



Leachate Pollutants Adsorption Using Potassium Hydroxide and Surfactant Modified Bentonite for Possible Use as Slow Release Fertiliser

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Abstract: Leachate pollutants adsorption using potassium hydroxide (KOH) and Surfactant Modified Bentonite (SMB) have been used as a new method for leachate treatment. KOH was used for removing the heavy metal elements and natural bentonite (NB) and SMB as adsorbents to adsorb ammoniacal-nitrogen, nitrate and phosphate. The suitable conditions for adsorbents are obtained using the percentage removal of colour, iron, COD, ammoniacal-nitrogen, nitrate and phosphate. The results obtained at optimum conditions for dosage and pH for NB was 233.3 g/L at pH 9. By comparison, for SMB they were 166.7 g/L at pH 8. For the contact time, using slow mixing and rapid mixing, SMB is better than NB. From the SEM-EDX analysis of weight percentage, after the NB and SMB treatments the elements of nitrogen, phosphorus and potassium for NB increased by 1.04, 1.32 and 5.13%; respectively; also for SMB 1.30, 2.25 and 6.81% respectively. It is clear that SMB gives better adsorption than NB and can be used for future application as a slow release fertiliser for plants.

Key words: Leachate • Natural bentonite • Surfactant modified bentonite • Adsorption • Fertiliser

INTRODUCTION

Landfill is one of the simplest methods for disposal of municipal solid waste around the world [1]. After solid waste is disposed into landfill, it undergoes physico-chemical and biological changes at the landfill site. Therefore, the degradation of the organic fraction of the waste is accomplished and this phenomenon generates a highly polluted wastewater called leachate [2, 3]. Leachate is defined as an aqueous effluent generated as a consequence of rainwater percolation through waste at the landfill site [4]. Leachate could contain a huge amount of pollutants such as organic substances measured as COD, biochemical oxygen demand (BOD), ammoniacal-nitrogen, heavy metals, major ions and inorganic salts [5].

In general, leachate generated from fresh acidogenic landfills; which is characterized by high BOD (3000-13000 mg/L), high strength COD (30000-60000 mg/L), high ammoniacal-nitrogen (500-2000 mg/L) and the ratio of BOD/COD is around 0.4 to 0.7. A high amount of COD

and BOD concentration and high BOD/COD ratio in fresh leachate makes it a candidate for anaerobic treatment prior to any aerobic process [3, 6]. The composition of landfill leachate greatly varies, depends on waste quantity and composition, decomposition rate and age of the waste. Also, it depends on method of landfilling or applied technology. The spread of leachate contamination from a landfill site is unacceptable and must be collected and treated before it is discharged. It must be treated close to the site to promote a sustainable closed-loop treatment strategy. This creates a need to develop on-site leachate treatment systems [7, 8].

The removal of metals from contaminated effluent is a matter of great interest in the field of environmental restoration, especially in this era of environmental concern. Several conventional methods are available for the treatment of effluents containing metals such as chemical precipitation, chemical oxidation, ion exchange, reverse osmosis and membrane filtration. However, most of these methods are ineffective for the removal of low concentrations (≤ 10 mg/L) of metal ions and resulted in

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toxic sludge production; which involves extra costs for treatment and disposal. On the other hand, adsorption is known as a cost effective and promising physico-chemical process for this purpose [9].

Currently, the adsorption process is believed to be a simple and effective method for water and wastewater treatment and the success of this method largely depends on the development of an efficient adsorbent. Activated carbon, clay minerals, biomaterials, zeolites and some industrial solid wastes have been widely used as adsorbents for adsorption of ions and organics in leachate treatment [10,11].

The aim of this study was to investigate the usage of SMB in adsorption process for the removal of ammoniacal-nitrogen, nitrate, phosphate and COD prior to eliminating the metals from the leachate. The generated sludge of adsorption can be used for the improvement of the soil fertility as slow release fertiliser.

MATERIALS AND METHODS

Sampling Location: Matang landfill is situated at 40°49'20.08" N and 100°40'44.08" E near the town of Taiping, Perak, Malaysia. The total area of this landfill site is about 12 hectare and it is equipped with a leachate detention pond. This landfill receives about 300 tonnes of solid waste daily and is classified as an improved anaerobic landfill. The landfilling operation started in 1995 and the landfill is now more than 17 years old [12].

The topography in the vicinity of the landfill is generally flat and low lying, with local elevations at the site ranging from 3.3 meters above sea level to as low as 1.8 meters. The climate of the area is classified as typical of Peninsular Malaysia, characterized by uniform temperature (daily mean minimum and maximum of 30 and 34°C, respectively) and high humidity (80 to 90%). This area is one of the wettest areas in Malaysia due to high average annual rainfall (4000 mm). Larut River and its tributary, Batu Tegoh River form the boundary of the landfill site on the south and east, respectively [13].

Leachate Sampling: Landfill leachate was collected manually from the leachate detention pond at an approximate depth of 1.0 m. The samples were kept in 25-litre plastic containers of high density polyethylene (HDPE). The samples were transported within 1 hour to the environmental laboratory and placed in a cool room (4°C) prior to experimental use, to minimise biological and chemical reactions in accordance with the Standard Methods for the Examination of Water and Wastewater

[14]. The on-site parameters were prepared in situ, to represent the actual condition of the raw leachate. Sensitive parameters of leachate such as total dissolved solids (TDS), electrical conductivity (EC), salinity, dissolved oxygen (DO), temperature and pH were determined during on-site sampling using YSI Multiparameter Probe. The metals in the landfill leachate were determined using Inductive Coupled Plasma (ICP) test method. Thereafter, only the highest metal concentration was considered in the leachate before and after treatment.

