**Adsorption of COD and BOD from slaughterhouse wastewater using stabilized solid waste materials**

**ABSTRACT**

Investigation on the use of agricultural and industrial wastes as locally available and economically viable adsorbents for wastewater treatment has been a focal point of studies in recent times. Consequently, landfill mining has become viable as a way of discovering the potential of recycling such materials. The stabilized solid waste used in this study was obtained from a closed landfill site of over 10 years which has become stabilized due to years of placement. The slaughterhouse wastewater chosen for the treatment process was obtained from a chicken slaughterhouse. The results showed that the residual concentration for COD and BOD was 160.2 and 54.9 mg/l from an initial concentration of 2720 and 960 mg/l which represents 94.8 and 95 % removal efficiency respectively from the wastewater. The treatment was carried out at ambient temperature and pH of 6.0 in less than 120 minutes with dosage of 8 g/10ml at 250 rpm. Both Langmuir and Freundlich isotherms were used to fit experimental data and the Langmuir model gave better correlations of r2 values close to 1, (0.9999 and 0.9999) Langmuir, and (0.9785 and 0.9557) Freundlich for COD and BOD. However in terms of the amount of pollutants adsorbed (Qe), the Freundlich model gave higher values which shows that the Freundlich model best describes the process as heterogeneous. In conclusion, the stabilized solid wastes material shows good potential to be used as an adsorbent, moreover, as a low-cost alternative for wastewater treatment as far as the optimal treatment conditions are well maximized.

***Keywords:*** Freundlich model; Langmuir model; isotherms; stabilized wastes; slaughterhouse wastewater; landfill; adsorption

1. **INTRODUCTION**

Environmental concern has increased over the years as a result of factors associated to climate change and global warming which stimulated a lot of studies in relation to environmental protection. One major factor for environmental concern is the ever increasing rate of solid waste management which has resulted in landfill congestion and subsequent closure without substantial alternatives. The need for recycling has championed studies in landfill mining which led to the discovery of the reuse potentials of materials from the landfill site including solid waste materials which has become stabilized due to several years of placement. The challenges experienced in effective wastewater management for slaughterhouses includes, the need to stay in business and make profit, which is the major priority, as well as minimizing associated environmental risks. The poultry industry in Malaysia is one of the fastest thriving businesses due to the ever increasing demand for chicken and chicken products resulting in the large number of chicken slaughterhouses within residential areas. Many authors have attempted to classify slaughterhouse wastewater composition which varies according to manufacturing process and water demand.

According to Matsumura and Mierzwa, (2008), slaughterhouses consume large volumes of water which are responsible for deterioration of water sources (De- Nardi et al., 2011). Bustillo-Lecompte et al., (2013) emphasized that most of the wastewater from these slaughterhouse are composed of blood, urine, faeces, fat, cadavers, non-digested food items and other leftovers as well as water from cleaning of the facilities. Sugito and Mohammad, (2016) stated that wastewater of a chicken slaughterhouse is in the form of gastrointestinal contents, excess blood, fat and washed water which has become a source of environmental pollution. Mittal (2006), stated that wastewater from slaughterhouses contains high degree of organic pollutants which are discharged into the communal sewer system while Baddour et al., (2016), concluded that such actions lead to an upsurge in organic load disposed to the wastewater treatment plants. This, according to Baddour et al., (2016) and Muhirwa et al., (2010) may possibly reduce the efficiency of such plants as well as contamination of both surface and groundwater sources arising from leaching action.

Furthermore, Rajakumar et al., (2012) indicated that the wastewater discharged by poultry slaughterhouse industries are characterized mainly by high Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), high suspended solids and composition of fats, proteins and fibres which should be treated before disposal. The BOD: COD ratio is a very important parameter which is significant in the design of wastewater treatment processes either biological or chemical treatment. According to the Malaysian sewage discharge standard, the standard BOD: COD ratio for disposal is 2.0: 1, however most of the sampled wastewater contain high organic contents and therefore highly exceed this range thereby making the wastewater difficult to treat due to the presence of non-biodegradable substances. Debik and Coskun, (2009) established that it is an economic, environmental and public health responsibility to carry out on-site treatment of wastewater from slaughterhouses and other meat processing plants before disposal. A summary of the composition of poultry slaughterhouse as evaluated by different researchers and BOD/COD ratios is shown in table 1.

