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Wastewater treatment using bentonite, the combinations of bentonite-zeolite, bentonite-alum, and bentonite-limestone as adsorbent and coagulant

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ABSTRACT

Health problems caused by aluminium salts have been recently reported. Various reports have mentioned the direct and indirect toxic effects of metals in the form of tumours, cancers, and allergies. In order to replace aluminium salts as adsorbents and coagulants, the capability of bentonite and combination of bentonite used as coagulants in wastewater treatment via adsorption, ion exchange, and coagulation-flocculation processes were investigated. The optimum conditions (pH and coagulants dosage) were identified for bentonite, the combinations of bentonite-zeolite, bentonite-alum, and bentonite-limestone. The investigation conducted found that bentonite can be a good coagulant which can absorb Chemical Oxygen Demand (COD) for 90.5% of removal. Based on the optimum dosage of the combinations of bentonite, bentonite-zeolite mixture gave high efficiency removal of iron (98%) and turbidity (95%) from others. Meanwhile, the bentonite-limestone mixture produced less sludge volume index and showed lowest zeta potential values. The zeta potential of treated bentonite and bentonite mixed were -26.7 mV for bentonite-alum, -20.7 mV for raw bentonite, -19.9 mV for bentonite-zeolite, and -17.6 mV for bentonite-limestone which demonstrated the coagulation and adsorption process occurred. On the other hand, the effects of contact time indicated that the adsorption capacity of combination bentonite was higher than raw bentonite.

Keywords: wastewater treatment; bentonite; zeolite; limestone; alum; coagulation and sorbent.

1. Introduction

Environmental regulation and public health concerns require that wastewater collected from municipalities and communities must be treated to a set standard before it is returned to surface waters or land or even reused (Jiang et al. 2004). Municipal wastewaters are still very important in the issue in waste management systems within Southeast Asia and the rest of the world. The COD, turbidity, Total Suspended Solids (TSS), and major cations are the main concerns of the characteristics of municipal wastewaters. Generally, high levels of COD results in low Dissolve Oxygen (DO) in water and this can lead to mortality of aquatic life. In addition to that, suspended solids such as organic and inorganic materials can result in the water being contaminated by dirt and odour.

Developing countries pay a high price to import chemicals including polyaluminium chloride and alum for water and wastewater treatment. Polyaluminium chloride and alum add impurities, such as epichlodine, which are carcinogenic. Besides that, aluminium is regarded as a major poisoning factor in encephalopathy dialysis and one of the factors which might

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contribute to Alzheimer disease. Some synthetic organic polymer, which has been used as coagulation agent such as acrylamide, has neurotoxicity and strong carcinogenic effects (Yarahmadi et al., 2009).

The use of clay mineral has undoubtedly become more popular and widely used as an adsorbent and ion exchange for water and wastewater treatment applications especially for removing heavy metal, organic pollutants, and nutrients (Abdelaal, 2004). Clay minerals, such as bentonite and zeolite, are some of the potential alternatives, as they have large specific surface areas with a net negative charge, which can be electrically compensated for by inorganic and organic cations from the environment (Konig et al., 2012) compared to polyaluminium chloride. Their sorption capabilities come from their high surface areas and exchange capacities (Babel and Kurniawan, 2003). It is a highly effective natural clay mineral, especially in granular form, used for the purification of wastewater and sludge dewatering.

Generally, there are two types of bentonite which are sodium bentonite and calcium bentonite. Sodium bentonite is usually a high-swelling type, derived from volcanic ash that is deposited in marine environments. While calcium bentonite is a low-swelling type, which evolved from volcanic ash deposited in freshwater environments (Dwairi and Al-Rawajfeh, 2012). However, calcium bentonite was used in this present study. The usage of natural clay minerals such as bentonite and zeolite for water and wastewater treatment are increasing because of their abundance, low price, and adsorption capabilities, as well as ion exchange that is highly capable of adsorbing all kinds of pollutants for some organic and inorganic compounds, including heavy metals in waters (Guimaraes et al.,2009). This outstanding capability is due to the presence of the mineral montmorillonite (Khenifi et al., 2009).

A part from that, bentonite is a natural material that contains essential compounds such as aluminium, iron and clay materials which are useful for the treatment of wastewater. Moreover, bentonite is cheaper than chemicals and it fulfils the economic benefits of the operators as well as environmental concerns (Al-Qunaibit et al., 2005).However, coagulants that are commercialised in the market are mostly chemical-based, which are non-environmental friendly and may create adverse impacts on the surrounding environments (Ozcan et al., 2007).

