figure 1.0 to find the best condition of treatment at fixed dosage of apple pectin.

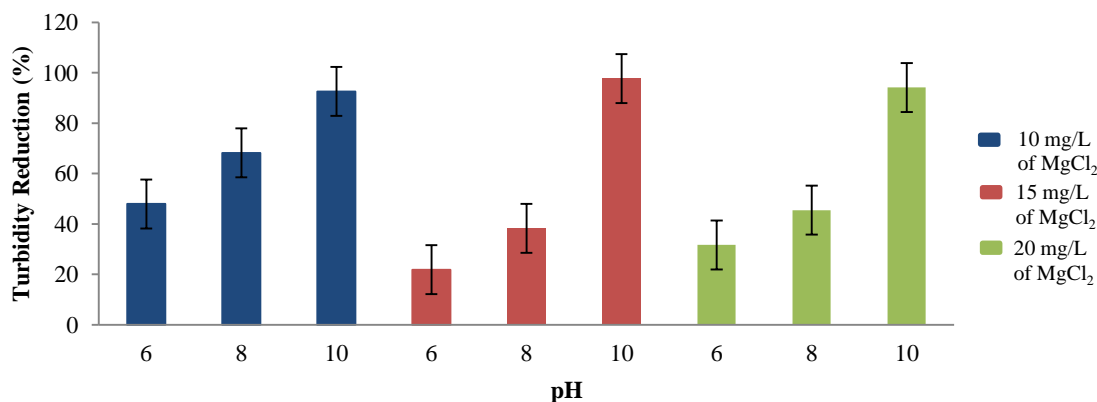


Figure 1. Turbidity reduction of well water treated by bioflocculant

Heavy Metals Content of Well Water

From Table 2, a result of heavy metal analysis is shown. From this table, five elements (Arsenic, Cadmium, Chromium, Iron and Lead) from this well water have been selected to undergone treatment by using apple pectin as a bioflocculant with dosage, 5 mg/L.

Table 2. Heavy metal analysis of well water by ICP-OES

Types of elements	Concentration of elements (mg/L)
Arsenic (As)	0.136
Beryllium (Be)	0.091
Calcium (Ca)	47.979
Cadmium (Cd)	0.076
Cobalt (Co)	0.072
Chromium (Cr)	0.089
Copper (Cu)	0.067
Iron (Fe)	1.374
Lithium (Li)	0.069
Magnesium (Mg)	4.981
Manganese (Mn)	0.082
Molybdenum (Mo)	0.327
Nickel (Ni)	0.140
Lead (Pb)	0.099
Antimony (Sb)	0.103
Selenium (Se)	0.083
Strontium (Sr)	0.227
Titanium (Ti)	0.119
Thallium (Tl)	0.115
Vanadium (V)	0.129
Zinc (Zn)	0.035

Table 3. Selected heavy metal for treatment

Types of heavy metal	Concentration of Heavy metals			National Guidelines for Raw Water Quality (Revised 2000)
	Before Treatment (mg/L)	After Treatment (mg/L)	Heavy metal removal (%)	
Arsenic (As)	0.136	0.103	24.42	0.01
Cadmium (Cd)	0.076	0.075	1.28	0.003
Chromium (Cr)	0.089	0.086	3.97	0.05
Iron (Fe)	1.374	0.107	92.23	0.3
Lead (Pb)	0.099	0.086	13.24	0.01

From the treatment, the result of five selected heavy metal concentration after the treatment shows in Table 3 and a plot of percentage of heavy metal removal shown in Figure 2.