In this regard, biological treatment of poultry slaughterhouse wastewater has been widely adopted due to its rate of success and economy as established in various studies including (Coskun et al., 2016; Kobya et al., 2006; Morales-Polo and Cledera-Castrom, 2016; De- Nardi et al., 2011; Vourch et al, 2008). These authors and several others utilized the available microorganisms in the wastewater and filter media for purification. However, attention has shifted in recent studies to the use of even more economically viable options such as bio-sorption reduction procedure for wastewater treatment using domestic waste materials from human and animal activities for cost reduction and as recycling options for such waste materials. Adsorption is the mostly used treatment method in recent times because it is both a physical and chemical process which gives an interphase for the wastewater and the porous media in which the pollutants in the wastewater are adsorbed on the surface of the media (adsorbent).

For this present study, an economically viable and locally available stabilized solid waste excavated from a closed landfill was used for the treatment of chicken slaughterhouse wastewater. Adoption method was applied as a removal technique option for BOD and COD removal from the wastewater as a way of establishing the potential of re-using such material. The influence of temperature, pH, treatment time and dosage on the removal efficiency was monitored.

**Table 1: Summary of BOD-COD Composition of Slaughterhouse Wastewater**

|  |  |  |
| --- | --- | --- |
| **BOD mg/l** | **COD mg/l** | **Reference** |
| 610-4635 | 1250-15,900 | Busellio-Lecompte et al, 2013. |
| 1500-2300 | 4700-5900 | Sombatsompop et al, 2011. |
| 750-1890 | 3000-4800 | Rajakumar et al, 2011 |
| 10888-14600 | 22000-27500 | Sunder and Satyanarayan, 2013. |
| 3000-3500 | 6185- 6840 | Kudu et al, 2013. |
| 12000-10000 | 29000-26000 | Kobya et al, 2006. |
| 727-29601684237511,5331,000-4000 | 2080-834525731223-969521,8942,000-10,000 | Nik Daud and Anijiofor 2017Sugito and Mohammad 2016Basitere et al, 2017. Soyong et al, 2010 Mike, 2006 |

1. **MATERIALS AND METHODS**

The Stabilized solid waste was excavated from the Air Hitam Sanitary Landfill (AHSL) site in Selangor Malaysia which has been closed for almost 10 years. The waste materials have been buried in the landfill site several years and as such have become stabilized due to several years of placement. After careful sorting such as removal of unwanted parts of the excavated material such as stoned, debris, wood, rubber, plastics, and the likes, the material was sieved in 2mm sieve size. Previous studies carried out showed that the treatment process favored the use of particle size of 2 mm and below

 Also, untreated chicken slaughter-house wastewater was obtained from a local chicken slaughterhouse located in Seri kerbamger, Selangor, Malaysia which is within the Vicinity of the University Putra Malaysia. The sample was collected from a discharge point which comprises wastewater from the entire cleaning process, and then stored in about 10 L plastic container. The wastewater was sieved to remove some of the undigested grains, feathers and the likes. Initial concentrations of COD and BOD were immediately determined in line with the APHA guidelines for water and wastewater analysis.

**Batch Experiments.**

The experiments were carried out in batch mode using a 250 ml flask and an electric shaker at 250 rpm under room temperature while other parameters such as pH, dosage and treatment time where monitored as influencing parameters. This involved varying one of the parameters while the others remained constant at the stipulated treatment time. At the end of the estimated treatment time, the sample was centrifuged at 3000 rpm for 8 minutes to further intensify the liquid/ solid separation and then filtered using whatman filter paper. A treatment time of 90 min was observed for each of the influencing parameters while the treatment time for the whole experiment was done between 30 – 180 minutes. The final concentrations of the samples obtained at different time intervals was measured.

1. **RESULTS AND DISCUSSION**

The composition of chicken slaughterhouse wastewater is shown in table 2.

