Peer-reviewed version available at Clean Technol. 2018, 1, 9; doi:10.3390/cleantechnol1010009

Removal of COD and Ammonia-Nitrogen by Sawdust/Bentonite Augmented SBR Process

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Abstract
Water pollutants removal by biomass adsorbent has been considered innovative and cost effective, thus commendable for application in industrial applications. However, certain important aspects have been overlooked by researchers, namely the efficiency in the operation time and pollutant removal. In this research, landfill leachate samples with organic components were treated using bentonite-enriched with sawdust augmented (SBR) process. By modifying the pH, the sawdust samples were categorized into three: the acidic, the alkaline, and the neutral. To bentonite samples, the pH-adjusted sawdust was added at 10%, 20%, and 30% amounts by mass respectively. At the optimum aeration rate of 7.5 L/min and contact period of 22 h, the treatment achieved 99.28% and 95.41% removal of COD and NH_3-N with bentonite respectively. For both pollutants, in the presence of sawdust, the removal reduced by about 17% with contact period reduced to 2 h which was a considerable achievement.

Keywords: Ammonia nitrogen; Bentonite; COD; RSM; Sawdust; SBR

1. Introduction

Solid waste disposal by sanitary landfilling is the rational and cost effective choice for most circumstances. However, despite the advantages, the generation of leachate aided by the precipitation or percolation through the landfill cap is the inevitable consequence of disposal by landfilling, and has been the main problem of this method [1]. The presence of a huge amount of organic substances measurable by the chemical oxygen demand (COD) and the biochemical oxygen demand (BOD) together with ammonia, inorganic salts, and high concentration of heavy metals such as lead and copper, could bring health issues to human [2] Re-circulating the leachate back into the landfill, discharging it into the sanitary sewer system, and treating it at site are some of the options for treatment that could also lead to surface and ground water contamination.

Leachate and waste water carry various pollutant concentrations that the treatment and the improvement procedures in qualifying them for direct discharge into surface water have not been easy. In a high quality treatment, a combination of physical, chemical, and biological methods is often applied [3-4]. The physical method may involve adsorption by clay soil, activated carbon, or zeolites; or the application of membrane techniques or air striping. The chemical method may use the coagulation–flocculation techniques, chemical oxidation, or ozonation; while the biological method may also involve the use of activated carbon [5-6]. The activated carbon in particular could be a carrier of micro-organisms, could enhance biomass settling properties, or

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could provide sorption of heavy metals and toxic organics, thus scientists have been encouraged to use it as the main purifying substance of landfill leachates. However, the high cost of the material has been the main impediment to its use thus alternative solutions such as using mineral additives and mineral clays became attractive [7].

Bentonite is an alluvial clay of weathered and aged volcanic ash and is belonged to the smectite group [8]. It is formed by the hydrous aluminosilicate minerals, each less than 2µ in size, making up the colloidal segments of it. The main reasons that bentonite has been preferred for various applications are its cost-effectiveness and availability throughout the world. Bentonite has been used as soil additive in agricultural engineering and mixture in construction fluid in civil engineering. It has also been used as a landfill liner in environmental engineering, as encapsulator of certain waste deposits, and as an adsorbent of heavy metals and phenol in the treatment of wastewater [9-12]. Its cation exchange capacity and dissociation capability of the hydrogen ions are the main reasons for the bentonite being negatively charged and therefore considered a good adsorbent [13]. In addition, bentonite is also capable of adsorbing bacteria constituents of the leachates.

One of the biological systems used for treatimg pollutants in leachates and waste water is the sequencing batch reactor (SBR) which merges all treatment units and processes into a single system, while the traditional methods of pollutant removal normally rely on various systems. Typically, a SBR accommodates five processing stages - fill, react, settle, draw, and idle [14]. Other than the landfill leachates, the SBR has been used for treating the domestic, municipal, industrial, dairy, synthetic, toxic and slaughterhouse wastewater [15].

Various methods are available in litrature and industry for removing organic pollutants from leachate or wastewater through improving physical, chemical, electrical, thermal and biological properties [16-20]. Oxidation, reverse osmosis, ion exchange, electro-dialysis, electrolysis, and adsorption are just a number of the treatment methods and excellent technologies available in the field. However, the cost of water traetment in the aformentioned technologies is at least twice as much as the cost of using the adsorption process [21]. Adsorption, due to its naturality, cost effectiveness, and ease of application is thus considered the preferred wastewater treatment method for removing soluble and insoluble organic pollutants.

The activated carbon has already been known as an adsorbent in the 1940's. However, the costly nature of the material has somehow limited its use [22]. Consequently, the search for the low cost adsorbents has continued [23-26]. The use of waste products in developing low cost adsorbents has also contributed to minimization of waste production and recovery of waste materials [27].

Sawdust and other agricultural products have been the lowcost, biomass adsorbents used in experiments since the 1980's for removing dyes [28-30]. The capacity of hardwood sawdust in the adsorption of basic dye increased with increasing temperature, i.e. from 82.2 mg dye/g of wood at 25 C to 105.7 mg dye/g of wood at 80 C.

About half of the matter produced by the photosynthesis process in plants becomes the major component of sawdust biomass; also called the lignocelluloses. The lignocelluloses are composed of the three polymers – cellulose, hemicelluloses, and lignin – which are strongly intermeshed and chemically bonded by the non-covalent forces and by the covalent cross-linkages. The cellulose and hemicelluloses are macromolecules from various sugars while the lignin is an aromatic polymer synthesized from phenyl-propanoid precursors. The composition and percentages of these components differ from one plant type to another. In addition, the composition within a single plant varies with age, stage of growth, and other conditions [31].