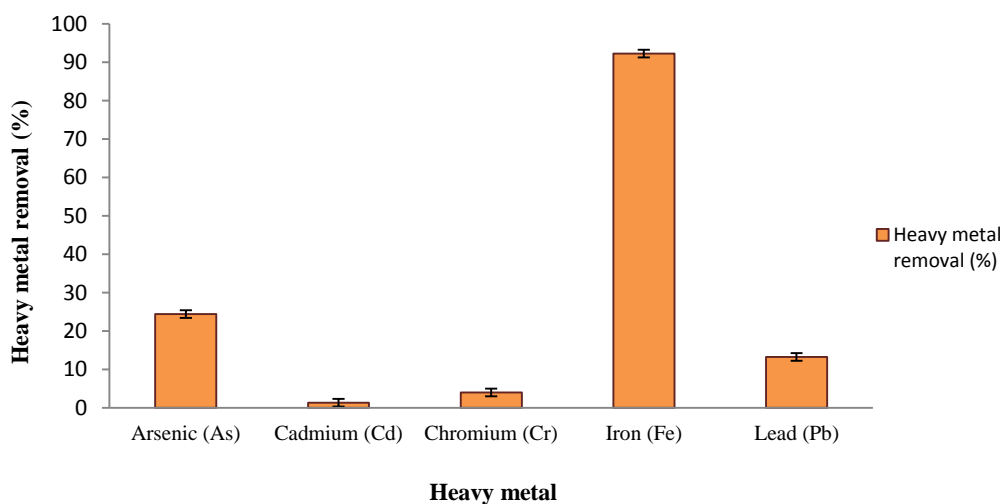


Figure 2. Heavy metal percentage removal

DISCUSSION

Jar Test Analysis

Based on Table 1.0, there are three different dosage of magnesium chloride (10 mg/L, 15 mg/L and 20 mg/L) have been tested with a different adjusted pH of well water (6, 8 and 10) with 5 mg/L of apple pectin. From the result, it can be seen that at pH 10, with using 15 mg/L of $MgCl_2$, the percentage of turbidity reduction are at the highest, 97.71% with final turbidity, 4.18 NTU as shown in Figure 1.0. According to National Water Quality Standards [14], turbidity of water below than 5 mg/L will be in class I which is no treatment are needed for that water supply. Furthermore, alkaline condition of well water which $MgCl_2$ works excellently in that pH ranges. From the research using magnesium chloride as a coagulant on treating waste water and for turbidity reduction; their maximum turbidity reduction is highest at higher pH reading of waste water [15]. Furthermore, at pH 10, with addition of higher dosage, the turbidity reductions decrease after reaching their optimum reduction. This is due to 'restabilizing' effect of the flocs, which reverse the charge on the colloid, and re-disperse it as a positive colloid affected from overdosing [16, 17].

In the flocculation process, there are many physicochemical factors that will affect the suspended particle in water which not only dependent on pH, surface morphology, cation concentration, functional groups, flocculant concentration and molecular weight, but also depends on adsorption density, charge density of the flocculants, and conformation of the adsorbed flocculants. Besides that, nature of adsorption of the polymer on the surface of particles, and also the conformation of the adsorbed polymer plays very significant factors that influence the extent and mechanisms of coagulation and flocculation [13]. From the Table 1.0 also we can see the addition of 5 mg/L of apple pectin to help the floc to settle down in flocculation process. It is state that biopolymer flocculants like pectin, the existence of galacturonic acid in biopolymeric acid will promote flocculation also with the help of its high molecular weight characteristic [18].

Heavy Metal Analysis

From Table 2.0, there are 21 elements listed out from heavy metal analysis and 5 (As, Cd, Cr, Fe and Pb) elements are chosen for further treatment. Based on Table 3.0, As, Cd, Cr, Fe and Pb show removal after treatment with the final values of 0.103 mg/L, 0.075 mg/L, 0.086 mg/L, 0.107 mg/L and 0.086 mg/L respectively. The percentage of the heavy metal removal are As (24.42%), Cd (1.28%), Cr (3.97%), Fe (92.23%) and Pb (13.24%). The binding of particles into the pectin surface are different. In the research of pectin binding of heavy metal ions in aqueous solutions, the affinity sequence for cation binding to pectin was found in these sequences, $Pb^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$ [19]. Besides that, the highest reduction of Fe removal can be related with its initial concentration in the groundwater. High concentration of Fe cause the binding to the pectin increase compared to other ions that contain in groundwater. In Figure 2.0, it can be seen that the reading of Fe complies with the standard limit Fe in the water, which is 0.3 mg/L with the highest removal, 92.23%. Heavy metal parameters in National Drinking Water Quality Standard listed by Malaysian Ministry of Health need to be complied in the water treatment to make sure drinking water supplied is secure for consumers.

CONCLUSION

It can be concluded from the experiments that magnesium chloride concentration at 15 mg/L and pectin concentration at 5 mg/L shows that the turbidity reduction of well water at optimum capacity with 97.71% reduction. In heavy metal removal of As, Cd, Cr, Fe and Pb, it can be seen that only Fe has the highest removal which are 92.23% and comply with National Drinking Water Quality Standard. This research shows that bioflocculant (Apple pectin) is able to be applied in groundwater treatment for heavy metal removal and turbidity reduction.

ACKNOWLEDGEMENT

The author acknowledges the Research University Grant (1001/PTEKIND/811314) by Universiti Sains Malaysia that has resulted in this article.