Therefore, this study aims to investigate the combination of clay minerals, bentonite and zeolite in comparison with aluminium sulphate, and zeolite. This study also investigates the comparative suitability of raw bentonite and combinations of bentonite as adsorbents and coagulants for wastewater treatment based on the removal of efficiencies of COD, iron, turbidity, as well as sludge volume index under the optimum conditions of both coagulants. Additionally, the sludge volume index (SVI) ratio of bentonite, bentonite-zeolite, bentonite-alum, and bentonite-limestone will produce a lower volume of sludge. The effects of pH and dosage were also taken under consideration. In addition to that, Freundlich and Langmuir's isotherm models were also examined for their applicability. There is no data available in the literature concerning the adsorption capability of raw bentonite and the combinations with zeolite.

2. Material and methods

2.1. Samples

Sewage water samples were collected from Indah Water Consortium Sewage Treatment Plants in Juru, Lebuh Kota Permai, Bukit Mertajam, Pulau Pinang. These treatment plants are biological plants, with an initial design capacity of 150,000 PE (Population Equivalent), with a possibility for future extension to 873,000, and receive about 216,000 litres/day of sewage water. Sewage samples were sampled at grit chamber (influent), in December 2009 and January 2010. In the laboratory, the sewage samples were preserved in the refrigerator at 4°C and examined when needed so that the potential for volatilization or biodegradation of the samples can be minimised. Collection and preservation of samples for the pH, COD, iron, and turbidity were done according to the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, and WEF 2005).

2.2. Materials

Bentonite material (40kg/pack) was bought from a company, Ipoh Ceramic Sdn. Bhd. in Ipoh, Perak. Then, the bentonite sample in the form of calcium bentonite was sieved using Vibrator Sieve Shaker to determine the particle size (63 µm) (Karapinar and Donat, 2009). Previous studies by Hussain et al., (2006) concluded that smaller particles of medium were more effective than larger ones because of greater available surface area and consequently higher adsorption capacity. Next, the bentonite was stored in a plastic container and ready to be used. The zeolite used was obtained from another company, PT. BRATACO Jakarta, Indonesia. The zeolite was sieved to obtain particle size of 63 µm before it was immersed in 1M aqueous NaCl for 24 hours to improve the natural zeolite cation exchange capacity and conditioning of zeolite (Rahmani et al., 2009). The zeolite was rinsed with distilled water for several times in order to remove dust and impurities. Then the zeolite was placed into an oven at 105^o C for 24 hours and subsequently dried in a desiccator for two hours.

2.3. Methods

Experimental work was initiated with sewage water sampling at the wastewater treatment plants and followed by the characterisation of sewage water. Next, the characterised sewage water was used to run the coagulation-flocculation experiments by using bentonite, aluminium sulphate (alum), zeolite, and limestone to achieve the optimum dosage. Coagulant dosage was optimised via a series of jar tests experimental works. Moreover, the responses for coagulant dosage such as the removal of efficiencies of COD, turbidity, iron, and sludge volume index (SVI) as well as its pH level were determined and compared among raw bentonite and its combination as coagulants.

A conventional jar test apparatus was used to perform these coagulation-flocculation experiments. In each set of batch testing, it accommodates a series of six beakers together with six-spindle steel paddles. Sewage water samples were measured to 500 mL and placed in a jar each. The pH of the wastewater was adjusted using NaOH and H_2SO_4 solutions. The speed of rapid mixing was set at 80 rpm for the duration of 5 minute while the speed of slow mixing was set at 50 rpm for the duration of five minutes. Screening or filtering as well as dilution processes were applied prior to the results analysis.

The experiments were tripled to obtain a more reliable result. Optimum dosage and pH for bentonite and its combination had been analysed to obtain the best condition for the removal of the parameters. Besides, the contact time was also investigated to determine the removal of all parameters towards the settling time at about two hours. Finally, zeta potential was investigated because the value can be related to the stability of colloidal dispersions.

A portable Turbidimeter (Hach 2100P) was used for turbidity determination. An Odyssey spectrophotometer (Hach DR 2500) was used for the determination of Iron (Fe). While, COD and pH of wastewater were determined using a Spectrophotometer (Hach DR 2800) and a Hach Sension 1 pH meter, respectively. The zeta potential measurement was performed with Zetasizer Nano. All methods were adapted from the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, and WEF, 2005).

3. Result and conclusion

3.1. Wastewater characteristics

Table 1 details the main characteristic of wastewater sample and it indicates that COD, turbidity, iron and pH levels was present in significant quantities with maximum concentrations of approximately 134 mg/L, 68 NTU, 4.7 mg/L and 7.82, respectively. These high values indicate that the wastewater can be categorised as a pollutant because it exceeded the Malaysian Environmental Quality Act (Sewage and Industrial Effluent) Regulations 1979, maximum effluent discharged limit. It can be concluded that the wastewater was quite concentrated and full treatment is necessary.