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1.1.Paper Contribution and Organization

The main aim of this study is to investigate the removal efficiency and contact time of two main organic components of leachates, the COD and ammonia nitrogen, by a biomass-clay matrix adsorbent. This paper is organized as follows: Section II discusses the materials and methods used throughout this research, results and discussions are presented in Section III, and the paper is concluded in Section IV.

2. Materials and methods

2.1. Adsorbents

2.1.1 Na-Bentonite

Bentonite clay provided by AMC Australia, was used in this research. It was first washed with deionized water several times in order to remove dust, unwanted materials, and water-soluble impurities. The sample was then oven dried at 150 to 200 C for 48 hours before being used as an adsorbent. At this point, the grey colored bentonite was in fine form passing mesh No. 30. Its physical properties such as specific gravity, particle size distribution, Atterberg limits, organic content, and moisture content were determined according to the ASTM D2216 [32]. Until the next stage, it was stored in cool, shaded, and dry environment. The sample was then air-dried and sieved through mesh No. 200 before headed for chemical analyses which were in accordance to the laboratory manual of the Geotechnical Research Center, McGill University. The cation exchange capacity (CEC) was determined using the $BaCl_2$ replacement method [33].

Table 1. Characteristics of bentonite sample

Physical Characteristics	Quantity measured	Geo-Environmental Characteristics	Quantity measured
Clay (%)	76	Mineral composition in decreasing abundance	Montmorilonite, Quartz, Calsit
Silt (%)	23	Carbonite content (%)	8
Sand (%)	1	Organic content (%)	1.4
Liquid limit (%)	423	CEC (cmol/kg soil)	80
Plastic Limit (%)	32	Specific surface area (10^{-3} m^2/kg)	425
PI (%)	391	PH (1:10 , Soil / Water ratio)	9.9
Activity (%)	3.73		
Soil Classification (%)	CH		
Water content (air-dried) (%)	5.9		
Water content (oven-dried) (%)	7.1		
G_s(%)	2.45		

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The X-ray diffraction (XRD) analysis was performed based on the method by Moore and Reynold [34]. The carbonate content was determined using the titration method [35]. The specific surface area (SSA) was determined according to the Brunauer–Emmett–Teller (BET) method [36]. The pH was measured on the bentonite-water solution of 1:10 ratio by mass – i.e. one portion of bentonite for every 10 portions of water. The resulting physical and chemical properties of the sample are given in Table 1.

2.1.2 Sawdust

The wood sample was of the Red-Meranti timber species. The sawdust was washed using deionized water multiple times and was oven-dried at 70 C for about 48 hours in order to remove the moisture content. The dried sample was converted to a fine powder using a ball mill. The resulting material was sieved to the 100-150 µm particle size according to the ASTM D4779 method [37-38]. A 0.5 M HCL solution was used to remove the color and water soluble substances by soaking at room temperature for 6 hrs. Eventually, the sawdust was filtered and washed multiple times by distilled water and then oven-dried at 70 C for about 48 hours. The adsorbent was stored in airtight container before headed for the application.

2.1.3 Alkali and acidic treatment of sawdust

Sawdust-water solutions of 1:10 ratio by mass were prepared and tested for pH using the EUTECH 700 pH measurement meter. The water was deionized. The solutions were placed in five different glass containers in adjusting them into pH 2, 4, 6, 8, and 10. To achieve this, the 0.1 M HCL reagent was used for the acidic adjustment while 0.5 M NaOH reagent was used for the alkali adjustment. The adjustment was carried out at room temperature while the solutions were shaken continuously. Different amounts of acidic and alkaline reagents were added to the containers based on the targeted pH of each. Until the pH became stabilized, the addition of HCL and NaOH drops continued. Once achieved, the solutions were kept overnight and the pH of each was again tested in the next day. This process was continued until the pH became consistent for 2 consecutive days. To eliminate the adsorbed acid or alkali, the sawdust was then washed several times with distilled water and acetone. The alkali-treated and acidic-treated sawdust was dried in a hot-air oven at 60 C for about 72 hours and kept in the desiccator for subsequent use. Care was taken to avoid bonding in sawdust that could turn into carbon.

2.2. Leachate sampling and characterization

Leachate samples were collected from the Pulau Burung sanitary landfill located 10 km away from the Engineering Campus of Universiti Sains Malaysia in the city of Nibong Tebal, Malaysia or approximately 20 km southeast of Penang Island [39]. The 64 hectare disposal site, located at 5°11'52.5"N 100°25'35.8"E, was first established in the 1980’s. In 1991, it was developed into a Level II semi-aerobic sanitary landfill and later in 2001 was upgraded to Level III, using controlled tipping with leachate reticulation system [40]. Only half of the area is currently operational and the daily incoming waste stands at 2200 tons per day. The bed is a natural marine clay which is also the liner. The landfill produces a dark black–green colored

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leachate which is classified as stable with high concentrations of COD and ammonia nitrogen and a low BOD/COD ratio [41].

The leachate samples were collected between May 2015 and August 2015. After each collection, the samples were immediately taken to the environmental engineering laboratory of the School of Civil Engineering and were kept in a cold room at 4 C to avoid any biological and chemical reactions. The properties of the leachate samples are given in Table 2. In order to evaluate the environmental risks of the leachate, the parameters were compared against the Malaysian Environmental Quality Regulations 2009 - Control of Pollution from Waste Transfer Station and Landfill – which were developed under the Malaysia Environmental Quality Act 1974 [42].