Preparation of Surfactant Modified Bentonite (SMB):

In this study, the amphoteric surfactant used is Miranol C2MSF 2M which is a very soft amphoteric surface-active agent, compatible with anionic, cationic (conditioning agent, germicides) and non-ionic materials [15]. The SMB was prepared with 0.02 mole (25.6 ml) of an amphoteric surfactant (Miranol C2MSF) that was mixed with 100 g NB and 1000 ml distilled water. Before the surfactant was mixed with the NB, the NB was washed several times with distilled water to avoid contamination. The mixtures were subjected to mechanical stirring for 4 hours at 250 rpm. After that, the mixture of SMB was left in a beaker for 3 days. After 3 days, the solution was filtered the solid residue was double washed with distilled water and then dried at 105 °C for about 24 hours. After being dried, the SMB was crushed to get the desired particle size and sieved using a mechanical shaker and 63µm sieve.

Leachate Treatment using KOH, NB and SMB:

Characterisations of the raw leachate before treatment were conducted as soon as possible after sampling. Measurement of the parameters was conducted in triplicate, according to the Standard Methods of Water and Wastewater [16]. In this experiment, KOH was used as a chemical reagent for the process of chemical precipitation. Four mole of KOH solution was used from a stock solution throughout the experiments. Chemical precipitation was performed with conventional jar test apparatus (Stuart Flocculator, Model: SW6, UK) comprising of six paddle rotors (2.1 cm × 7.5 cm) each equipped with six 1000 mL beakers, using a variable speed mixer (0 to 350 rpm). The leachate samples were left for 2 hours at ambient temperature before each experiment was conducted. For each experiment, each beaker used for testing was filled with 300 mL of leachate sample. Jar test equipment in the physico-chemical treatment experiments was used to investigate the effect of KOH at various pH on removing the iron, colour, COD and turbidity content

of the leachate. During the treatment, the pH of the leachate sample was readjusted to the desired level using the KOH reagent. The pH varied from pH 9 to 13. One beaker was used as a control. Rapid mixing for 4 min (200 rpm), slow mixing for 20 min (60 rpm) and 30 min settling time was applied sequentially in the chemical precipitation. The supernatant of leachate from the treatment with KOH was filtered with a glass microfiber filter (90 mm) using the filtered media before analysis of the iron, colour and COD removal according to the standard methods using a DR2800 Spectrophotometer. The percentage removal of all the parameters versus pH coagulant was plotted. The highest removal point indicated the suitable pH condition for the leachate treatment with KOH. After the suitable pH from the leachate treatment with KOH was obtained, the supernatant from the chemical precipitation process was subjected to adsorption tests with NB and SMB. Before the leachate underwent the second stage of treatment with NB and SMB; the leachate effluent was filtered again to make sure that the suspended solids were removed. The batch studies for NB and SMB were conducted in order to find suitable conditions for dosage, pH and contact time. The dosages ranged between 10 to 90 g for both NB and SMB in the batch studies. After the suitable dosage was obtained, the leachate treatment was continued with batch studies for pH variation in the range of 6 to 11. The application of contact time by rapid mixing, slow mixing and the settling time were the same as in the KOH treatment. After treatment with NB and SMB, the effluent was filtered again with a glass microfiber filter (size 90 mm) before the concentration of colour, COD, iron, ammonia, phosphate and nitrate was measured.

RESULTS AND DISCUSSION

Landfill Leachate Characterisation: According to the Standard Methods for the Examination of Water and Wastewater, the characterisation of the raw leachate, such as pH, turbidity, colour, BOD₅, COD, ammoniacal-nitrogen, nitrate, phosphate, potassium and metals such as iron, copper, nickel, manganese and zinc were determined before the leachate was treated. Table 1 shows the raw leachate characterisation of Matang landfill from the laboratory analyses. The characteristics of the landfill leachate from this study were obtained before the landfill leachate treatment stage commenced. From Table 1, the colour, COD, BOD, NH₄-N, arsenic, manganese and nickel concentrations exceeded the

parameter limits of standard discharges of leachate. Iron with maximum concentration 6.41 mg/L had the highest concentration of all measured metals in the leachate.

The leachate collected could be classified as alkaline since the pH values varied from 7.86 to 8.43. Generally, the pH of a stabilised leachate is higher than a fresh leachate. The pH for fresh leachate is less than 6.5, intermediate leachate is in the range of 6.5 to 7.5 and stabilized leachate is greater than 7.5 [17]. Moreover, the data obtained indicated that despite the short landfill lifetime, some parameters such as high pH (on average 8.15), low COD concentration (<2000 mg/L COD), low BOD₅/COD ratio (<0.4) and low heavy metal concentration indicated that the landfill was already characterised by methanogenic conditions at the beginning of the monitoring period [18].

The colour of the leachate sample in this study was orange brown or dark brown. The maximum value of colour for Matang landfill leachate was 8510 Pt-Co, while the minimum value was 4200 Pt-Co. The high concentration of colour in the landfill leachate is due to the high presence of organic substances. In general, the leachate produced by an old landfill with low biodegradability is classified as stabilised leachate. Stabilised leachate contains a high level of organic substances such as humic and fluvic compounds, which can be indicated by leachate colour [19]. Landfill leachate is a very dark coloured liquid formed primarily by the percolation of precipitation through open landfill or through the cap of the completed site. The decomposition of organic matter such as humic acid may cause the water to be yellow, brown or black [20].