Table 1: Characteristics of wastewater

Parameter	Minimum	Maximum	Average *	Effluent Discharged Standard **
COD (mg/L)	72	134	105.43	100
Turbidity (NTU)	38	68	53.17	5
pH	6.69	7.82	7.26	5-9
Iron (mg/L)	2.72	4.7	3.74	2.0

**Average values for period of collecting between December 2009 and January 2010*
***Standard Discharge Effluent Regulation, Second Schedule, EPA (2002)*

3.2. Bentonite composition

The composition of bentonite was determined using X-Ray Florescence instrument (XRF). They were sieved into particle size of 63 µm using a vibrator sieve shaker no. 230 because that size was found to be appropriate for maximum adsorption (Karapinar and Donat 2009). Based on the results obtained, it shows that most constituents of bentonite were SiO_2 with 61.65% followed by Al_2O_3 (13.08%), MgO (2.48%), CaO (1.78%), Fe_2O_3 1.52%), K_2O (0.17), Na_2O (0.13%) and SrO (0.03%).

3.3. Effect of dosage and pH on bentonite

The reduction in COD and thus the biodegradable organics is one of the objectives of wastewater treatment (Jiang et al., 2004). Based on that study, jar tests were performed to determine dosage optimal in terms of COD removal in various concentration of bentonite between 0.2 and 1.2 grams. After being separated by Whatman cellulose filter papers, supernatant was tested and resulted in maximum percentage of COD removal as shown in Figure 1. It is evident from the figure that as the amount of bentonite dosage increases up to 0.4g/L, the maximum COD removal which is 90.6% was attained and it was used for further experiments. The presence of bentonite notably improves the removal of COD. According to Bourliva et al., (2010), almost 80% of the total COD can be removed by treating with chemical coagulations after the addition of clay. The effective adsorption of organic matter in the large surface area of the clay was distributed to the more efficient removal of COD by bentonite.

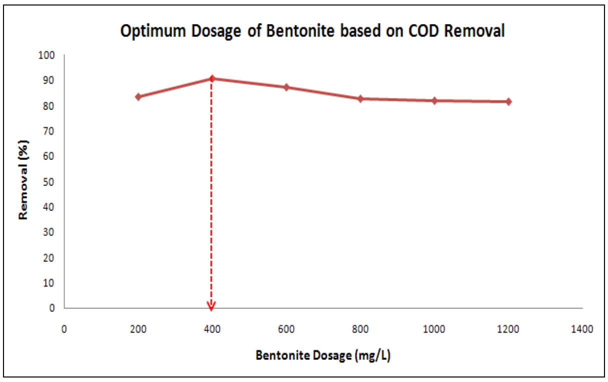
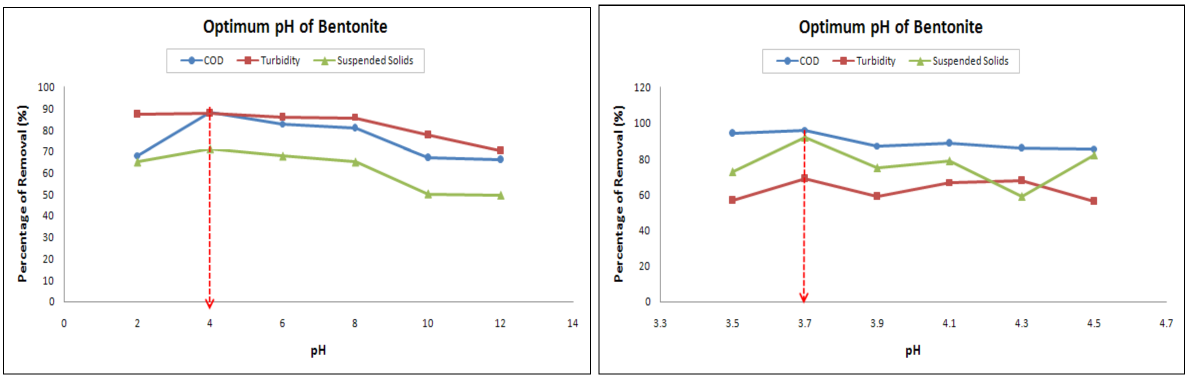


Figure 1: Effect of bentonite dosage for COD removal

The pH level of the aqueous solution is also an important variable which controls the adsorption of the organic constituents at the solid-water interfaces (Inglezakis et al. 2007). Hence, optimum dosage of bentonite was studied over a pH range of 2.0 – 12.0 as shown on Figure 2(a) and furthermore, detailed pH value (pH 3.5 - pH 4.5) with an initial bentonite concentration fixed at 0.4 g/L. Figure 2.(a) indicated that by increasing the pH value, the adsorption was decreased (Tahir and Rauf, 2004). Likewise, detailed pH values (pH 3.5 ~ pH 4.5) as shown on Figure 2(b) was further determined by using the same responses in order to obtain a more accurate reading. It indicated that, the highest removal efficiency values were achieved at pH 3.7. The extent of pH value does not only depend on the type and concentration of coagulants but also depended on the characteristics of wastewater itself. Under acidic condition, the amount of cationic ions (Al^{3+}) was increased, resulting with a high coagulation activity since the charge neutralisation effect between negatively charged suspended or colloidal particles was maximised (Aziz et al. 2007).