Table 2. Characteristics of leachate sample

Parameter	Unit	Standard	Sampling average
Temperature	°C	40	33
pH Value	-	6.0 – 9.0	9
COD	mg L^{-1}	400	2955
BOD	mg L^{-1}	20	269
Ammonia Nitrogen	mg L^{-1}	5	120
Arsenic	mg L^{-1}	0.05	0.04
Manganese	mg L^{-1}	0.20	0.12
Nickel	mg L^{-1}	0.20	0.017
Iron	mg L^{-1}	5.0	0.48
color	ADMI*	100	1220
Suspended solids	mg L^{-1}	50	710
TDS	%	-	5.72

2.3. Operation of the reactors

The treatment was carried out in twenty 1700 mL plexiglass reactors. Each of the cylindrical reactors has a 1000 mL working capacity with 'Couple Bottom Aeration System' or simply two air pressure inputs. The reactors were filled with 1000 mL leachate sample while the different mix designs of the Na-bentonite and the pH-adjusted sawdust were as described earlier. The ratio of sawdust plus bentonite against the untreated leachate put together in each reactor was constant at 1:50 by mass.

Therefore, each solid part of the reactor system consisted of 20 g bentonite plus an odd from the 9 sawdust samples with pH of 2, 6, or 10 and with a percentage of sawdust of either 10%, 20%, or 30% by mass of the 20 g bentonite. Furthermore, for each group contact time, an additional reactor was run with just the bentonite, while each of the other twenty reactors had the bentonite enhanced with either the acidic or the alkaline sawdust content.

To supply the air, a pump was used with the following specifications: voltage of 240 V, frequency of 50 Hz, input power of 61 W, and pressure of 0.012 MPa. The regulation of the air rate was manually done by an air flow meter. Based on a previous study, an aeration rate of 7.5

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L/min was applied with 3 possible contact times of 2, 12, and 22 h [43]. The room temperature during tests was set at 30 C.

Fill, react, settle, draw, and idle were the sequential operation phases of the reactor system. The times for filling and mixing, settling, and drawing and idling times were 20, 90, and 10 min respectively, thus totaling 2 h, for the shortest. The removal efficiencies of COD and NH_3-N, are defined in Equation 1.

$$Removal\ efficiency\ (\%) = \frac{(Ci-Cf)*100}{Ci} \quad (1)$$

Where C_i and C_f are the initial and final concentrations of the parameters respectively

2.4. Experimental design

In this study, the response surface methodology (RSM), and central composite design (CCD) were used for the gathers mathematical and statistical techniques that are useful for the modeling and analysis of problems, in which responses of interest are influenced by some variables and statistical design of experiments and data analysis respectively. The design included of k^2 factorial points completed by 2k axial points and a centre point, where k is the number of variables. Thereupon, CCD and RSM were applied in order to evaluate the association between the variables i.e. percentage of sawdust (%), pH of the sawdust, and contact time (h) and their responses.

In other word, the main scope of this design is to optimizing the appropriate situation of operating variables to predict the best value of responses. Aeration rate was 7.5 L/min in all the reactors and 2 dependent parameters (COD, and NH_3-N) were measured as the responses Table 3.

Table 3. Experimental variables and results for SBR

	Variable			Responses	
Run	A: Contact time(hr)	B: pH	C: Sawdust (%)	Ammonia Removal (%)	COD Removal (%)
1	2	2	30	52.5	76.58
2	2	10	30	45.8	79.6
3	22	10	10	97.7	99.2
4	12	10	20	61.2	78.5
5	22	6	20	97.9	84.4
6	12	6	20	35	82.9
7	2	2	10	60	83
8	22	2	10	98.3	99.4
9	22	10	30	97.7	98.9
10	22	2	30	98.3	99.2
11	2	10	10	40.8	56
12	12	6	30	67.9	82.7
13	12	6	20	39.1	84
14	12	2	20	63.7	83.6
15	12	6	10	67.5	83.4

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16	12	6	20	64.1	83.8
17	2	6	20	78.3	59.3
18	12	6	20	42.3	83.6
19	12	6	20	47.5	84.2
20	12	6	20	42.9	84
Blank1*	**2**	**-**	**-**	**37.5**	**12.13**
Blank2*	**12**	**-**	**-**	**68.75**	**83.55**
Blank3*	**22**	**-**	**-**	**95.41**	**99.28**

A reactor was considered without any sawdust in order to compare with others and to monitor the effect of the sawdust on the COD and ammonia removal. The following equation explains the quadratic equation model for estimating the optimum conditions:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X^2 + \sum_{i_i<j}^{k} \sum_{j}^{k} \beta_{ij} X_i X_j + \cdots + e \quad (2)$$

where Y is the response; Xi and Xj are the variables; β_0 is a constant coefficient; β_j, β_{jj}, and β_{ij} are the interaction coefficients of linear, quadratic and second-order terms, respectively; k is the number of studied factors; and e is the error.

The aeration rate was a constant 7.5 L/min for all reactor systems. Another reactor was run free of sawdust as the control. The values of the independent variables and the resulting responses are given in Table 3.

2.5. Experimental method

All experiments were carried out according to the Standard Methods for the Examination of Water and Wastewater [44]. A spectrophotometer (DR/2800 HACH) was used for measuring color (Pt.Co), NH3-N (mg/L), magnesium (mg/L), total iron (mg/L Fe), Nickel (mg/L Ni), and Arsenic (mg/L As). COD concentration was determined using the closed reflux and colorimetric Method No. 5220D. YSI 556 MPS (YSI incorporated, USA) was used for recording the values of pH, temperature (◦C), and TDS (%).

3. Result and discussion

3.1. COD removal

3.1.1 Adsorption by clay mineral

For an SBR system with 20g bentonite, no sawdust, 1000 ml leachate, an aeration rate of 7.5 L/min, the COD removal was 12% after 2h; and 99% after 22h. For a system with 20g bentonite, 20% sawdust of pH 6, and everything else remained the same, the COD removal was 83% after 2hrs; and 84.2% after 12hrs. Eventually, the maximum COD removal was 99.4% after 22hrs, i.e. with 10% sawdust of pH 2. More detailed results are given in Table 3 and Figure 1.