From the characterisations of the landfill leachate, it was shown that the concentrations of arsenic, manganese, nickel and zinc were relatively low on average 0.21, 0.26, 0.27 and 0.36 mg/L respectively. Meanwhile the concentration of iron was the highest among the heavy metal elements contained in landfill leachate which average 4.62 mg/L. In general, the concentration of heavy metals in landfill leachate is fairly low. The concentration of heavy metals in landfill is generally higher at the earlier stages because of greater metal solubility as a result of low pH caused by production of organic acids [18].

The COD value for the landfill leachate varied from 867 to 1572 mg/L. The landfill for this study can be classified as a stabilised landfill as the COD value was less than 4000 mg/L, in accordance with results of a previous study on stabilized landfill [19]. The COD values obtained from our study seem to have exceeded the permissible limits issued by the Environmental Quality

Table 1: Characterisation of raw landfill leachate

Parameter	Units	Value				
		Minimum	Maximum	Average*	Standard Deviation	Standard**
pH	-	7.86	8.43	8.15	0.26	6.0-9.0
Turbidity	NTU	136	177	156.5	19.10	-
Colour	PtCo	4200	8510	6355	1878.45	100
Chemical Oxygen Demand (COD)	mg/L	867	1572	1219.5	324.01	400
Biological Oxygen Demand (BOD ₅)	mg/L	108	360	234	114.34	20
Ratio BOD/COD	-	0.12	0.23	0.18	-	-
Ammoniacal Nitrogen (NH ₄ -N)	mg/L	1145	1620	1382.5	221.75	5
Nitrate (NO ₃ ⁻)	mg/L	45	80	62.5	14.72	-
Phosphate (PO ₄ ³⁻)	mg/L	88	160	124	31.82	-
Potassium (K)	mg/L	725	909	817	65.71	-
Arsenic (As)	mg/L	0.10	0.32	0.21	0.09	0.05
Iron (Fe)	mg/L	2.83	6.41	4.62	1.52	5.00
Manganese (Mn)	mg/L	0.23	0.28	0.26	0.02	0.20
Nickel (Ni)	mg/L	0.14	0.40	0.27	0.11	0.20
Zinc (Zn)	mg/L	0.21	0.46	0.36	0.11	2.00

*Average reading for the period of leachate sampling between January and March 2013

** Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009 (PU (A) 433), Second Schedule (Regulation 13), Acceptable Conditions for Discharge of Leachate

(Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009 (PU (A) 433), Second Schedule (Regulation 13), Acceptable Conditions for Discharge of Leachate wherein the acceptable COD value standard is 400 mg/L. A contributing factor to the high COD level could be attributed to non-biodegradable compounds and inorganic oxidisable compounds [21].

The concentration of ammoniacal-nitrogen is in the range of 1145 to 1620 mg/L. This high concentration of untreated ammonia leads to stimulated algae growth, decreased performance of biological treatment systems, accelerated eutrophication, promoted dissolved oxygen depletion and increased toxicity of living organisms in water bodies [22]. Nitrogen removal is important to control eutrophication and adsorption is an efficient treatment process.

The concentration of nitrate in the leachate from this landfill site was 62.5 mg/L. The nitrate concentration from this study was higher than previous studies published by Aziz *et al.* [23]. Microbial decomposition of organic carbon influenced many processes of the nitrogen cycle. With time, the nitrogen concentration decreased due to microbial utilisation of nitrate compounds and there was denitrification of ammonia gas [19]. The phosphate concentration in this study varied from 88 to 160 mg/L and potassium was 817 mg/L. The phosphate value in this study was consistent with previous studies with a range of 57 to 197 mg/L [22].

Batch Studies for First Stage of Leachate Treatment:

Batch studies for the first stage of leachate treatment were started using KOH as a chemical precipitation process and Granular Activated Carbon (GAC) as an adsorption process to remove heavy metals and COD [24]. This treatment used jar test equipment with three types of contact time applied: rapid mixing at 200 rpm for 4 min; slow mixing at 60 rpm for 20 min; and settling time for 30 min. The percentage removal of iron, colour and COD using KOH and GAC were compared to determine the suitable conditions for proceeding to the second stage of leachate treatment using NB and SMB as adsorbents. Fig. 1 shows the percentage removal of colour, iron, COD, turbidity, ammonia, nitrate and phosphate against the pH for KOH. Meanwhile Fig. 2 shows the percentage removal of colour, iron, COD, ammonia, nitrate and phosphate against the GAC dosage.

The initial concentration of raw leachate for colour, iron, COD, ammonia, nitrate and phosphate before treatment with KOH were 8350 Pt-Co, 6.27, 1000, 696.67, 65 and 41.83 mg/L, respectively. Fig. 2 shows the highest percentage removal of colour, iron, COD, nitrate and phosphate were 40.12, 46.12, 10.0, 27.87 and 33.86% at pH 13, respectively. The highest percentage removal of ammonia was 48.72% at pH 11. From the pattern of the graph shown, it can be seen that increasing the pH of the leachate with KOH caused the percentage removal of colour, iron, COD, turbidity, nitrate and phosphate to increase.

