Limestone-Zeolite Biocomposite as Potential Low-Cost Adsorbent for Landfill Leachate Remediation

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Abstract. A novel approach for the low-cost bioadsorbent for the removal of leachate pollutants is presented herein. In this study, limestone is combined with zeolite in order to fabricate biocomposite media with different ratios. Results revealed that limestone-zeolite biocomposite adsorbed ammoniacal nitrogen (NH₃-N) and COD, which could possibly be used for the adsorption of NH₃-N and COD efficiently from leachate. The optimum mixing ratio by means was carried out using series of batch experiments for limestone and zeolite to measure the remediation of NH₃-N and COD in a stabilized leached. The optimum ratio for limestone and zeolite in the remediation of NH₃-N and COD obtained were at 25:15 (82%) and 30:10 (75%), respectively. Indeed, the prepared limestone-zeolite biocomposite is a low-cost and effective adsorbent was potential used to derive the NH₃-N and COD for a promising adsorption efficiency from stabilized landfill leachate.

1. Introduction

Leachate is a major problem to be faced in the management of the landfill. Characterized as the fluid leachate resulting from the decomposition of biochemical and physical processes from solid waste and contains organic and inorganic materials, metals, colloidal, disintegrated solids and a variety of pathogenic contaminants that could pollute groundwater sources and surface water [1]. The nature of the earth in numerous creating nations especially in urban zones is quickly falling apart. Lacking municipal solid waste management is surely one of the significant contributing factors to the degrading environment quality [2]. There are two problematic of organic contaminants from landfill leachate which are NH₃-N and COD [3]. Thus, there is a need to develop efficient wastewater treatment technologies that eliminate the problematic pollutants from landfill leachate wastewater and recalcitrant matter are not easily removed by the chemical and biological methods.

The biological treatments is difficult to operate because is a highly favored treatment system, and recommended for long-term leachate treatment but these methods are costly. In addition, these processes cannot effectively matter and varied substances such as ammonia that inhibit biological activity [4]. Some research has been reported on [5], the results showed that the high concentrations of ammonia can slow down the biodegradation process. Based on the changes in biodegradation process, the biodegradable organic content of the leachate tends to decrease, because a landfill stabilizes with
the passage of time. In this regard, the decreased effectiveness of biological processes, physicochemical processes could be viewed as more appropriate options [3], [4]. Compared to many expensive methods, adsorption is preferred due to its flexibility, compatibility, low-cost, and regeneration ability [6]. It is demonstrable that the adsorbents which is low-cost, easy to find, and does not require special maintenance while operating [7]. However, few studies have indicated that limestone, a low-cost adsorbent, could effectively remove ammonia and metals from landfill leachate wastewater [2, 3].

Several studies indicated that composite materials could be effectively used as an adsorbent for the remediation of stabilized leachate wastewater [8]. It is a new composite materials of zeolite-carbon (Z-C), which combines the excellent properties of zeolites and carbon and could be prepared by simple inexpensive method [9]. However, the surface of zeolite is hydrophilic with regular aligned molecular level pores and cationic exchange ability, which makes it a good adsorbent for metallic ions and catalyst [3]. Conversely, it is expected that combination of low-cost adsorbent like limestone with zeolite should compensate for the drawback of individual materials and may develop a sustainable adsorbent for large-scale application [10].

This work aims to fabricate the potential of limestone-zeolite as a low-cost biocomposite to replace conventional adsorbent (zeolite) and evaluate their applicability in remediating NH$_3$-N and COD from stabilized landfill leachate was investigated. Moreover, effect of limestone and zeolite of biocomposite ratio toward NH$_3$-N and COD adsorption efficiency also was explored throughout this study.

2. Materials and Methods

2.1. Landfill leachate sampling

The samples of landfill leachate wastewater was obtained manually from Simpang Renggam landfill site (SRLS) located in Kluang district, Johore, Malaysia [11]. The sampling and preservation of leachate sample was carried out based on the standard method outlined by [12]. Table 1 presents the characteristics of landfill leachate at SRLS using laboratory tests.

| Parameter                     | Initial Characteristics |
|-------------------------------|-------------------------|
| BOD$_5$ at 20°C (mg/L)        | 156-379                 |
| COD (mg/L)                    | 2440-2990               |
| SS (mg/L)                     | 143-213                 |
| Color (mg Pt-Co/L)            | 4061-4748               |
| NH$_3$-N (mg/L)               | 1555-2010               |
| BOD$_5$/COD ratio             | 0.06-0.13               |
| Fe (mg/L)                     | 6.45-8.94               |

2.2. Materials

Limestone chips was purchased locally from marble factory which cost about RM40 per ton while zeolite (clinoptilolite) from PT. Anugerah Alam Sdn. Bhd. was commercially available for at a cost of RM2-4 per kg, respectively. Afterwards, the preparation of adsorbent was performed based on the procedure outlined by [2, 8].