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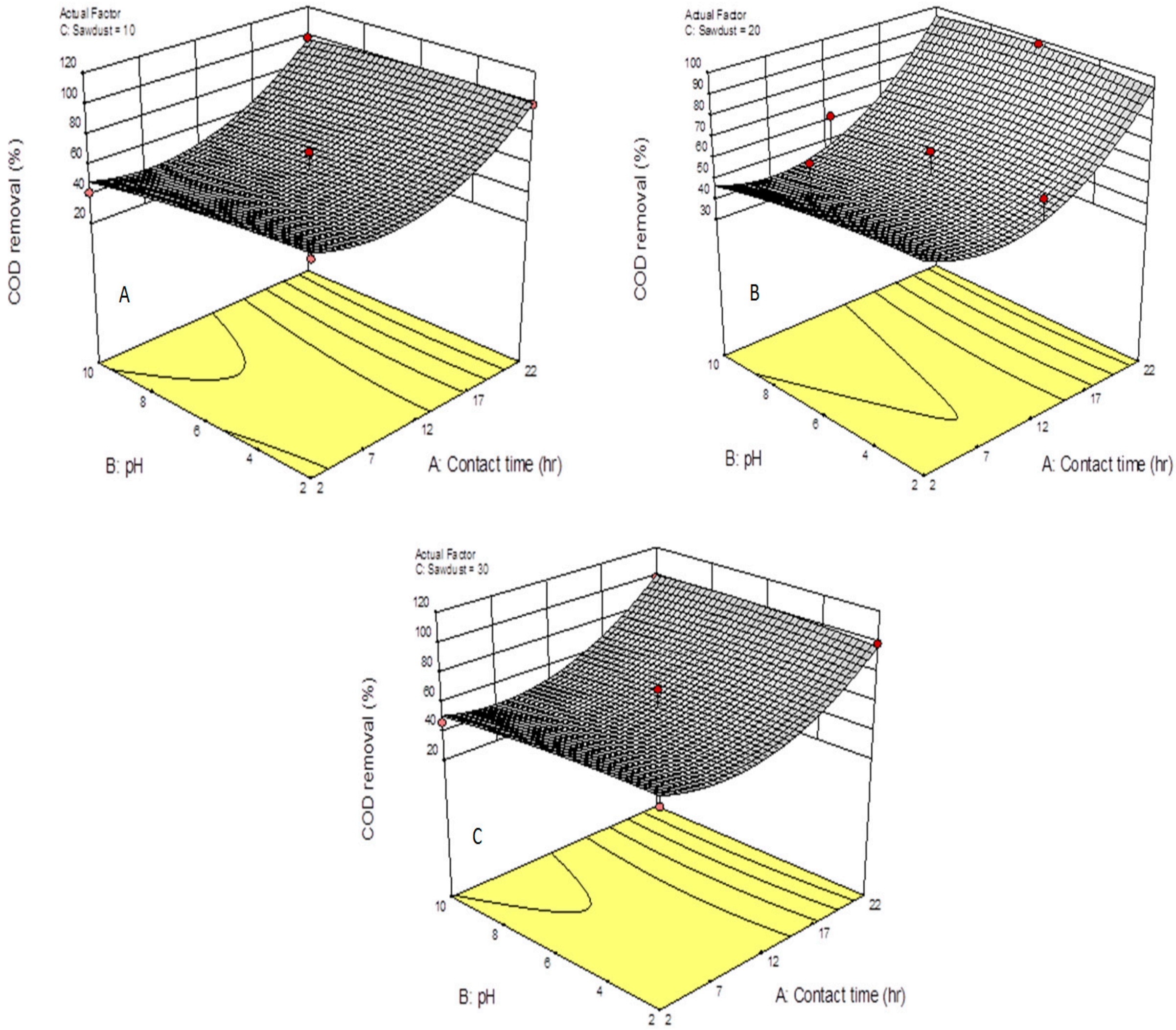

Fig. 1. Plot of COD removal (A) with sawdust content of 10%, (B) with sawdust content of 20%, and (C) with sawdust content of 30%

A decrease in the non-biodegradable organic pollutant in waste water translates to a decrease in COD [45]. The complex interaction between the clay minerals and the organic compounds results in a decrease in COD in a process involvs the roles of the silicate layers, the inorganic cations, the water, and the organic molecules. First, between the organic matter and the clay minerals, there is the ion exchange which is either the cation exchange or the anion exchange. Cation exchange is the term describing the adsorption of the organic cations by the clay minerals with the inorganic cations leaving. The interaction of positive charge sites, at oxide surfaces or edge sites of clays with carboxylate (COO^-), sulfonate (SO_3^-) groups, and phenolate (aromatic-O^-) by replacement of univalent exchangeable anions (e.g., Cl^- or NO_3^-) bounds to a protonated surface hydroxyl (OH_2^+) [46-47]. Because of the weakness of the electrostatic bonds, this organic adsorption mechanism is not observed often. On the other hand, the presence of the metal oxides at clay fractions can make this mechanism as a one [48]. Adsorption by dispersion forces is so important, since it is not only acts separately, but also as a supplier in the other

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mechanisms. There is a parallel relationship between the adsorption degree of this mechanism and the molecular weight of the adsorbate. Van der Waals interaction occurs between the adsorbed molecules rather than the surface and adsorbed molecules [49-50]. Protonation of organic molecules at clay surfaces mechanism makes many compounds cationic. The acidity of the clay surface is the main factor to make the organic compound in cationic form. The main source of the protons and the protonation reactions are exchangeable H^+ occupying cation exchange sites, water associated with metal cations at the exchange sites, and proton transfer from another organic cation [51]. Hemisalt formation mechanism occurs while neutral organic bases are adsorbed on H-clays in excess over the number of protons available and in this case two molecules have a competition for the proton [52-53]. Coordination by cation bridging and water bridging are the other organic matter adsorption by clay minerals. Organic molecules may be coordinated to the inorganic saturating cations by a direct bonding which is called cation bridging or through water, which depends on the water content of the clay mineral and is known as water bridging. When the water content is reduced in the system, there will be a competition between the water and the polar molecules for ligand position around the metal cation initially through a water bridge and then through a direct interaction [46-48].