(a) (b)

Figure 2: (a) and (b) Optimum pH of bentonite

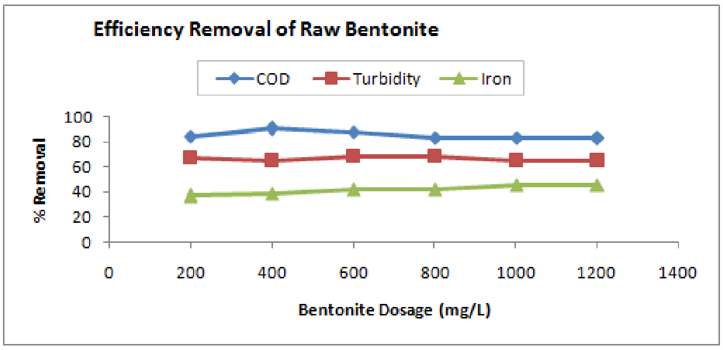
3.4. Mechanism of removal

The results on the removal of COD, turbidity and iron against concentration of bentonite are shown in Figure 3(a). This figure shows that the optimum concentration of bentonite for coagulation of 0.4 g/L was found in terms of COD removal. Therefore, effective coagulation was achieved with much lower doses of bentonite that would be required for complete charge neutralization of bentonite, and this process was guided by combined effects of electrostatic patch and bridging mechanisms. This phenomenon is in agreement with Chatterjee et al. (2008) that further increase in bentonite concentration reduces the coagulation process.

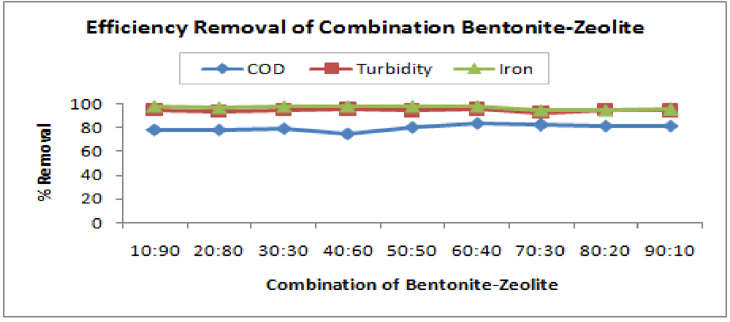
Based on Figure 3(a), the bentonite can be used as a good adsorbent for COD because it can achieve about 90.5% of removal. Accordingly, the treatment process should be optimised for COD removal when the organic matter is the major contaminant (Zhou et al. 2008). However, the turbidity gradually increased with the increase in bentonite dosage of up to 0.8 g/L and visual inspection also showed that with the increase in bentonite dosage, the supernatant became clearer. As more coagulant is added, electrostatic forces began to minimise and more flocs were formed, resulting in a decrease in turbidity. Besides that, in previous studies, it showed that 95% of Fe(II) removal was achieved by using 2.0 g of the bentonite (Tahir and Rauf 2004). Therefore, for further increase in the removal of Fe(II) the concentration of bentonite has to increase to more than 1.2 g/L.

3.4.1. Combination of bentonite and zeolite

Based on Figure 3(b), the best mixture ratio of bentonite and zeolite with the maximum COD removal of 83.33% was achieved at initial concentration of 320 mg/L using the bentonite-zeolite mixture ratio of 60:40. The COD removal rose with the increase of bentonite concentration. In other words, increasing the bentonite concentration by certain extent increases the number of vacant adsorption sites attractive towards organic constituents. This behaviour is compatible with what has been reported in the literature of adsorption regarding the effects of bentonite concentration by Al-Bastaki and Banat (2004). Hence, optimum mixture ratio was studied over a pH range of 2.0 – 12.0 with the maximum percentage of COD removal at pH 3.7 (93.06%). In the other hand, the removal efficiency of combination bentonite and zeolite gave better results than raw bentonite. Figure 3(b) showed that more than 95% of turbidity and iron and about 83% of COD were removed by bentonite-zeolite mixture (60:40 by volume).