**Table 2: Physio-Chemical Composition of Poultry Slaughterhouse Wastewater**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Composition** | **\*Discharge Standard** |
| pH | 7.17 | 5.5 – 9.0 |
| Temperature oC | 29.2 | 40 |
| Turbidity NTU | 124 | 5 |
| TSS mg/L | 312 | 100 |
| TDS mg/L | 702 | 1000 |
| COD mg/L | 2720 | 100 |
| BOD mg/L | 960 | 50 |
| Colour mg/L | 10600 | 300 |

TSS – Total Suspended Solids; TDS – Total Dissolved Solids; COD – Chemical Oxygen Demand; BOD – Biochemical Oxygen Demand; \*\*Malaysian sewage and industrial standard 2000

Table 2 shows the wastewater is highly polluted with organic load which is not suitable for disposal without prior treatment. The study also revealed that the wastewater is discharged into the domestic sewage system without any form of treatment. One major problem of such disposal is increase in the domestic load and consequently, the clogging of the piping system which affects the general performance of the treatment plants. Also the design period for the treatment plant is also affected due to the concentration of these organic constituents. The COD and BOD concentration as shown in table 2 were very high when compared with the permissible discharge limits as prescribed by the Malaysian sewage and industrial standard 2000. However, in our previous study, (Nik Daud and Anijiofor 2017), the COD and BOD values were 4979 and 1360 mg/l respectively, as compared to values obtained in this study which were 2720 and 960 mg/l for COD and BOD respectively. This difference in values is due to the sampling periods, higher values of pollutants are usually obtained during period of low rainfall because less water is used for cleaning which also generate lesser volunes of wastewater when compared to monsoon periods (June –August) where larger volumes of wastewater is generated but lesser concentration.

Also, the characteristics of the waste material showed that it is composed of 29.5 % moisture content which provides the required oxygen, porosity level of up to 51 %, which would prevent fouling and clogging and also Cation Exchange Capacity (CEC) of 26.9 mmol kg-1. The texture is similar to loamy clay, with the abundance of microbes at 7.1 x 106 CFU/100ml which would enhance biodegradation. The EDX showed specific surface area of 3.376 m2 g-1 and some major elements as classified in table 3.

**Table 3: Chemical Composition of Stabilized Solid Waste Material**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Element** | **Weight %** | **Atom %** | **Formula Compound %** |  |
| O K | 42.50S | 63.11 | -- -- |
| Al K | 8.78 | 7.73 | Al2O3 16.58 |  |
| Si K | 30.45 | 25.76 | SiO2 65.15 |  |
| In L | 11.59 | 2.40 | In 11.59 |  |
| Tb L | 6.67 | 1.00 | Tb 6.67 |  |
| Total | 100.00 | 100.00 | -- 100.00 |  |
|  |  |  |  |  |

Oxygen plays a major role in aerobic bio-degradation which stabilizes the growth of microorganisms and forms an integral part of most biological wastewater treatment systems. Also the presence of silicon compounds present a high adsorptive property which has ability to remove some heavy metals present in wastewaters. These compounds will influence nutrient supply thereby increasing microbial degradation of organic substances.

**3.1 Factors affecting efficiency of BOD and COD removal**

As stated earlier, the operating conditions taken into account in this study are treatment time, dosage, pH, initial concentration of the wastewater, agitation speed and particle size. However, the effect of particle size and agitation speed were monitored in our earlier study (Nik Daud and Anijiofor, 2017) and did not differ in this study.

The rate of adsorption is largely dependent on the physical and chemical properties of adsorbents as well as the concentration of the adsorbate.

Percentage removal of pollutants was calculated from Equation 1:

$Adsorption efficiency \left(\%\right)= \frac{C\_{i}-C\_{f }}{C\_{i}}x 100$ **Eq. 1**

Where; *Ci* and *Cf* = initial and final concentration of the pollutants, respectively.

1. **Influence of pH**

Most biological treatment processes have been influenced by pH of the sample and the treatment media. The pH of the wastewater was almost neutral at 7.17 0C and the treatment was not very successful at this stage. The pH was adjusted using dilute solutions of NaOH and H2S04 to either increase or reduce the pH as the case may be for the selected pH values of 4-8. This range of pH values selected to monitor this study have been stated in various studies (Devi and Dariya, 2008; Devi et al., 2008; Sivakumar, 2013) as being successful for biological treatment of wastewaters. The effect of pH on BOD and COD removal efficiency is demonstrated in figure 1 (a).