Surface complexation of organic anions is formed between the organic ions or molecules and functional groups and divided into two main groups. If no water intervened between the surface functional group and ion it bind, the complex is inner-sphere, while in the presence of the water it will be the outer-sphere one. The outer sphere surface complexes involve the electrostatic bonding mechanisms and are less stable than the inner-sphere which involves ionic and covalent bonding.

One of the most important adsorption mechanisms in clay soils is Hydrogen bonding which occurs at edge and surface sites. Mortland [46] suggested three main groups for this mechanism as follows:

- Water Bridge involves the linking of a polar organic molecule to an exchangeable metal cation through a water molecule in the primary hydration shell. One or both protons of water molecule can participate in the bonding.
- Organic-organic hydrogen binding occur when the exchangeable cation on the clay is an organic one. Organic-clay hydrogen bonding mechanism acts, when the hydroxyls of the exposed siloxane (Si-O) and aluminol (Al-OH) planes of clay minerals interact with a polar organic molecule [54].
- Adsorption by donation of π electrons [55] and hydrophobic bonding [56], are the other mechanisms of organic adsorption with clay minerals.

3.1.2 Sawdust adsorption mechanism

In this study, various mix designs of bentonite and pH-adjusted sawdust are considered with different operation procedures in order to monitor the effect of sawdust on the melioration of adsorption efficiency. As given in Table 3 and Figure 1, the sawdust has a positive effect in reducing the contact time with the same high removal efficiency. In 2h, the addition of 10% sawdust with pH 2 increased the COD removal by bentonite alone from 12.13% to 83%. On the other hand, in 12h, the addition of 20% sawdust with pH 6 increased the removal by 1% while in 22 h, the addition of 10% sawdust with pH 2 the removal is decreased by 0.2%.

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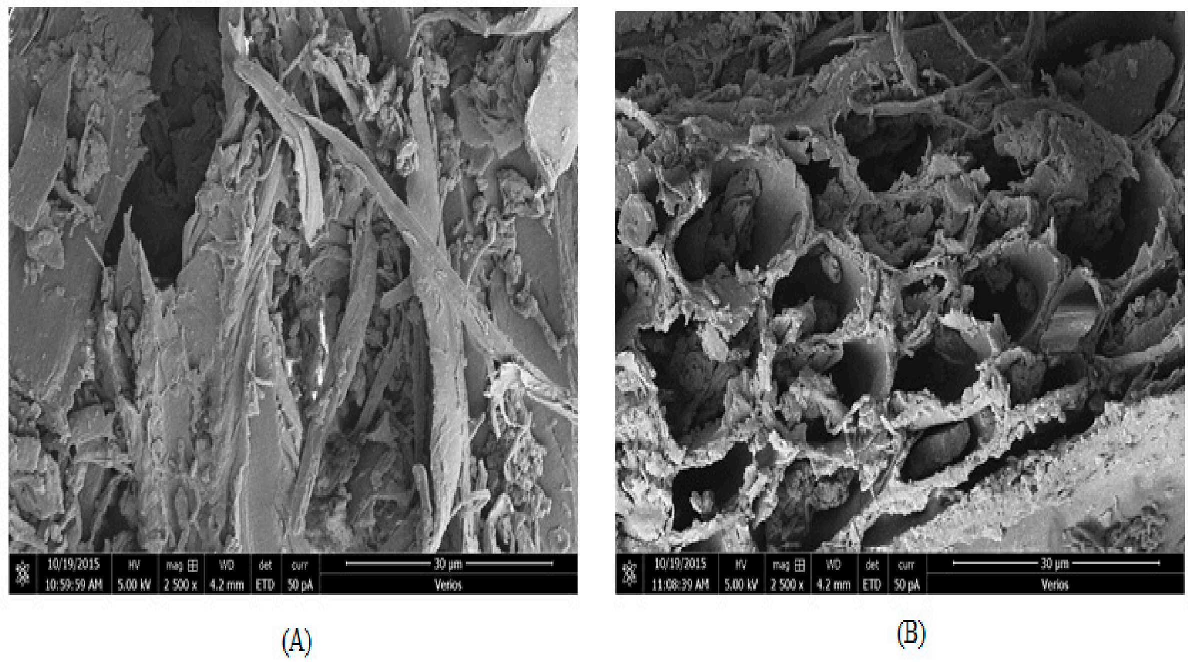

Fig. 2. Scanning Electron Microscope; A) Sawdust before treatment, B) Sawdust after acidic treatment

Chemical and physical adsorption mechanisms are two main adsorption mechanisms of sawdust in contact with unwanted materials. Chemically adsorption is related to the structural components of sawdust relating to the lignin, cellulose, hemicellulose, and active groups on the surface, while physical adsorption behavior is activated by treatment of sawdust with chemical materials. The cell wall of the sawdust mainly consists of cellulose, lignin, and hydroxyl groups which are active ion exchange compounds [47]. Ion exchange, Hydrogen bonding, and electron donating nature of O-, S-, and P-containing groups in sawdust materials are the main indirect adsorption mechanisms of organic matters by sawdust with cation and anion exchanging and different bridging mechanisms respectively. As explained earlier, the optimum efficiency in the early and final contact time occurred with sawdust pH (2). An acidic treatment of sawdust from 6 to 2 led to the generation of cylindrical tubes which could capture the organic matters as shown in Figure 2. The size of organic matters and the diameter of the tubes can affect the physical adsorption mechanism.