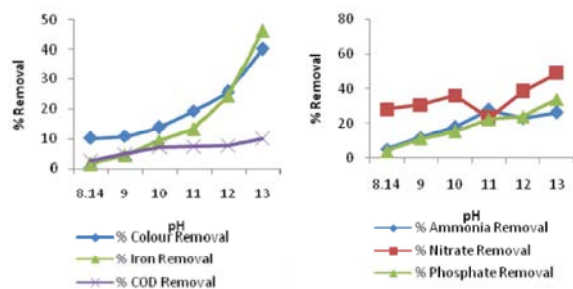


Fig. 1: Percentage removal of colour, iron, COD, turbidity, ammonia, nitrate, and phosphate against dosage for KOH

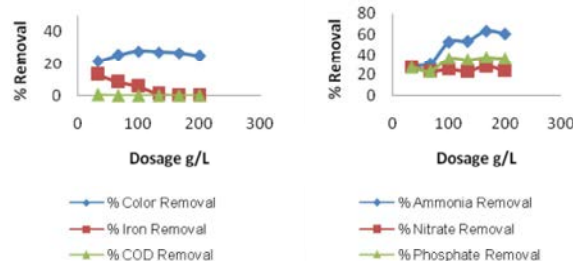


Fig. 2: Percentage removal of colour, iron, COD, ammonia, nitrate, and phosphate for GAC

The initial concentration of raw leachate for colour, iron, COD, turbidity, ammonia, nitrate and phosphate before treatment with GAC were 8350 Pt-Co, 6.12, 1271 mg/L, 187 NTU, 696.67, 65 and 41.83 mg/L, respectively. Fig. 2 shows the highest percentage removal of colour, iron, COD, ammonia, nitrate and phosphate were 28.14, 13.26, 0.66, 63.25, 28.21 and 37.30%, respectively. The graph shows that the percentage removal of colour, iron and COD decreased when the dosage increased. The percentage removal of ammonia, nitrate and phosphate increased when the dosage was increased.

Batch Studies for Second Stage of Leachate Treatment:

After comparing the percentage removal of colour, iron, COD and turbidity between landfill leachate treatment with KOH and GAC, it was found that the leachate treatment with KOH was much better than GAC in removing colour, iron, COD and turbidity. Meanwhile, GAC was better for adsorption of ammonia, nitrate and phosphate than KOH. The aims for this study in the first stage of leachate treatment were to remove more colour, iron, COD and turbidity and less adsorption of ammonia, nitrate and phosphate. This was because more adsorption of ammonia, nitrate and phosphate were needed in the

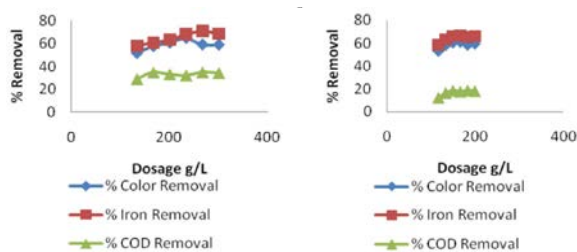
leachate treatment with NB and SMB in order to make NB and SMB into a slow release fertiliser product for future application.

Before the second stage of leachate treatment commenced, the leachate was treated with KOH at pH 13 and then the effluent in the leachate was filtered using filtering media to remove suspended solids. After filtering, the leachate was treated using NB and SMB as adsorbents. For these batch studies, there were three factors that were considered: the effect of dosage, pH and contact time (rapid mixing, slow mixing and settling time). The suitable conditions for dosage, pH and contact time were determined in order to compare the adsorption process of ammonia, nitrate and phosphate between NB and SMB.

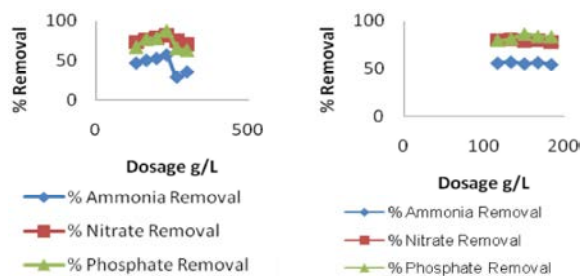
Effect on Dosage: Fig. 3 shows the percentage removal of colour, iron and COD against dosage using NB and SMB. The dosage was varied from 133.3 to 300 g/L for NB and from 116.7 to 200 g/L for SMB. The leachate sample used in this treatment was 300 mL for both adsorbents. The adjusting pH for these batch studies was pH 8.5 and the pH of the raw leachate averaged pH 8.15. The least chemical reagent was used for adjusting the pH in the leachate treatment as it resulted in a saving in the cost of the reagent. The constant rapid mixing was 200 rpm for 4 min, the slow rapid mixing was 60 rpm for 20 min and the settling time was 30 min.

Fig. 3 also shows the percentage removal of colour, iron and COD increased when the dosage increased. The highest colour removal percentages for NB and SMB were 64.95 and 61.18% at dosage 233.3 and 166.7 g, respectively. The highest percentage removal of iron for NB and SMB were 71.18 and 66.88% at dosage of 266.7 and 166.7 g/L, respectively. The percentage removal of colour and iron, at more than 50%, while the highest percentage removal of COD for NB and SMB were only 35.17 and 18.8% at dosage 166.7 and 183.3 g, respectively. From the results, it can be seen that NB produces a higher percentage removal of colour, iron and COD than SMB. However, in terms of the amount of dosage used to achieve the most suitable conditions, the SMB was considered to be an excellent adsorbent, since it obtains a higher removal of colour, iron, COD and turbidity with a lower adsorbent dosage when compared to NB.

