Adsorption of Anionic Surfactant Presence in Synthetic Car Wash Wastewater by Limestone

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Abstract: Limestone (LS) is a natural carbonated rocks that is porous with the scatterings of minerals on the surface with potentially active surface. In this study, raw LS were observed to perform efficiently in treating synthetic car wash wastewater (CWW) that was prepared using commonly used anionic surfactant (AS); sodium dodecyl sulphate (SDS). The point zero charge (PZC) of LS were determined using salt addition method and resulted with the result of pH PZC 8.05. Overall, the LS used in this study was found to perform efficiently at pH 2, with the removals of chemical oxygen demand (COD) and AS at around 30% and 50% respectively and the adsorption capacity of COD and AS around 0.25 and 0.30 mg/g respectively. Overall, LS shows promising potential to be used in the treatment of AS presence in wastewater with requirement of additional optimization of other parameters (such as dosage, contact time, salt addition, etc.) to enhance the efficiency.

Keywords: Limestone, point zero charge, pH PZC, car wash wastewater, anionic surfactant, chemical oxygen demand.

1. Introduction

Car wash wastewater (CWW) has high contaminants level that exceeds the standard discharge limit established by Malaysia’s regulatory limit. This includes the parameter of chemical oxygen demand (COD), oil and grease (O&G), solids, anionic surfactants (AS), pH, heavy metals and others. Reviews shows that the concentration of pH [1]–[3] COD [1, 3–6], O&G [1, 7, 8] and AS [2, 8, 9] were mostly over the standard discharge limit as referred to the Environment Quality Act 1974 – industrial effluent discharge limit.

Surfactants are one of the most versatile products present in several industrial segments, such as manufacturing of motor oils and cleaning products; which includes its application in car wash services [10]. Among the class of surfactants, AS is very important as it accounts for 60% of the world production. Though seems harmless, it was reported that increasing concentration of ASs and other organic compounds resulted in the considerable enhancement of phytoplankton biomass, density and productivity in polluted seas [11,12]. Moreover, the AS produced from CWW can greatly affect the marines as it can destroy the mucus membrane and gills of fishes thus interrupting oxygen transfer [13]. Furthermore, sodium dodecyl sulphate causes severe skin dehydration and complete recovery from the irritation can only be achieved 17 days after exposure [14]. In addition, ASs themselves show marked biological activity too either by binding to various bioactive macromolecules such as starch [15] and proteins [16] or being inserted into various cell fragments thus causing malfunction as reported accordingly. This list of implications on the exposure of AS to the livings calls out for proper treatment before being released to the water body.

Adsorption is a well-known method used to treat industrial waste gas and effluent mostly due to its low cost, high-efficiency and easy to operate. The adsorption process is generally suitable for decontaminating low or high concentrations of toxic compounds [17]. For adsorption of AS by LS, the idea is viewed as interference interaction in Enhanced Oil Recovery (EOR) procedure. In this procedure, AS were injected into the oil mixture to reduce the interfacial tension thus improving the oil extraction process. However, instead of interacting with the oil, AS interacts with the LS near the extracting site, thus, reducing the extracting efficiency [18-19]. This phenomenon was a setback for the oil production industry. However, for the wastewater treatment industry, this occurrence provides idea for the usage of LS in adsorbing AS.

Limestone is a widely available sedimentary rock, which composed of minerals calcite and aragonite with a different crystal forms of calcium carbonate (CaCO3). LS was known to be used as adsorbent for wide spectrum of adsorbates due to high porosity which enable it to show high efficiency towards adsorption of many types of dyes, anionic surfactants and other
adsorbents [20]. The dissociation of calcite and calcium oxide will cause the formation of Ca2+. In the treatment of AS, the role of Ca2+ is very crucial as it represents the cation that is in charge for LS to form electrostatic interaction with the polar head of AS as reported is previous studies [18–22]. Though it seems simple, the application of LS is highly sensitive to the pH of the solutions to be treated as the surface charges is dependent on the pH of solutions.

Overall, the objective of this study is to evaluate the capability of LS in treating synthetic CWW which was made up of AS. The removals efficiency and adsorption capacity of AS and COD using LS will be properly explained in the next section. Moreover, the relationship between the pH PZC of the LS and its performance will be explained appropriately.