(a)



(b)

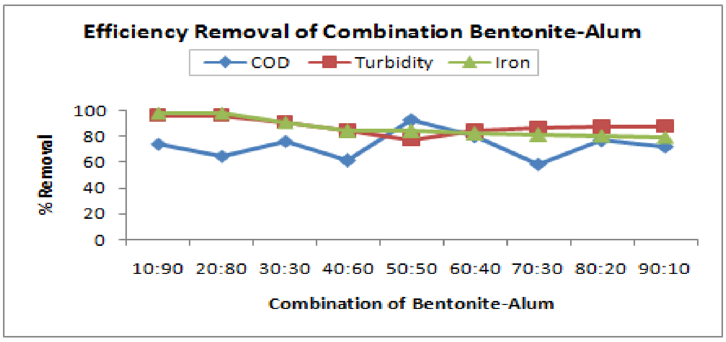
Figure 3: Removal efficiencies of (a) bentonite-alum mixture and (b) bentonite limestone mixture

3.4.2. Combination of bentonite and alum

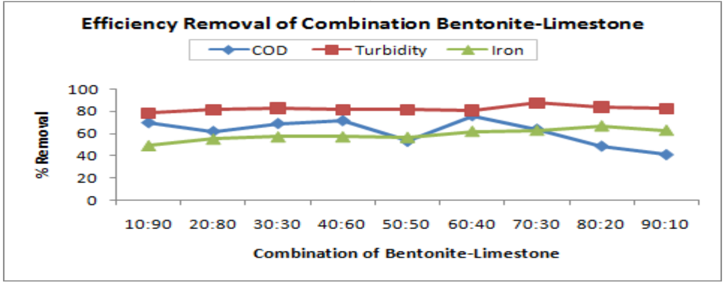
Inorganic metal salts such as aluminium sulphate is generally used in coagulation-flocculation in wastewater and water treatment (Ghafari et al. 2009). However, Chatterjee et al. (2009) reported that extensive intake of alum may cause Alzheimer's disease. Therefore, by combining the alum with bentonite it will minimise the negative effects associated with the use of the alum. The result shows that the best mixture ratio of bentonite-alum due to highest COD removal of 93.09% was at ratio of 50:50 by volume with a favourable pH of eight. Figure 4(a) indicated that the removal of turbidity was decreased at the initial stage but started to increase after it reached 50% of bentonite concentration. This phenomenon is in agreement with Chatterjee et al. (2009) that the increase in bentonite dosage may produce some acceleration in self-coagulation. Meanwhile, OD removal was slightly unstable due to addition of NaOH and H_2SO_4 solutions used to obtain an optimum pH during the coagulation process (Aziz et al. 2007).

3.4.3. Combination of bentonite and limestone

The best mixture ratio of bentonite and limestone with the maximum COD removal of 76.20% was achieved at the initial concentration of 480 mg/L using the bentonite-limestone mixture ratio of 60:40 as shown on Figure 4. (b). This results showed that, the COD removal was unstable at initial stage and started decreased after reached maximum removal and this is due to the addition of NaOH and H_2SO_4 solutions to control the pH (pH 7.0). This result indicates that the adsorption of COD increases from pH 2.0 to pH 6.0 and then decreases at pH 8.0 to 12.0. This decrease in the adsorption probably reflects a reduction in the quantity of negative surface charges on the bentonite surface (Karapinar and Donat 2009). This phenomenon is in agreement with Jiang et al., (2004) that this negative charge density on the surface of the adsorbent decreases as the pH increases and this leads to low adsorption of COD from water at high pH. This combination exhibits better removal results for all parameters except COD compared with the use of raw bentonite as shown in Figure 4(b).



(a)



(b)

Figure 4: Removal efficiencies of (a) bentonite-alum mixture and (b) bentonite limestone mixture

3.5. Adsorption isotherm model

The application of the Langmuir equation assumes that the adsorption site is homogeneous, with each site accommodating one molecule or one atom; the adsorption is monolayer coverage, and there is no interaction among adsorbed molecules (Hu et al. 2007). Meanwhile, the Freundlich isotherm describes equilibrium on a heterogeneous surface where energy of the adsorption was not equivalent for all adsorption sites, thus allowing multi-layer adsorption. The larger value of adsorption capacity, k_f, thus the higher the adsorption (Darus et al. 2007).

The intensity parameter, 1/n indicates the deviation of the adsorption isotherm from linearity. While n=1 indicates that the adsorption is linear with homogenous adsorption sites and there is no interaction within the adsorbed. The 1/n < 1 shows that the adsorption is favourable, new adsorption sites are available and the adsorption capacity increases. The 1/n >1 indicates that the adsorption bonds are weak, adsorption capacities is decreased and unfavourable (Aziz et al. 2008). The Langmuir isotherm determines the adsorption favourable or unfavourable. While, the Freundlich isotherm is used for modelling the adsorption on a heterogeneous surface. The results shown in Table 2 indicate the constant value of both equations. Values of correlation coefficients (R^2) were used to compare the isotherm models. Therefore, the Langmuir model is more suitable than the Freundlich model for the representation of adsorption data because it has higher R^2 values in all cases (Karadag et al. 2007).

