Evaluation on adsorption isotherms of alizarin red S dye removal by nickel/aluminium layered double hydroxide

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Abstract. The textile industry is one of the swiftest thriving industries contributing to the economic growth of Malaysia, particularly in east coast peninsular state. As the popularity of industry increases, the water usage was found to be elevated and eventually causes high expel rate of wastewater with excessive dye pollutants. In this study, anionic clay of nickel/aluminium layered double hydroxide (NiAL), was chosen to be studied as a potential adsorbent for anionic dye, namely Alizarin Red S (AR). The NiAL was synthesised via co-precipitation method and were characterized using powder X-Ray diffraction (PXRD) and Fourier Transform Infrared spectrophotometer (FTIR). NiAL was then used as adsorbent for the removal of AR dye in aqueous solution which was tested at different NiAL dosages. The experimental data were analysed using adsorption isotherm models and the AR adsorption was found to obey the Langmuir model.

1. Introduction
The textile and clothing industries is a vital part of the manufacturing production, trade and employment in numerous evolving countries. It is one of the industry that helps provide economic growth in Malaysia. Handmade textile industry is very popular in the East Coast of Peninsular Malaysia and Sarawak region. This industry is highly commercialized and contributes positively to the economic growth for some of the states, mainly Kelantan and Terengganu. However, this industry has increased water usage and eventually generate expel rate of wastewater with excessive amount of pollutants. During textile dyeing and finishing process, dyes residues are released as the main water pollutant [1]. A numerous amount of these dyes have been identified as toxic substances or sometimes even carcinogenic [2]. The existence of dyes in water causes damage to the environment especially aquatic life as it retards photosynthetic activity and causes disturbance in the re-oxygenation capacity because it blocks sunlight, which cause anaerobic condition that restricts the aquatic plants’ growth. Also, there could be contamination in groundwater and surface water that makes the water ill-suited for other uses as it may cause mutagenic effects [3].

There has been multiple treatment techniques such as solvent extraction, chemical precipitation, coagulation, and adsorption being used as metal ions remover from aqueous solutions. Due to economic
limitation, cost efficient and clean processes is preferred, for example, electrolysis, solvent extraction, ion exchange, and reverse osmosis. But these methods have a certain number of disadvantages, such as high energy requirement, incomplete removal, and high operational cost. Therefore, it has been proven that the most effective method is adsorption.

Anionic clay known as layered double hydroxides (LDH) attract significant attention from the academia and industries. LDH have also attracted attention on several fields of study, such as biomedical uses, polymer nanocomposites, water treatment, and catalysis [4]. LDH have relatively weak interlayer bonding which allows it to showcase outstanding ability to trap organic and inorganic anions [5]. It also have derived attention because of its great ionic exchange capacities and can be used as an efficient adsorbent for the removal of an assortment of anions from aqueous solution as it has anions in the interlayer that can be exchanged by other anions [6]. Hence, it is possible to use the LDH as an adsorbent for anionic dyes in wastewater. Previous researches reported the utilization of LDH as an adsorbent for dyes including eriochrome black T [4], acid red 27, direct red 23, disperse red 9 and methylene blue [7].

In this study nickel/aluminium layered double hydroxide (NiAL) is investigated as an adsorbent for the removal of Alizarin Red S (AR) dye from aqueous solution. AR, also known as sodium alizarinesulfonate which has a molecular formula of C_{14}H_{7}NaO_{7}S (Figure 1) is a type of anthraquinone dye that is commonly used in the textile industries to produce a deep red colouring. It could not be degraded completely via general biological and physicochemical processes due to its complex structures of aromatic rings that can sustain high thermal, biological and optical stability [8]. The removal of AR dye from water were previously reported by using activated carbon from Achyranthes aspera plant [8], activated carbon/γ-Fe_{2}O_{3} nano-composite [9], alumina [10], and photocatalyst ZnO and TiO_{2} [11]. However to best authors knowledge, there is no study on the adsorption of AR by LDH.