The chemical compositions of limestone and zeolite were carried out by using the analysis of X-Ray Fluorescence spectrometry (XRF) (Model Philip PW 1404/10) prior to the experiment. All media were sieved to obtain particle size (<150 μm) by using ceramic ball mill in accordance to the procedure outlined by [2, 8]. Table 2 displays the result of XRF of limestone and zeolite, respectively.
Table 2. Composition of limestone and zeolite.

| Formula | CaCO$_3$ | CaO | SiO$_2$ | Al$_2$O$_3$ | MgO | K$_2$O | Fe$_2$O$_3$ | TiO$_2$ | P$_2$O$_5$ | SO$_3$ | Others |
|---------|----------|-----|---------|-------------|-----|--------|-------------|--------|---------|-------|--------|
| Limestone | 95.0 | 2.3 | 1.1 | 0.31 | - | - | - | - | - | 0.5 | - |
| Zeolite | - | 3.29 | 72.3 | 14.7 | 0.84 | 4.64 | 2.72 | 0.26 | 0.11 | 0.26 | - |

2.3. Optimum ratio of limestone-zeolite biocomposite analysis

In the beginning of the test, the optimum ratio of limestone-zeolite biocomposite identified. Tests carried out in the presence of mixed adsorbent limestone:zeolite (0:40, 5:35, 10:30, 15:25, 20:20, 25:15, 30:10, 35:5, and 40:0). The batch adsorption experiment was used to measure the removal efficiencies based on the existing literature [2], [8] at pH7, 200 rpm, and 2 hours at room temperature. The purpose of determining the optimum ratio is to select the most optimum combination for limestone and zeolite in the removal of NH$_3$-N and COD. The combination of limestone and zeolite that has the highest removal of this parameters selected as the optimum ratio. The optimum ratio for limestone and zeolite was used for the preparation of limestone and zeolite biocomposite. The percentage of NH$_3$-N and COD removal in the solution was computed as follows [2]:

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\text{Percentage of NH}_3\text{-N and COD removal} = \left[\frac{C_0 - C_e}{C_0}\right] \times 100
\]

Where, $C_0$: initial leachate of NH$_3$-N and COD concentration (mg/L); $C_e$: residual of NH$_3$-N and COD concentrations of the leachate (mg/L) at equilibrium.

2.4. Leachate analysis

NH$_3$-N and COD were conducted in accordance with the Nesslerization method and reactor digestion closed reflux colorimetric method [1], respectively. Three replicates were used for each test at room temperature [2].

3. Result and Discussion

3.1. Leachate characterization

SRLS was generally lower for BOD$_3$ and COD in the range 156 to 379 mg/L and 2440 to 2990 mg/L, respectively. The lower concentration of BOD$_3$ and COD in landfill leachate is different depends on the period of landfill leachate operation [11]. Due to its pH (more than 7.5) and the high concentration of NH$_3$-N is in the range 1555 to 2010 mg/L and the BOD$_3$/COD ratio is very small (lower than 0.1), which is considered as stable [3]. Hence, the option of landfill leachate treatment depends on the characteristic of the landfill leachate. One of the appropriate method via physicochemical processes through an adsorption for stabilized landfill leachate treatment.

3.2. Optimum mix ratio

From the result of the removal efficiencies of NH$_3$-N and COD, respectively in figure 1 and figure 2, the variation of the sample with the different ratio of limestone with zeolite in 4.0 g at fixed conditions representing as a function of optimum mix ratio for limestone-zeolite biocomposite. Altogether, it can be seen that after the maximum point, a rapid decrease of NH$_3$-N (82%) and COD (75%) was observed, followed by a continuous increment of zeolite ratio. The increase of NH$_3$-N and COD removal efficiency with increasing the dosage of limestone adsorbent can be explained by the ratio obtained show a significant replacement of the conventional (zeolite) adsorbent, which indeed without affecting the remediation of pollutant [9]. Similar findings have been observed in other studies [2, 3].

3
4. Conclusions
In this work, the biocomposite of limestone-zeolite was manufactured and batch experiments were designed using the conventional mix ratio method act as a promising low-cost adsorbent to reduce NH$_3$-N and COD from stabilized leachate. As a consequence, the limestone recorded lower at adsorption capability by referring to single media and the combination with a lower percent of zeolite during the determining the optimum ratio, the presence of both adsorbents aiding the process to result high percentage removal of NH$_3$-N and COD in the stabilized leachate treatment. The suggested optimum mixture ratio of limestone:zeolite at 25:15 to obtain higher NH$_3$-N removal of 82% while at 10:30 with the highest COD removal of 75%. The results obtained from this study have laid an important platform from which to improve the adsorbates present in the effluent, but this would be recommended for future work as it could provide further improvement by formulating a wide range of efficient composite. Therefore, for future work would attempt to involve adsorption efficiency of the composites to describe the different inorganic matters present in the landfill leachate effluent.

Acknowledgements
This work is ostensibly supported by the MyBrain15 (MyPhD) of the Ministry of Higher Education, Malaysia and also Dean, Faculty of Civil Engineering and Built Environment, Universiti Tun Hussein Onn Malaysia, for providing research facilities.
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