1. **Influence of adsorbent dosage**

 The amount of the material used for treatment is also an important parameter to monitor, hence the effect of the dosage of the waste material on the COD and BOD removal efficiency was studied. The treatment time was kept constant at 90 minutes under room temperature and at a pH of 6, while dosage was varied between 2-10g as shown in figure 1(b).

1. **Influence of treatment time on removal efficiency.**

The treatment time is a very important parameter to be observed during adsorption because the rate of removal of pollutants is a function of the contact time between the adsorbent and adsorbate. The effect of treatment time on the removal efficiency of COD and BOD from the wastewater is demonstrated in figure 1 (c).

The effect of treatment time on pH was observed which showed that the pH increased slightly during the adsorption process which caused a slight increase in the pH of the sample after treatment as shown in figure 1 (d).

0

20

40

60

80

100

120

0

2

4

6

8

10

12

**% Efficiency**

**Dosage in g**

**COD**

**BOD**

1. **Effect of pH** **(b)** **Effect of adsorbent dosage**

1. **Effect of treatment time (d) Effect of time on pH**

**Figure 1: Effect of parameters on the removal efficiency of COD and BOD from poultry slaughterhouse wastewater.**

Figure 1 (a) shows that % efficiency of treatment for the wastewater increased gradually as the pH increased with over 70 % removal up to pH of 6. The maximum removal efficiency of 90.2 and 94.7 % was recorded at PH of 6 for COD and BOD respectively. As the pH gradually increased the efficiency of removal dropped significantly to 50 and 48.5 % at pH of 8 for COD and BOD respectively. Other conditions for this treatment were dosage of 8g/100ml, treatment time of 90 minutes at room temperature.

Figure 1 (b) shows that as the dosage of the stabilized soil was increased, efficiency of both COD and BOD increased significantly, therefore, increase in dosage of the treatment material also leads to an increase in efficiency of treatment. Removal efficiency of 52.1 and 67.9 % was achieved for COD and BOD respectively when 2g/100 ml dosage was used after 90 min of treatment time. However, maximum removal of 94.1 and 94.2 % for COD and BOD respectively, was reached corresponding to 8g/100ml at 90 minutes of treatment time. Though equilibrium can be said to be reached at 89.9 % removal 6g/100 ml for BOD, saturation for COD was reached at 8g/ 100ml which was the climax for removal for both parameters signifying that the adsorption site has been saturated and any further increase beyond this point did not record any significant changes. Also, the soil-like nature of the material may influence some other parameters like turbidity and total suspended solids if the sorption process takes longer time as experienced in previous study (Nik Daud and Anijiofor, 2017). Therefore optimum condition for this treatment are 8g/100 ml, pH 6, agitation speed of 250 rpm, particle size of ≤0.6 mm, observed at contact time of 90 minutes at room temperature.

Figure 1(c) showed a steady increase in the removal efficiency of both COD and BOD until equilibrium was reached at 90 min of contact time. The efficiency obtained after 90 min was 92.9 and 93.2 % for COD and BOD respectively at pH 6, dosage of 8g/100 ml, agitation speed of 250 rpm and at room temperature. It was observed that after this saturation point was reached there was no visible difference in the rate of adsorption, however, maximum removal efficiency reached was 94.8 and 95 % for COD and BOD respectively achieved at the end of treatment. For similar studies which used other forms of cheap adsorbents obtained from waste materials, Devi and Dariya (2008), achieved maximum removal efficiency of 95.8 and 97.45 % using mixed adsorbent carbon (MAC) and 99.05 and 99.54 % using commercial activated carbon (CAC), from domestic wastewater for COD and BOD respectively. Al-Jlil (2009), achieved 92.17 and 97.66 % removal from domestic wastewater using activated sludge for COD and BOD respectively. Devi et al, (2008) also achieved 98.20 and 99.18 removal efficiencies for COD and BOD from Coffee wastewater using activated carbon from Avogadro peels. Idris et al., (2012) recorded 65.15 % COD removal from dye wastewater using poultry wastes while Kamalpreet et al., (2016) achieved 79 % removal of COD from landfill leachate using cow dung ash.