3.2. Ammonia nitrogen removal mechanism

3.2.1 Clay mineral adsorption mechanisms

The NH_3-N removal from the leachate sample is in the range of 35% to 98.3% Table 3 and Figure 3. The maximum removal of ammonia nitrogen occurred with 10% sawdust pH (2) in 22h contact time with constant operation conditions. In contrast, 20% sawdust pH (2) in 12h contact time leads to a negative effect on the efficiency of the system.

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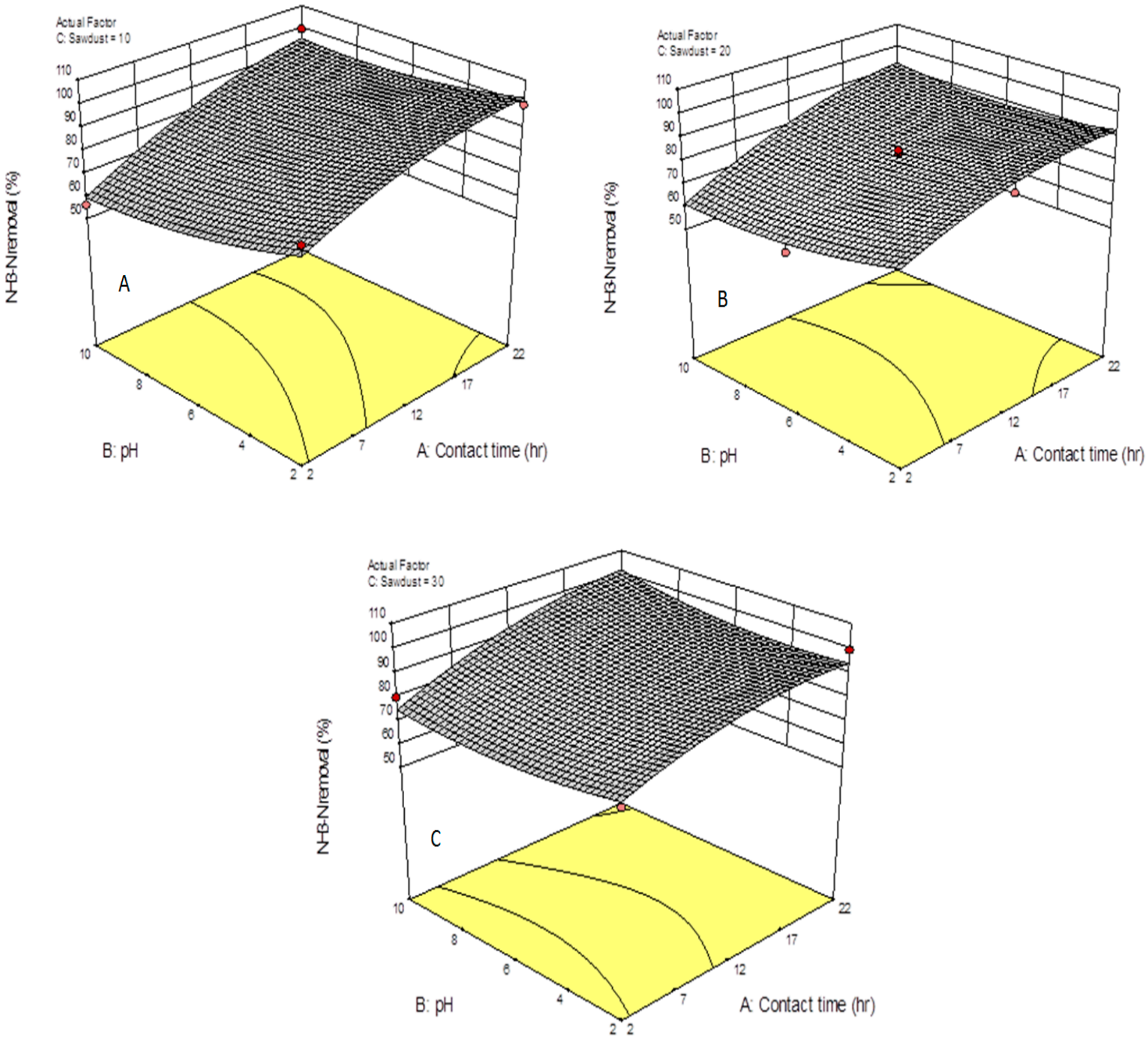

Fig. 3. Plot of ammonia removal (A) with sawdust content of 10%, (B) with sawdust content of 20%, and (C) with sawdust content of 30%

Ion exchange and adsorption are two main mechanisms of ammonia removal from wastewaters by clay minerals. One of the advantages of using clays as the adsorbent for ammonia removal is the layered structure of the clay allows expansion (swelling) when contacted with water, which exposes an additional mineral surface capable of ammonium ion (NH_4^+) adsorption [57]. Specific surface area (SSA), cation exchange capacity (CEC), and the functional groups of the different fraction of soils are the surface characteristics of the soil solids. Some exchangeable cations such as K^+, Na^+, $Mg^{2+}$and Ca^{2+} are available in the structure of bentonite molecules, and these cations can easily exchange with other cations such as NH^{4+}. The stage of the cation in the lyotropic series, concentration of the cations, and the diameter of the cation molecule are the effective factors in the ion exchange mechanism. Similar to the other mechanism, the reaction between the cation and the negative charge surface of the soil fractions leads to the adsorption of

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the cation by clay. Consequently, bentonite which includes montmorillonite clay mineral with high cation exchange capacity (CEC), and specific surface area (SSA), is one of the most important clay adsorbents.