Table 2: Parameters of Langmuir and Freundlich adsorption isotherm models

	Freundlich constants				Langmuir constants			
	K_f	**1/n**	**R^2**	**Equation (q_{eq})**	**Qo**	**b**	**R^2**	**Equation (q_{eq})**
B	4.443	-0.575	0.439	$4.443C^{-0.575}$	-0.092	-5.747	0.751	$\frac{0.529\ C_{eq}}{1-5.747\ C_{eq}}$
B+A	-0.131	-4.673	0.157	$-0.131C^{-4.673}$	-7.505	-0.034	0.746	$\frac{0.255\ C_{eq}}{1-0.034\ C_{eq}}$
B+Z	-1.131	1.887	0.176	$-1.131C^{1.887}$	12.828	0.028	0.186	$\frac{0.359\ C_{eq}}{1+0.028\ C_{eq}}$
B+L	-0.033	-2.193	0.786	$0.033C^{-2.193}$	-15.060	-0.007	0.979	$\frac{0.105\ C_{eq}}{1-0.007\ C_{eq}}$

Notes: B=bentonite, B+A=bentonite-alum, B+Z=bentonite-zeolite, and B+L=bentonite-limestone

3.6. Comparative of coagulants under optimized condition

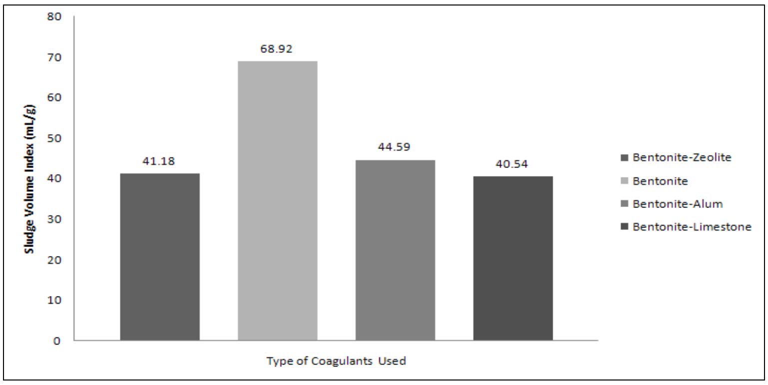
Based on the optimum dosage for each coagulant, comparison had been done for efficiency removal due to COD, turbidity and iron to obtain the best coagulant. The bentonite-zeolite mixture gave higher efficiency of iron (98%) and turbidity (95%). Meanwhile, bentonite-alum mixture gave only high efficiency removal for COD (93%). This indicates that, the efficiency removal of combination of bentonite was higher compared with raw bentonite. Therefore, it can be concluded that the best coagulants is bentonite-zeolite mixture.

3.7. Sludge volume index under optimized condition

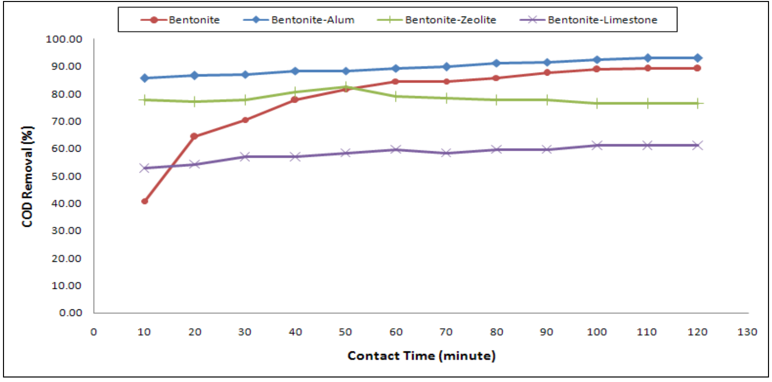
The sludge volume index (SVI) is the ratio between the volume and the weight of sludge formed after 30 minutes of settling and measures the compaction of the sediment (Gonzalez et al 2007). The abundant amount of sludge produced during coagulation-flocculation process by using chemical coagulants remains a serious problem to the operator in handling the sludge (Wang et al. 2007). Mishandling of chemical sludge will lead to quality deterioration of the environment (Anselme et al. 1995). Therefore, various types of coagulants with little sludge at final discharge of the plant should be developed. The experimental results for SVI are summarised in Figure 5(a). It indicates that the sludge generated by raw bentonite was higher with 68.92 mL/g. Meanwhile, bentonite-limestone mixture gave lower SVI of 40.54 mL/g.

4. Effect of contact time

The adsorption data for the uptake of COD versus contact time of different types of coagulants are presented in Figure 5(b). The results indicate that the adsorption capacity increases with the increase of contact time and becomes almost constant after 100 minutes. However, for subsequent experiments, the samples were left for two hours to ensure equilibrium. These results also indicate that the extent of adsorption increased rapidly in the initial stages but slowed in the later stages until attainment of equilibrium. Similar results were reported by Jamali et al. (2009) and Banat et al. (2000). This phenomenon is in agreement with Darus et al. (2007) that after reaching the equilibrium, the adsorbate species normally form a surface layer, which is only a molecule thick, on the surface of the adsorbent which prevents further attachment to it. It also shows that the adsorption capacity of combination bentonite is higher than raw bentonite.