REFERENCES

- [1] Hafiza, N. A. R., Praveena, S. M., Zaharin, A. A. and Zailina, H. (2015). Drinking water studies: A review on heavy metal, application of biomarker and health risk assessment (a special focus in Malaysia). *Journal of Epidemiology and Global Health*, 5, 297–310.
- [2] Mahirah, K., Alias, R., and Khalid, A. R. (2016). Household preferences for improved water services in Kelantan, Malaysia: A choice experiment approach. *Journal of Business and Social Development*, 4, 43-54.
- [3] Muthuraman, G., Sasikala, S. and Prakash, N. (2013). Proteins from Natural Coagulant for Potential Application of Turbidity Removal in Water, *International Journal of Engineering and Innovative Technology*, 3(1).
- [4] Stephen, A., Stacey, F. Y. Y., Lim, Y. A. L., Wah, M. J., Chen, D. K. F., Ooi, S. S., Lee, S. P., Tan, T. M., Goh, M. Y. and Danapidha, N. (2014). The chemical, heavy metal and microbial quality of well water in an urbanised village in the Klang Valley. *International e-Journal of Science, Medicine & Education*, 8(3), 28-44.
- [5] Husam, M., Hadidoun, M., Al-Khatib, M., Al-Rimawi, F. and Al-Qutob, M. (2014). Assessment of Groundwater Pollution with Heavy Metals in North West Bank/Palestine by ICP-MS. *Journal of Environmental Protection*, 5, 54-59.

- [6] Tangahu, B. V., Rozaimah, S. S. A, Hassan, B., Mushrifah, I., Nurina, A., and Mukhlisin, M. (2011). A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation. *Hindawi Publishing Corporation, International Journal of Chemical Engineering*, 31.
- [7] Hashim, M.A., Soumyadeep, M., Jaya, N. S. and Bhaskar, S. (2011). Remediation technologies for heavy metal contaminated groundwater. *Journal of Environmental Management*, 92, 2355-2388.
- [8] Kamarudin, S., Tadza, M. A. R., Ismail, A. and Mohamed, H. I. (2012). Heavy metals profiles in a groundwater system at a solid waste disposal site, Taiping, Perak. *Bulletin of the Geological Society of Malaysia*, 58, 9 – 14.
- [9] Sneh, L. and Samadder S. R. (2014), Removal of Heavy Metals Using Rice Husk: A Review, *International Journal of Environmental Research and Development*, 4(2), 165-170.
- [10] Baghvand, A., Zand, A. D., Mehrdadi, N. and Karbassi, A. (2010). Optimizing Coagulation Process for Low to High Turbidity Waters Using Aluminum and Iron Salts. *American Journal of Environmental Sciences*, 6 (5), 442-448.
- [11] Al-Sameraiy, M. (2012). A Novel Water Pretreatment Approach for Turbidity Removal Using Date Seeds and Pollen Sheath. *Journal of Water Resource and Protection*, 4, 79-92.
- [12] Yokoi, H., Obita, T., Hirose, J., Hayashi, S. and Takasaki Y. (2002). Flocculation properties of pectin in various Suspensions. *Bioresource Technology*, 84, 287–290.
- [13] Ho, Y. C, Norli, I., Alkarkhi, A. F. and Morad, N. Y. C. (2009). Analysis and optimization of flocculation activity and turbidity reduction in kaolin suspension using pectin as a biopolymer flocculant. *Water Science Technology*, 60(3), 771-81.
- [14] Water Environment Partnership in Asia (WEPA), National Water Quality Standards for Malaysia, (2000). http://www.wepa-db.net/policies/law/malaysia/eq_surface.htm (22 Febuari 2017).
- [15] Gobinath, R., Aswathy, V. G., Arun, O. S., Arun, C. P. and Vijayakumar, S. (2013), Coagulation performance of magnesium chloride in education institutional waste water. *Scholars Journal of Engineering and Technology*, 1(3), 140-148.
- [16] Louis, R. (1993), Everything you want to know about Coagulation & Flocculation, Zeta-Meter, Inc.
- [17] Emma, L. S., Peter, J., Simon, A. P. and Bruce, J. (2006). The Impact of Zeta Potential on The Physical Properties of Ferric-NOM Floccs. *Environmental Science & Technology*, 40, 3934-3940.
- [18] Wu, J. Y. & Ye, H. F. (2007). Characterization and flocculating properties of an extracellular biopolymer produced from a *Bacillus subtilis* DYU1 isolate. *Process Biochemistry*, 2, 1114 –1123.
- [19] Kartel, M. T, Kupchik, L. A. and Veisov, B. K. (1999). Evaluation of pectin binding of heavy metal ions in aqueous Solutions. *Chemosphere*, 38, 2591 – 2596.