Fig. 4 shows the percentage removal of ammonia, nitrate and phosphate for NB and SMB with an increase in the dosage. The highest percentage removal



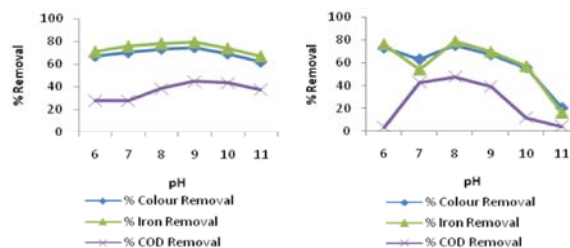
(a) (b)
Fig. 3: Percentage removal of colour, iron, COD, and turbidity against dosage for (a) NB and (b) SMB



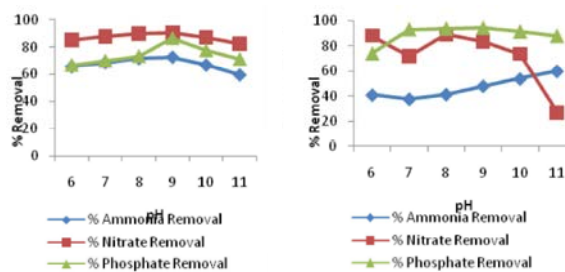
(a) (b)
Fig. 4: Percentage removal of ammonia, nitrate, and phosphate against dosage for (a) NB and (b) SMB

20f ammonia, nitrate and phosphate for NB was 57.1, 88 and 81.66% at dosage 233.3 g/L, respectively. The highest percentage removal of ammonia, nitrate and phosphate for SMB was 56.88, 79.98 and 86.47% at dosage 133.3, 166.7 and 150 g/L, respectively. SMB has a higher percentage removal for phosphate than NB. Meanwhile for ammonia and nitrate, NB has a higher percentage removal than SMB.

SMB can be excellent adsorbents in terms of adsorption of ammonia, nitrate and phosphate since it can adsorb at a lower dosage when compared to NB. The SMB, as an adsorbent for ammonia, nitrate and phosphate in this study, can be used for future application as a slow release fertiliser for plants, since they need nitrogen, phosphorous and potassium for growth. After considering all the parameters in terms of removal, the suitable dosages were 233.3 and 166.7 g/L for NB and SMB, respectively. For the effect of dosage, the general patterns of colour, iron, COD, turbidity, ammonia, nitrate and phosphate removal were consistent and increased with larger dosages. However, an exception was the removal of COD by NB and ammonia by SMB, which both decreased rapidly and fluctuated when the dosages were increasing.



(a) (b)
Fig. 5: Percentage removal of colour, iron, and COD against pH for (a) NB and (b) SMB

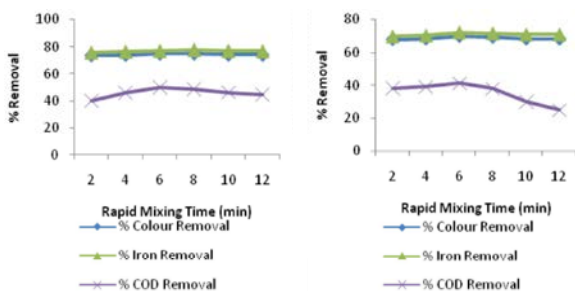


(a) (b)
Fig. 6: Percentage removal of ammonia, nitrate, and phosphate against pH for (a) NB and (b) SMB

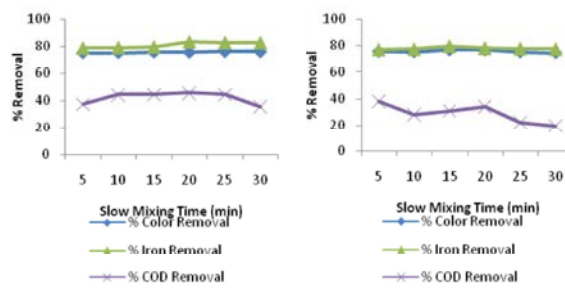
Effect on pH: Fig. 5 shows the percentage removal of colour, iron, COD and turbidity against pH for NB and SMB. The pH was varied from pH 6 to pH 11. The suitable dosages of 233.3 and 166.7 g were applied for NB and SMB, respectively. The contact time applied in this treatment was the same as in the previous experiment on the effect on dosage.

Fig. 5 shows the highest percentage removal of colour, iron and COD for NB were 75.05, 79.4 and 44.85%, at pH 9, respectively. Meanwhile for SMB, the highest percentage removal of colour, iron and COD were 75.44, 78.85 and 47.61% at pH 8, respectively. The percentage removal of colour and iron for SMB fluctuated at pH 7 and decreased rapidly at a higher pH. Meanwhile, the graph of NB was smooth and the percentage removal of colour, iron and COD increased slowly and was higher than for SMB.