2.0 Materials and Chemicals

2.1 Materials

LS were collected from Perwaja Steel Sdn. Bhd., located in Telok Kelong Industrial Area, Kemaman, Terengganu. The obtained LS were washed with ultrapure water and then dried at 105 °C for 24 hours [23, 24]. This process was done in order to remove any dirt or particulate that adheres to the media before being used for batch study. Later, the LS were crushed and sieved to be in the size of between 1.0-5.0 mm in size [24, 25].

2.2 Chemicals

Sodium dodecyl sulphate (SDS), chloroform, and methylene blue, sodium hydroxide (NaOH), hydrochloric acid (HCl), sulphuric acid (H2SO4), silver nitrate, potassium dichromate, mercury sulphate, ferroin indicator solution and ferrous ammonium sulphate (FAS).

3.0 Methodology

3.1 Preparation of Synthetic CWW

Preparation of the synthetic CWW was based on the characterization of CWW taken from local car wash stations, with the average of 80 mg/L of AS as MBAS. The 80 mg/L of AS synthetic CWW was prepared by dissolving 0.08 g of SDS solution with concentration of 10 ppm, 7 ppm, 5 ppm, 3 ppm, 2 ppm, and 1 ppm were prepared and extracted using the same method and the data obtained were used for plotting a calibration curve. The concentration of the samples were then calculated using the calibration curve and linear regression obtained.

3.2 Evaluation on the Effect of pH in Treatment of Synthetic CWW using Limestone

The pH of the aqueous solution is a controlling factor in the adsorption process. The batch adsorption experiments were conducted in a series of 250 ml conical flasks containing 150 ml of synthetic CWW. The pH of synthetic wastewater was adjusted using 0.1M NaOH or 0.1N HCl. Next, 0.5g of LS were added to each respective flasks. The flasks were then agitated in the orbital shaker at 300 rpm for 24 hours at 170 rpm. The changes in pH, ΔpH, were then determined using Eq. (1). The pH PZC of LS was determined using immersion methods [30–32]. In this method, the Na⁺ solution was used as background electrolyte, sodium chloride, NaCl. 50 mL of 0.1 M NaCl were prepared and then the pH were varied to 3, 5, 7, 8, 9, 10, 11 and 12 using 0.1M HCl and 0.1M of NaOH. Next, 0.5g of LS were added to each flasks and the system were shaken for 24 hours at 170 rpm. The changes in pH, ΔpH, was then determined using Eq. (1). The pH PZC of LS will be at ΔpH=0.

\[ \Delta pH = pH_{final} - pH_{initial} \]  

(1)

4.0 Data Analysis

4.1 Determination of Anionic Surfactant (AS) as Methylene Blue Absorbing Substance (MBAS)

The methods to determine the concentration of anionic surfactant in the treated and untreated samples were as according to the standard method APHA (2010) [16]. 10 mL of samples were pipetted into the separatory funnel. The samples were mixed with methylene blue prior to chloroform extraction. The solvent layer were then filtered through a phase separator filter paper (Whatman 1PS). The filtrates (chloroform + methylene blue) were then checked for its absorbance using UV Spectrophotometer at the wavelength of 652 nm. A series of SDS solution with concentration of 10 ppm, 7 ppm, 5 ppm, 3 ppm, 2 ppm, and 1 ppm were prepared and extracted using the same method and the data obtained were used for plotting a calibration curve. The concentration of the samples were then calculated using the calibration curve and linear regression obtained.

4.2 Determination of Chemical Oxygen Demand (COD, APHA (5220C))

The determination of COD was done accordingly to the APHA standard method [29]. Ultrapure water were used as blank and titrated against FAS solution prepared according to the APHA standard method.

4.3 Determination of Point of Zero Charge (pH PZC) of Limestone

The pH PZC of LS was determined using immersion methods adapted from previous studies [30–32]. In this method, the Na⁺ solution was used as background electrolyte, sodium chloride, NaCl. 50 mL of 0.1 M NaCl were prepared and then the pH were varied to 3, 5, 7, 8, 9, 10, 11 and 12 using 0.1M HCl and 0.1M of NaOH. Next, 0.5g of LS were added to each flasks and the system were shaken for 24 hours at 170 rpm. The changes in pH, ΔpH, was then determined using Eq. (1). The pH PZC of LS will be at ΔpH=0.