From figure 1(d), the pH of a treatment medium can increase during the treatment process which could influence the treatment efficiency if not properly monitored. The initial pH of 6 reduced slightly in the first minutes of treatment but subsequently increased slightly up to 6.12 as the treatment progressed. However, the slight increase did not produce any negative effect on the overall treatment efficiency because the pH was within the range and favorable results were obtained.

**3.2 Adsorption Isotherms**

Freundlich and Langmuir equations were used to evaluate the experimental results of this study. According to Freundlich isotherm, adsorption usually occurs on heterogeneous surfaces, while Langmuir model refers to the interaction between the adsorbent and the adsorbate. The Langmuir’s equation applied is in the form as stated in Equation 2

$\frac{C\_{e}}{q\_{e}}=\frac{1}{bq\_{m}}+\frac{C\_{e}}{q\_{m}}$ **Eq. 2**

Where; *Ce* and *qe* are the equilibrium solute concentration in the solution (mg/L) and equilibrium adsorption capacity (mg/g), respectively. The linear plots *Ce/qe* versus *Ce* of the Langmuir’s equation for COD and BOD are shown in Figure 2 (a) and (b), while the calculated values of Langmuir constants qm and b are shown in Table 4.

**Figure 2 (a) and (b). Langmuir adsorption plot for COD and BOD reduction using stabilized solid waste materials as adsorbent.**

The Freundlich isotherm equation used is in the form as Equation 3:

$q\_{e}=K\_{f}C\_{e}^{^{1}/\_{n}}$ **Eq. 3**

Where; *qe* (mg/g) is the amount of pollutants removed, *Ce* (mg/l) is pollutant concentration after adsorption, *k* and *1/n* represents Freundlich constants as shown in Table 4. Isotherm plots for Freundlich equation is in the form of In *qe* versus In Ce as shown in Figure 3 (a) and (b).

**Figure 3 (a) and (b): Freundlich adsorption plot for BOD reduction using stabilized solid waste materials as adsorbent.**

**Table 4: Isotherm parameters for COD and BOD adsorption from poultry wastewater**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  **Langmuir** | **Model** |  |  **Freundlich** | **Model** |  |
| Parameter | qm | b | R2 | K | n | R2 |
| COD | 29.85 | 0.091 | 0.9999 | 46.45 | 13.66 | 0.9785 |
| BOD | 10.74 | 0.360 | 0.9999 | 16.12 |  11.35 | 0.9557 |

For the Freundlich model, the slope 1/n is dependent on the order of change that occurs during the adsorption process while the intercept k describes the extent of removal of BOD/COD by the adsorbents. These values have been calculated from the linear plot of the Freundlich isotherm and the values are represented in table 4. For the Langmuir model, qm and b calculated from the slope and intercept respectively, are the Langmuir constants which signifies adsorption capacity and energy of adsorption respectively. The regression analysis for the two isotherms studied gave good correlation and describes the adsorption model perfectly however the Langmuir model gave better R2 values than the Freundlich model. On the other hand, the Freundlich model gave higher values for Qe (quantity of COD and BOD adsorbed) than the Langmuir model as calculated from equations 2 and 3. The Qe values for COD were 28.28 and 68.32 mg/g and for BOD 10.22 and 22.94 mg/g for Langmuir and Freundlich models respectively. In this regard, the Freundlich model suits the data perfectly and also shows that the adsorption is a physical and heterogeneous process.

1. **CONCLUSION AND RECOMMENDATION**

This present studyon the useof stabilized solid waste materials as adsorbents for the treatment of poultry slaughterhouse wastewater was very successful. Maximum efficiencies of 94.8 and 95 % were achieved for COD and BOD respectively in less than 120 min of treatment time. Residual concentrations of 160.2 and 46.4 mg/l were obtained from initial concentrations of 2720 and 960 mg/l for COD and BOD respectively. The pH increased slightly during treatment but had negligible effect on the overall treatment efficiency. However, careful selection of design criteria for this treatment is very important since the operating conditions play a very important role in the reduction of organic pollutants from the wastewater. The optimum conditions for this study were pH 6, agitation at 250 rpm, particle size of ≤ 0.6 mm, dosage of 8 g/100ml and temperature fluctuating within room temperature. The adsorbent is very cheap, readily available and its use will promote landfill remediation and reclamation.

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