(a)



(b)

Figure 5: Comparative of (a) SVI and (b) settling time

4.1 Zeta potential under optimized condition

Table 3 summarised the results of zeta potential for each coagulant under optimised conditions. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If the particles have a large negative or positive zeta potential, they will repel each other and there is dispersion stability. Meanwhile, if the particles have low zeta potential values then there is no force to prevent the particles coming together and there is dispersion instability. This phenomenon is in agreement with Salopek et al. (1992) that stability is at the lowest in the vicinity of a point where the value of zeta potential is approximately equal to zero. Therefore, if the suspension is to be destabilized, one of the ways is to lower the zeta potential i.e. to reduce the electronegative of a particle. Although the bentonite-alum mixture gave a higher value but it was still under the stabilisation condition of the colloid.

Table 3: Summarized of zeta potential value under optimized condition

Materials	Zeta Potential (mV)
Diionized water (control)	-2.07 (± 13.4)
Wastewater sample	-15.60 (± 8.26)
Bentonite + Alum	-26.70 (± 4.87)
Bentonite	-20.70 (± 4.05)
Bentonite + Zeolite	-19.90 (± 5.45)
Bentonite + Limestone	-17.60 (± 3.87)

5. Conclusions

Bentonite can be a good adsorbent for COD because it can achieve more than 75% of removal with a favourable dosage of 400 mg/L at pH 3.7. Furthermore, from the comparison of coagulants under optimised conditions it indicates that the best coagulant was bentonite-zeolite mixture with high efficiency removal of iron (98%) and turbidity (95%). However, bentonite-limestone and bentonite-zeolite mixture gave lower value of SVI (40-41 mg/L) and zeta potential under optimised conditions compared with other coagulants. Apart from that, the adsorption capacity rises with the increases of contact time and become almost constant after 100 minutes. In conclusion, the adsorption capacity of combination bentonite shows better performance than raw bentonite.

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6. References

1. Abdelaal, A.M., (2004), Using a natural coagulant for treating wastewater. Eighth International Water Technology Conference, IWTC8, Alexandria, Egypt.

2. Al-Bastaki, N., and Banat, F., (2003), Combining ultra filtration and adsorption on bentonite in a one-step process for the treatment of coloured waters. Resources, conversation and recycling, 41, pp 103-113.

3. Al-Qunaibit, M.H., Mekhemer, W.K., and Zaghloul, A.A., (2005), The adsorption of Cu (III) ions on bentonite – a kinetic study. Colloids Interface Sci., 283, pp 316-321.

4. Anselme, N., Subba Narasiah, N., and Brian, G.T., (1995), Active agents and mechanism of coagulation of turbid water using Moringa Oleifera. Wat. Res., 29, pp 703-710.

5. APHA, AWWA, WFE., (2005), Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association (APHA), Washington, D.C.

6. Aziz H.A., Alias S., Asaari F., and Adlan M.N., (2007), The use of alum, ferric chloride and ferrous sulphate as coagulants in removing suspended solids, colour and COD from semi-aerobic landfill leachate at controlled pH. Waste management research, 25, pp 556-565.

7. Aziz H.A., Adlan M.N., and Ariffin K.S., (2008), Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III) removal from water in Malaysia: Post treatment by high quality limestone. Bioresource technology, 99, pp 1578-1583.

8. Babel, S., and Kurniawan, T.A., (2003), Low-cost adsorbent for heavy metals uptake from contaminated water: a review. Journal of Hazardous Materials, B97, pp 219-243.

9. Banat, F.A., Al-Bashir, B., Al-Asheh, S., and Hayajneh, O., (2000), Adsorption of phenol by bentonite. Environmental pollution, 107, pp 191-198.

10. Bourliva, A., Michailidis, K., Sikalidis, C., Filippidis, A., and Apostolidis, N., (2010), Municipal wastewater treatment with bentonite from Milos Island, Greece. Bulletin of the geological society of Greece, proceeding of the 12th International Congress.

11. Chartterjee, T., Chartterjee, S., and HanWoo, S, (2009), Enhanced coagulation of bentonite particles in water by a modified chitosan biopolymer. Chemical engineering journal, 148, pp 414-419.

12. Darus, F.M., Laiman, R., and Yusof, M.N., (2007), The removal of basic dye (methylene blue) from aqueous solutions by adsorption on activated carbon prepared from palm oil fibre. Department of environmental technology, Universiti Teknologi MARA, Shah Alam.