4.4 Determination of Removal Efficiency and Adsorption Capacity

The removal efficiency and adsorption capacity for COD and AS were determined using Eq. (2) and Eq (3), which has been widely used in determining the performance of adsorbents.

Removal Efficiency

\[ \% = \left( \frac{C_o - C_f}{C_o} \right) \times 100 \]  

(2)

Where:

- \( C_o \) = Initial COD/AS concentration (mg/L)
- \( C_f \) = Final COD/AS concentration (mg/L)

Adsorption Capacity
Where:
\[ q = \frac{(C_o - C_f) \cdot V}{m} \]  
(3)

5.0 Results and Discussions

The LS used in this study was analysed for its composition and surface morphology using FESEM instrument. Figure 1 and Table 1 shows the morphology and elemental analysis of the LS used in this study.

![Figure 1: Morphology of LS surface using FESEM instrument](image)

**Table 1: Elemental analysis of LS using EDX instrument**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt. %)</td>
<td>13.70 ± 6.15</td>
</tr>
<tr>
<td>O (wt. %)</td>
<td>44.09 ± 23.79</td>
</tr>
<tr>
<td>Ca (wt. %)</td>
<td>34.71 ± 16.67</td>
</tr>
</tbody>
</table>

In this section, the effect of pH of the synthetic CWW and its interaction with LS were evaluated. Foremost, the pH\(_{PZC}\) of the LS were determined using the method described in previous section. Figure 2 shows the point zero charge, pH\(_{PZC}\) of LS against 0.1M of NaCl solution. From the figure, it shows that the pH\(_{PZC}\) of LS used in this study was at pH 8.05. Similar pH\(_{PZC}\) of LS was also reported in previous study with the pH\(_{PZC}\) value of 8.1 [24]. This means that, when the pH of the water exceeds pH 8, the surface charge of the LS will become negative, thus, explains the low LS performance in this current study as the pH was adjusted from 2-12. As the of the adsorbent and the adsorbed species is usually considered to be led mainly by electrostatic interactions, chemical interactions, hydrophobic lateral interactions, hydrogen bonding or desolvation energy, while not every system contains all the five aspects. As the electrostatic interaction is not available at alkaline condition, the adsorption occurs might be due to the other interaction stated [33].

In addition, the effect of pH value of the synthetic CWW on the performance of LS was done with the adjustment of the synthetic CWW to pH of 2, 3, 5, 7, 9 and 11 using 1N HCl and 1N NaOH prior being placed on top of an orbital shaker to be shaken at 160 rpm for 30 minutes.

![Figure 2: Determination of pH\(_{PZC}\) of LS](image)

**Figure 3: Optimization of operating pH using LS on synthetic CWW.**

![Figure 4: The adsorption capacity of COD and LS using LS in treating synthetic CWW](image)
Overall, the findings shows that the LS was able to perform better at pH 2, a very acidic pH value. The removals of COD and AS were the highest at pH 2, at 35.3% and 53.2% accordingly. As the targeted contaminant in the synthetic CWW was AS, a negatively-charged contaminant, at acidic condition, the LS surface will become positively-charged, thus promoting electrostatic interaction. This explains the low adsorption of AS at higher pH value [24]. Current finding was subsequent with the statement, that net charge of rock or mineral surfaces is strongly dependent in pH; where, above pH of point zero charge (pHpzc), the net charge of the surface will be negative and vice versa [19].

5.0 Conclusion

Overall, the LS used in this study was found to perform efficiently at pH 2, acidic, same as the previous studies, where acidic conditions, the surface charges of LS are positively-charged, thus, enabling the electrostatic interaction with the negatively-charged AS. Moreover, the removals of COD and AS presence in the synthetic CWW were found to be around 30% and 50% respectively. Furthermore, the adsorption capacity of COD and AS by LS were found to be around 0.25 and 0.3 mg/g respectively. Overall, LS shows promising potential to be used in the treatment of AS presence in wastewater with additional optimization of other parameters (such as dosage, contact time, salt addition, etc.) to enhance the efficiency.

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Reference