3.2.2 Sawdust adsorption mechanism

In this study, the maximum adsorption of ammonia nitrogen, at 98.3%, was achieved by the bentonite with 10% sawdust of pH 2, and after 22h of contact, as given in Table 3 and Figure 3. Thus the conditions for maximum ammonia nitrogen removal were the same as for maximum COD removal. The main point however was in having an acceptable removal by a reduced contact time. Thus the bentonite with 20% sawdust of pH 6 could remove 78.3% ammonia nitrogen after 2h, while the bentonite without sawdust could remove 37.5% after the same 2h, 68.8% after 12h, and 95.3% after 22h. With only 17% more removal after 22h, the bentonite with 20% sawdust of pH 6 was obviously a design with considerable benefit in terms of saving the contact time. At lower pH, the positively charged ammonium has a competition with the H^+ and by ion exchange mechanism, adsorbed into the surface of the sawdust. With an increase in pH, the ammonium may be adsorbed by hydrogen bonding mechanism along with ion exchange.

The basic chemical phenylpropane units of lignin (primarily syringyl, guaiacyl and *p*-hydroxy phenol) are bonded together by a set of linkages to form a very complex matrix. This matrix comprises a variety of functional groups, such as hydroxyl, methoxyl and carbonyl, which impart a high polarity to the lignin macromolecule. So lignin is the constituent of lignocellulose materials which participate in the adsorption process. Figure 4 illustrates the FTIR results of the sawdust pH (2) and pH (4). The graph shows an increase in the peaks at 1599, 1511, 1467, 1429, 1157, and 1054 which belong to lignin. A strong aromatic ring stretch, phenylpropanoid polymer, deformation (methyl and methylene), glycosidic linkage, and vibrational stretching are a number of bonds which are present in the lignin [58-59].

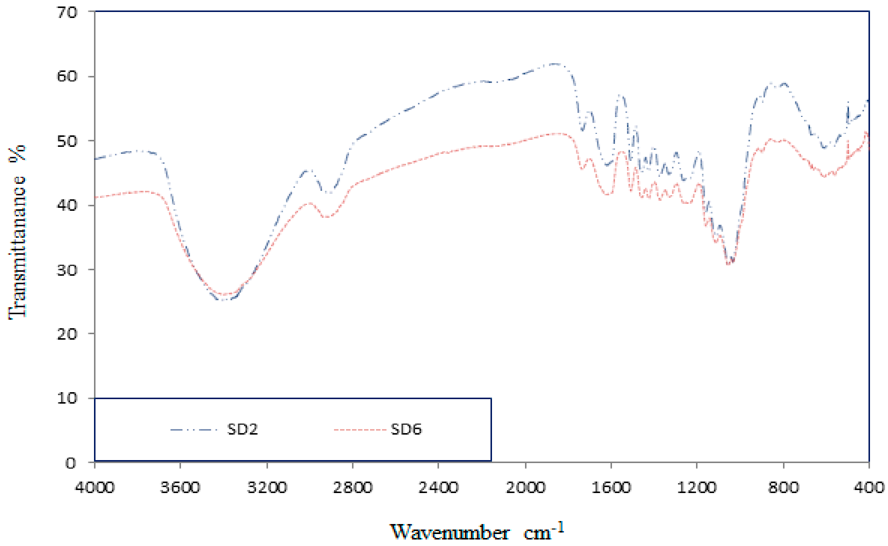

Fig. 4. Fourier Transform Infrared spectroscopy (FTIR) of sawdust pH (2), and sawdust pH (6)

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3.3. Statistical analysis

Response surface methodology (RSM) is used to analyze the correlation between the variables, i.e., contact time, pH, and sawdust content; COD and NH_3-N removals. Considerable model terms were preferred to achieve the best fit in a particular model. CCD permitted the development of mathematical equations where predicted results (Y) are evaluated as a function of contact time (A), pH (B), and sawdust (C). The results are computed as the sum of a constant, three first order effects (terms in A, B, and C), three interaction effect (AB), (AC), and (BC), and three second-order effects (A^2, B^2, and C^2), as shown in Equation (1), Tables 3 and Table 4. In order to determine the accuracy of fit, the results were analyzed by ANOVA statistical technique. Equations from the first ANOVA analysis are adapted by neglecting the terms found statistically irrelevant. The reduced quadratic models in terms of actual factors are illustrated in Table 4.

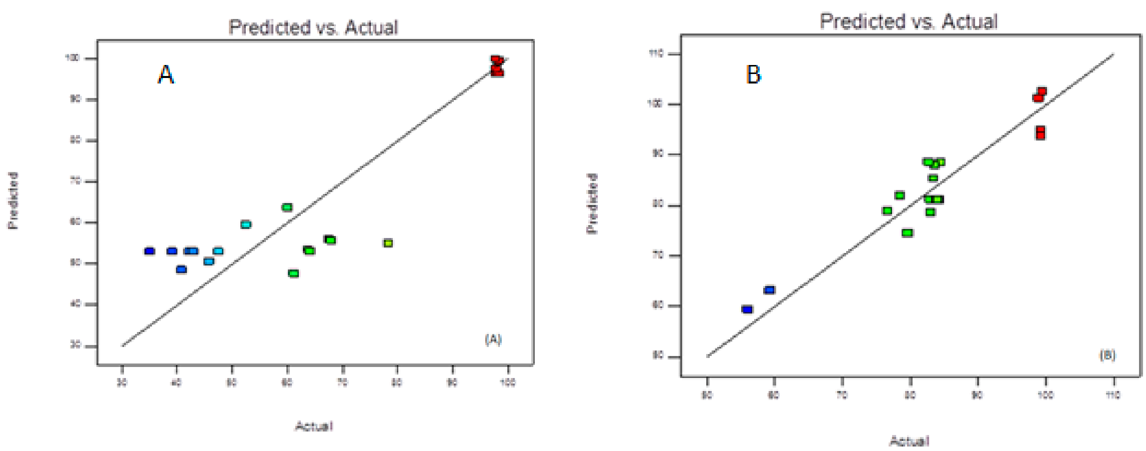

Fig. 5. Design-expert plot; predicted vs. actual values plot for (A) COD removal, and (B) NH_3-N removal