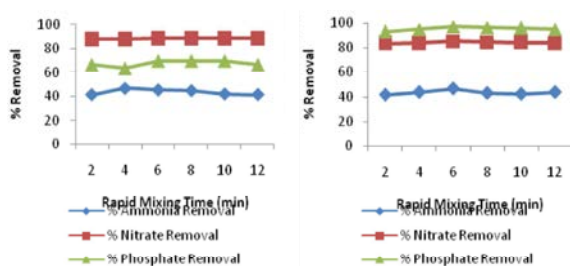
Fig. 6 shows the percentage removal of ammonia, nitrate and phosphate for NB and SMB with an increased pH. The highest percentage removal of ammonia, nitrate and phosphate for NB was 72.71, 90.6 and 86.67% at pH 9, respectively. The highest percentage removal of ammonia, nitrate and phosphate for SMB was 59.97, 89.58 and 94.25% at pH 11, 8 and 9, respectively.



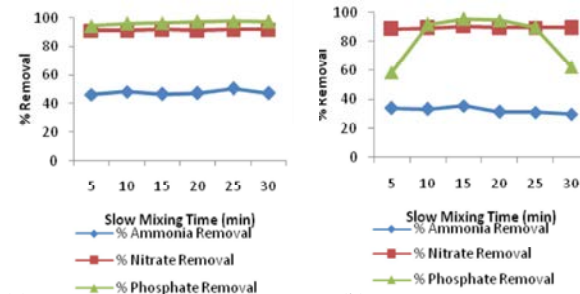
(a) (b)
Fig. 7: Percentage removal of colour, iron, COD, and turbidity against rapid mixing time for (a) NB and (b) SMB



(a) (b)
Fig. 9: Percentage removal of colour, iron, and COD against slow mixing time for (a) NB and (b) SMB



(a) (b)
Fig. 8: Percentage removal of ammonia, nitrate, and phosphate against rapid mixing time for (a) NB and (b) SMB



(a) (b)
Fig. 10: Percentage removal of ammonia, nitrate, and phosphate against slow mixing time for (a) NB and (b) SMB

In comparing NB and SMB, NB is better than SMB in adsorption of ammonia and nitrate. Meanwhile SMB is better than NB in adsorption of phosphate. The pH value needed for plant growth is in the range of 6-9. Therefore, NB and SMB are able to be used as a slow release fertiliser since they can supply the nutrients plants need, which are nitrogen, phosphorus and potassium. The suitable pH for NB and SMB were 8 and 9, respectively after considering all the parameter removals.

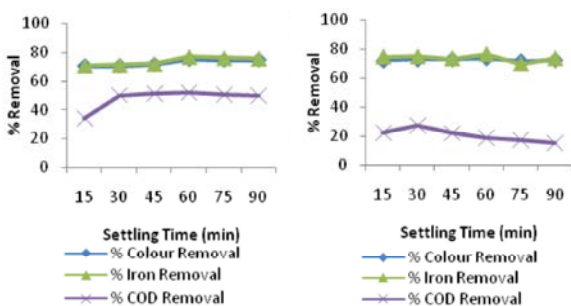
Effect on Contact Time

Rapid Mixing Time: Figures 7 and 8 show the percentage removal of colour, iron, COD, ammonia, nitrate and phosphate at the rapid mixing time for NB and SMB. The ranges of rapid mixing time were 2 to 12 min at 200 rpm. The adsorbent dosage and pH were adjusted to their suitable condition determined previously, where the dosage and pH applied for NB in rapid mixing was 233.3 g/L at pH 9. However, for SMB the dosage and pH applied was 166.7 g/L at pH 8. Figures 7 and 8 show the percentage removal increased as time increased, but with little difference. The highest percentage removal of

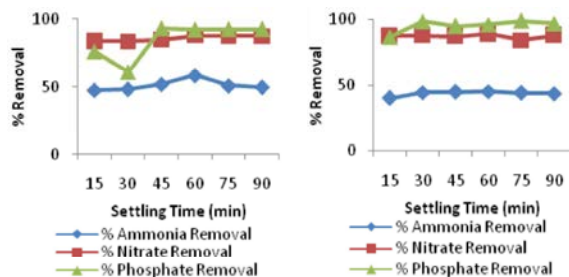
colour, iron and COD for NB was 75.21, 77.67 and 50.09% and for SMB was 69.68, 72.15 and 41.21%, respectively. The highest percentage removal of ammonia, nitrate and phosphate for NB was 46.75, 88.49 and 69.67% and for SMB was 46.5, 85.07 and 96.91%, respectively.

Slow Mixing Time: Figures 9 and 10 show the percentage removal of colour, iron, COD, turbidity, ammonia, nitrate and phosphate at the slow mixing time for NB and SMB. The range of slow mixing time was between 5 and 35 min at 60 rpm. The adsorbent dosage, pH and slow mixing times were adjusted to their suitable condition determined previously, where the dosage, pH and slow mixing time for NB was 70g, pH 9 and 8 min, respectively. For SMB, the suitable dosage, pH and slow mixing time were 50 g at pH 8 and 6 min.

Based on Figures 9 and 10, the percentage removal increased as time increased but there was little difference in the percentage removal between the intervals of slow and rapid mixing times. The highest percentage removal of colour, iron and COD for NB was 75.97, 83.44 and 45.66% and for SMB were 76.73, 79.56 and 33.81%, respectively.



(a) (b)
Fig. 11: Percentage removal of colour, iron, and COD against slow settling time for (a) NB and (b) SMB



(a) (b)
Fig. 12: Percentage removal of ammonia, nitrate, and phosphate against settling time for (a) NB and (b) SMB

The highest percentage removal of ammonia, nitrate and phosphate for NB was 50.67, 97.49 and 91.77% and for SMB it was 35.6, 95.69 and 90.52%, respectively.