13. Dwairi, R.A.A., and Al-Rawajfeh, A.E., (2012), Removal of cobalt and nickel from wastewater by using Jordan low-cost zeolite and bentonite. Journal of university of chemical technology and metallurgy, 47(1), pp 69-76.

14. Environmental Quality (Sewage and Industrial Effluents). Regulations, (1979), under the Laws of Malaysia-Malaysia Environmental quality act 1974 (ILBS, 1998).

15. Ghafari S., Aziz H.A., Isa M.H., and Zinatizadeh, A.A., (2009), Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. Journal of hazardous materials, 163, pp 650-656.

16. Gonzalez, T., Dominguez, J.R., Betran-Heredia, J., Garcia, H.M., and Sanchez-Lavado, F., (2007), Aluminium sulphate as coagulant for highly polluted cork processing wastewater: Evaluation of settleability parameters and design of a clarifier-thickener unit. Journal of hazardous materials, 148, pp 6-14.

17. Ferreira, G.A.M., Ciminelli, V.S.T., and Vasconcelos, W.L., (2009), Smectite organo functionalized with thiol groups for adsorption of heavy metal ion. Applied clay science, 42, pp 410-414.

18. Hu, Q., Xu, Z., Qiao, S., Haghseresht, F., Wilson, M., and Lu, G.Q., (2007), A novel color removal adsorbent from hetero coagulation of cationic and anionic clays. Journal of colloid and interface science, 308, pp 191-199.

19. Hussain, S., Aziz, H.A., Isa, M.H., Adlan, M.N., and Asaari, F.A.H., (2006) Physico-chemical method for ammonia removal from synthetic wastewater using limestone and GAC in batch and column studies. Bio resource technology, 98, pp 874-880.

20. Inglezakis, V.J., Stylianou, M.A., Gkantzou, D., and Loizidou, M.D., (2007), Removal of Pb (II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents. Desalination, 210, pp 248-256.

21. Jamali, H.A., Mahvi, A.H., and Nazmara, S., (2009), Removal of Cadmium from aqueous solutions by Hazel Nut Shell. World applied science journal, 5, pp 16-20.

22. Jiang, J.Q., Zeng, Z., and Pearce, P., (2004), Evaluation of modified clay coagulant for sewage treatment. Chemosphere, 56, pp 181-185.

23. Karadag, D., Akgul, E., Tok, S., Erturk, F., Kaya, M.A., and Turan, M., (2007), Basic and reactive dye removal using natural and modified zeolites. Journal chemical engineering, 52, pp 2436-2441.

24. Karapinar, N., and Donat, R., (2009), Adsorption behavior of Cu^{2+} and Cd^{2+} onto natural bentonite. Desalination, 249, pp 123-129.

25. Khenifi, A., Zohra, B., Kahina, B., Houari, H., and Zoubir, D., (2009), Removal of 2,4-DCP from wastewater by CTAB/bentonite using one-step and two-step methods: A comparative study. Chemical engineering journal, 146, pp 345-354.

26. Konig, T.N., Shulami, S., and Rytwo, G., (2012), Brine wastewater pretreatment using clay minerals and organ clays as flocculants. Applied clay science, 67(68), pp 119-124.

27. Ozcan, A., Omeroglu, C., Erdogan, Y., and Ozcan, A.S., (2007), Modification of bentonite with a cationic surfactant: An adsorption study of textile dye Reactive Blue 19. Journal of hazardous materials, 140, pp 173-179.

28. Rahmani, A.R., Samadi, M.T., and Ehsani, H.R., (2009), Investigation of clinoptilolite natural zeolite regeneration by air stripping followed by ion exchange for removal of ammonium from aqueous solutions. Iran journal of environmental health and science engineering, 6(3), pp 167-172.

29. Salopek, B., Krasic, D., and Filipovic, S., (1992), Measuement and application of zeta-potential. Geology and petroleum engineering, 4, pp 147-151.

30. Tahir, S.S., and Rauf, N., (2004) Removal of Fe (II) from the wastewater of a galvanized pipe manufacturing industry by adsorption onto bentonite clay. Journal of engineering management, 73, pp 285-292.

31. Wang, J.P., Chen, Y.Z., Ge, X.W., and Yu, H.Q., (2007), Optimization of coagulation-flocculation process for a paper-recycling wastewater treatment using response surface methodology. Colloids and surface A: Physicochemical Engineering, 302, pp 204-210.

32. Yarahmadi, M., Hossieni, M., Bina, B., Mahmoudian, M.H., Naimabadie, A., and Shahsavani, A., (2009), Application of Moringa Oleifer Seed Extract and Polyaluminium Chloride in Water Treatment. World applied sciences journal, 7 (8), pp 962-967.

33. Zhou, Y., Liang, Z., and Wang, Y., (2008), Decolorization and COD removal of secondary yeast wastewater effluents by coagulation using aluminum sulfate. Desalination, 225, pp 301-311.