Table 4. ANOVA results for response parameters

Response	Final equations in terms of actual factors	prob	R^2	Adj. R^2	Adec. P.	SD	CV	Press
NH_3-N removal	+102.79375+2.54999* A-6.38364* B-2.47927* C+0.073375* A* B-0.022100* A* C+0.093500* B* C-0.053418* A^2+0.24114* B^2+0.058582* C^2	0.0010	0.8897	0.7905	11.822	5.16	6.19	3322.24
COD removal	+83.16323-3.99044* A-0.67818* B-1.44924* C+0.077188* A * B+3.12500E-003* A * C+0.039063* B * C+0.23291* A^2-0.14744* B^2+0.028909* C^2	0.0228	0.7777	0.5777	5.036	14.66	22.57	9050.76

According to the probability value (less than 0.05), all models were significant at the 5% confidence level. R^2 values close to 1 were favorable, and a high R^2 coefficient ensured acceptable modification of the quadratic model to the experimental data. The correlation coefficient (R^2) gave the proportion of total variation in the response predicted by the model, indicating the ratio of sum of squares due to regression (SSR) to total sum of squares (SST). Adequate precision compared the range of the predicted values at the design points to the mean prediction error [60]. Figure 5 shows the predicted versus actual value plots of the response

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parameters for the COD and ammonia removal. These plots signified a sufficient agreement between the real data and the values achieved from the models.

3.4. Optimization of the system

The final experimental results involving COD and NH_3-N removals with various mix designs of adsorbents and operation conditions were analyzed using RSM and CCD in order to determine a specific operation system that could lead to the optimum removal of both organic compounds.

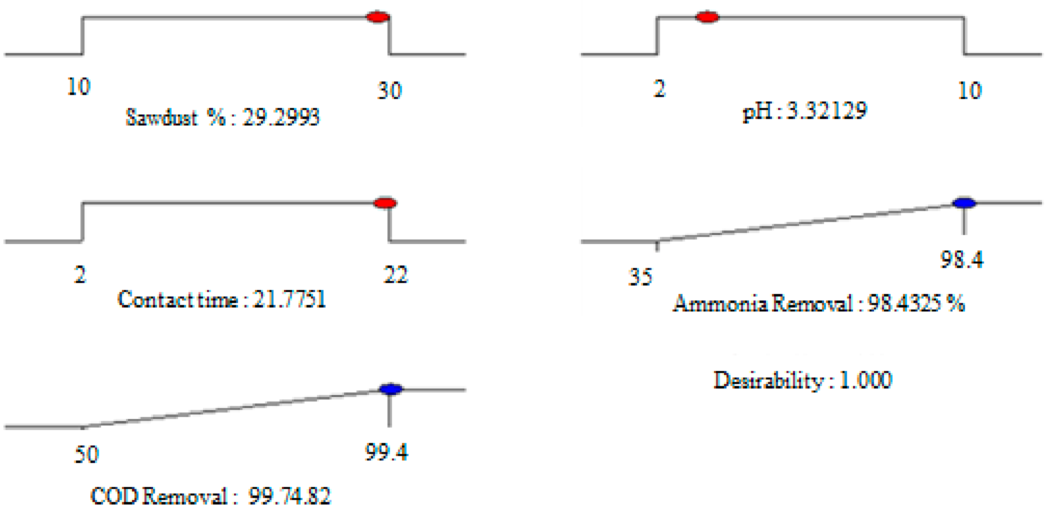

Fig. 6. Desirability response of removal system

The resulting responses from optimizing the COD and NH_3-N removals are given in Figure 6. Accordingly, the optimized conditions were the sawdust content of 29.3% with pH of 3.3 and the contact time of 21.8h, which would result in 99.7% COD removal and 98.4% NH_3-N removal.

4. Conclusion

The development of sawdust-enriched bentonite as pollutant removal of organic compounds of Pulau Burung sanitary landfill has been investigated in this research. The roles of pH-adjusted sawdust of various designs have been studied using the augmented SBR processes. The COD and NH_3-N of Pulau Burung landfill effluent exceeded the permissible discharge limits and needed efficient removal. Using the SBR system, the COD removals by bentonite without sawdust were 12.13%, 83.55%, and 99.28% for the COD and 37.5%, 68.75%, and 95.41% for the NH_3-N after 2h, 12h, and 22h contact times respectively. The COD removals by bentonite with the proper pH-adjusted sawdust, on the other hand, were 83%, 84.2%, and 99.4% for the

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COD and 78.3%, 67.9%, 98.3% for the NH_3-N after the same contact times respectively. The results indicated that an acidic treatment of the sawdust and adding it at 10% of the bentonite mass to the system could lead to a sufficient and efficient removal of the pollutant parameters even with the contact time reduced to 2h.

Acknowledgement

This research is funded by University Sains Malaysia (USM) under Ionic grant scheme (Grant no. 1001/CKT/870023) for research associated with the Solid Waste Management Cluster, Engineering campus, University Sains Malaysia. The authors would like to acknowledge the University Sains Malaysia (USM) for provision of research grant to conduct this work.

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