Settling Time: Figures 11 and 12 show the percentage removal of colour, iron, COD, turbidity, ammonia, nitrate and phosphate against settling time for NB and SMB. The range of settling time was from 15 to 90 min. The adsorbent dosage, pH, rapid mixing time and slow mixing time were adjusted to their suitable condition determined previously. For NB the suitable dosage, pH, rapid mixing time and slow mixing time applied in settling time were 233.3 g/L, pH 9, 8 min and 25 min, respectively. For SMB the suitable dosage, pH, rapid mixing time and slow mixing time were 50 g, pH at 8 for 6 and 15 min, respectively.

Based on Figures 11 and 12, the percentage removal increased as time increased with little difference of percentage removal between settling time in rapid and slow mixing times. The highest percentage removal of colour, iron and COD for NB was 74.92, 76.87 and 51.8% and for SMB was 73.96, 76.53 and 27.49%, respectively.

Meanwhile, the highest percentage removal of ammonia, nitrate and phosphate for NB was 58.65, 88.04 and 93.37% and for SMB was 45.16, 88.85 and 98.71%, respectively. For the effect of contact time, we can conclude that it has less influence on all parameters for removal. For the effect on dosage and pH, it has considerable influence on all parameters for removal, since the percentage removal for variation of dosage and pH were higher than the effect on contact time.

Analysis of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX): In this study, samples of NB and SMB before and after treatment were analysed using SEM and EDX. The SEM analysis defined the morphology of shape and structure of NB and SMB while the EDX analysis defined their chemical compositions. SEM-EDX analyses are conducted in order to show the different elements contained in NB and SMB before and after treatment. These analyses were performed on clean surfaces to avoid any contamination.

Fig. 13 shows the surface of NB before treatment (x 10000, SEM) and is approximately 14 μm in size. The result of the SEM analysis shows that the shape of NB before treatment has a smooth surface and coating. The biggest constituent elements in NB before treatment were silicon and oxygen, with an average of 43.27 and 31.45% by weight. Meanwhile, other element content such as carbon, aluminium and magnesium in NB in terms of percentage by weight are shown in Table 2.

Fig. 14 shows the surface of NB after treatment (x 5000, SEM) and is approximately 20 μm in size. The shape of NB after treatment is rough. This is because of the increase of ions in the adsorption process and pollutant ions from the leachate are attached to the raw NB morphology structure. The biggest constituent elements in NB after treatment are silicon and oxygen and these are 44.98 and 33.65%, respectively (Table 3). The elements in NB after treatment are increased, with the presence of nitrogen, phosphorus and potassium. This indicates that the process of adsorption has occurred in the leachate treatment using NB.

Fig. 15 shows the surface of SMB before treatment (x 5000, SEM) and is approximately 22 μm in size. The SEM micrographs and the shape of SMB before treatment is different to the raw NB. The surface of the raw NB was disturbed by the added surfactant. The anionic and cationic surfactant has changed the shape of the raw NB. The greatest constituent elements in SMB before

Table 2: Elements in NB before treatment

Element	Wt %	At %
Carbon (C)	16.6	24.49
Oxygen (O)	31.45	37.67
Magnesium (Mg)	2.02	1.60
Aluminium (Al)	6.65	4.73
Silicon (Si)	43.27	29.52

Table 3: Elements in NB after treatment

Element	Wt %	At %
Carbon (C)	2.9	5.24
Nitrogen (N)	1.04	1.61
Oxygen (O)	33.65	45.60
Magnesium (Mg)	2.59	2.31
Aluminium (Al)	8.39	6.74
Silicon (Si)	44.98	34.73
Phosphorus (P)	1.32	0.92
Potassium (K)	5.13	2.84

Table 4: Elements in SMB before treatment

Element	Wt %	At %
Carbon (C)	4.79	8.53
Oxygen (O)	31.80	42.52
Magnesium (Mg)	2.61	2.30
Aluminium (Al)	11.22	8.89
Silicon (Si)	49.58	37.76

Table 5: Elements in SMB after treatment

Element	Wt %	At %
Carbon (C)	6.06	10.73
Nitrogen (N)	1.30	1.98
Oxygen (O)	31.71	42.13
Magnesium (Mg)	3.04	2.66
Aluminium (Al)	9.70	7.64
Silicon (Si)	39.11	29.60
Phosphorus (P)	2.25	1.54
Potassium (K)	6.82	3.71

treatment were silicon and oxygen with an average of 49.58 and 31.80%. Other elements such as carbon, oxygen and magnesium in SMB in terms of percentage by weight are shown in Table 4.

Fig. 16 shows the surface of SMB after treatment (x 5000, SEM) and is approximately 20 μm in size. The shape of SMB after treatment is like NB after treatment. The biggest constituent elements in SMB after treatment are silicon and oxygen with a value of 39.11 and 31.71%, respectively (Table 5). The elements in SMB after treatment are also increased, with the presence of nitrogen, phosphorus and potassium. This shows that the process of adsorption of ammonia, nitrate, phosphate and potassium in leachate treatment using SMB had occurred, similar to NB. Nevertheless, percentage weight of elements nitrogen, phosphorus and potassium in SMB

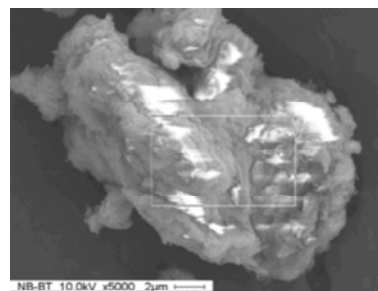


Fig. 13: SEM analysis for NB before treatment

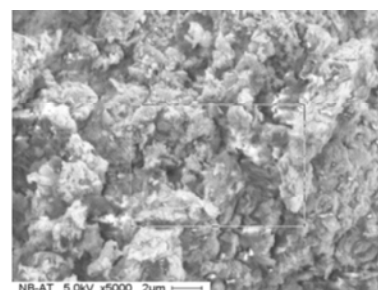


Fig. 14: SEM analysis for NB after treatment

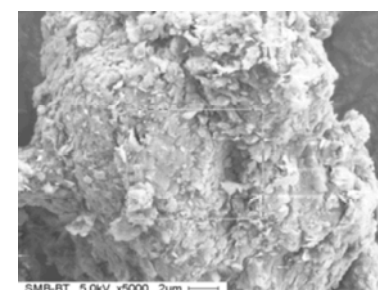


Fig. 15: SEM analysis for SMB before treatment

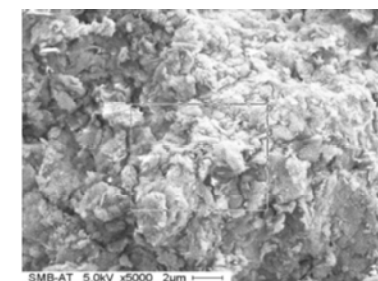


Fig. 16: SEM analysis for SMB after treatment

after treatment was greater than in NB with 1.30, 2.25 and 6.81%, respectively (Table 5). By comparison, in NB they were 1.04, 1.32 and 5.13%, respectively (Table 3).

CONCLUSION

From this study, in the first stage of leachate treatment by using KOH to remove the heavy metals and COD from raw leachate were achieved. The initial

concentrations in raw leachate of colour, iron, COD, ammonia, nitrate and phosphate were 8350 Pt-Co, 6.27, 1000, 696.67, 65 and 41.83 mg/L, respectively. Meanwhile, the highest percentage removal of colour, iron, COD, nitrate and phosphate were 40.12, 46.12, 10.0, 27.87 and 33.86% at pH 13, respectively. The highest percentage removal of ammonia was 48.72% at pH 11. In the second stage was achieved by subjecting the KOH treated leachate to NB and SMB, which were used as adsorbents. After considering all the percentage removal parameters for NB, the suitable condition for dosage, pH and contact time of adsorption for ammoniacal nitrogen ($\text{NH}_4\text{-N}$), phosphate (PO_4^{3-}) and nitrate (NO_3^-) were at dosage 233.3 g/L, pH 9, 8 min (rapid mixing time), 25 min (slow mixing time) and 60 min (settling time). Meanwhile, for SMB they were at dosage 166.7 g/L, pH 8, 6 min (rapid mixing time), 15 min (slow mixing time) and 30 min (settling time). From SEM-EDX analysis, NB and SMB were an increase in elements (nitrogen, phosphorus and potassium) after pollutants leachate adsorption. The percentage weight of these elements in SMB were 1.3, 2.25 and 6.81% while for NB were 1.04, 1.32 and 5.13%, respectively.

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Persian Abstract

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چکیده

جذب آلاینده های شیرابه با استفاده از هیدروکسید پتاسیم (KOH) و سورفکتانت بنتونیت اصلاح شده (SMB) به عنوان یک روش جدید برای عملیات تصفیه شیرابه استفاده شده است. هیدروکسید پتاسیم به عنوان جاذب جهت حذف فلزات سنگین استفاده شده و همچنین بنتونیت طبیعی و سورفکتانت بنتونیت اصلاح شده جهت جذب نیترژن آمونیاکی، نیترات و فسفات استفاده شده است. شرایط مناسب برای جاذب با استفاده از درصد حذف کلر، آهن، COD، نیترژن آمونیاکی، نیترات و فسفات بدست آمده اند. نتایج بدست آمده در شرایط بهینه برای مقدار بنتونیت طبیعی برابر ۲۳۳/۳ گرم بر لیتر و pH برابر با ۹ می باشند. در مقابل، این مقادیر برای سورفکتانت بنتونیت اصلاح شده برابر ۱۶۶/۷ گرم بر لیتر و pH برابر با ۸ می باشند. در مورد زمان تماس با استفاده از اختلاط آهسته و تند، سورفکتانت بنتونیت اصلاح شده نسبت به بنتونیت طبیعی بهتر عمل کرده است. با استفاده از نتایج آنالیز SEM-EDX درصد وزنی، عناصر نیترژن، فسفر و پتاسیم برای بنتونیت طبیعی به ترتیب برابر ۱/۰۴، ۱/۳۲ و ۵/۱۳٪ و برای سورفکتانت بنتونیت اصلاح شده به ترتیب برابر ۱/۳۰، ۲/۲۵ و ۶/۸۱٪ به دست آمده اند. نتایج نشان می دهند که سورفکتانت بنتونیت اصلاح شده نسبت به بنتونیت طبیعی، جذب بهتری نشان داده و می تواند در آینده به عنوان آزاد کننده آهسته کود شیمیایی برای نباتات به کار گرفته شود.