![Figure 1. Structural formula of Alizarin Red S](image)

2. Materials and methods
All chemicals were used as purchased without further purification. Nickel(II) nitrate hexahydrate (Ni(NO_{3})_{2}.6H_{2}O, Merck), aluminium nitrate nonahydrate (Al(NO_{3})_{3}.9H_{2}O, Merck), sodium hydroxide (NaOH, Merck), alizarin red S (C_{14}H_{7}NaO_{7}S, R&M).

A direct synthesis method, which is the co-precipitation method, was used to synthesis the NiAL with the Ni/Al molar ratio of 2:1. The synthesis process was conducted under constant flow of nitrogen gas while the pH of the solution was adjusted to 6 by dropwise addition of 2M NaOH solution into the mother liquor. Then the solution was aged in oil bath for 18 hours and the resultant slurry was washed with distilled water before being filtered, and dried in an oven at 70°C. The NiAL synthesized were then grinded and characterized by using Powder X-Ray Diffractometer (PXRD), Rigaku Miniflex II, and Fourier Transform Infra-Red (FTIR) spectrophotometer, Perkin Elmer Precisely, Spectrum 100 in the range of 400 to 4000 cm\(^{-1}\). The adsorption study was conducted at different amount of NiAL (0.05 – 0.5 g) which were placed in contact with 100 mL of 40 ppm AR dye solution for 60 minutes. The remaining dye concentration was determined at \(\lambda = 260\) nm using UV-Vis spectrophotometer, Shidmadzu UV1800.
3. Results and Discussion

X-ray diffractogram of NiAL (Figure 2) shows typical peaks of layered double hydroxide with poor crystallinity which is similar to the one reported by previous study [12]. The broad reflections of the planes also indicate that amorphous phase might be present in sample [13]. However the basal spacing value for (003) plane ($d_{003}$) which twice the basal spacing of (006) plane ($d_{006}$) showing that the materials comprise of layered structure. The $d_{003}$ of NiAL is 0.90 nm, indicates the thickness of a single layer of the NiAL and the charge balancing interlayer anion [14] which is nitrate.

![Figure 2. PXRD pattern of NiAL](image)

A broad band was observed in the FTIR spectrum of NiAL (Figure 3) centred at around 3400 cm$^{-1}$ is assigned to OH stretching due to the presence of hydroxyl groups in NiAL layers and interlayer as well as adsorbed water molecules [15]. A peak at approximately 1627 cm$^{-1}$ is attributed to the HOH deformation ($\delta_{\text{H-O-H}}$), thus confirming the presence of water molecules in the interlayer region of NiAL [16]. The presence of the nitrate anion located in the interlayer region of NiAL is shown by the appearance of a sharp peak at 1384 cm$^{-1}$, attributed to the bending vibration of N-O. The peaks within the region lower than 1000 cm$^{-1}$ are assigned to the metal-oxygen vibrations (M-O, O-M-O, M-O-M) within the layers of NiAL.

The ability of NiAL as an adsorbent for the removal of dye was tested using anionic dye of alizarin red S (AR) at different dosages of NiAL. As the mass of NiAL increases it provides greater number of vacant sites, which contributes to the increase of the number of binding site and surface area [17] for dye adsorption hence the removal percentage of AR increases (Figure 4). The removal percentage continues to increase with the increase of NiAL mass but the graph line starts to plateau when it reaches optimum mass at 0.25 g with 73% of AR was removed and no significant changes can be observed beyond this mass. This may be due to the overloading of adsorbent particles hence the binding sites available in NiAL were overlapped [18] and not accessible for dye molecules.
Figure 3. FTIR spectrum of the NiAL

Figure 4. Removal percentage of AR against mass of NiAL

The data were then fitted into two widely used adsorption isotherm models namely Langmuir and Freundlich. The Langmuir isotherm model presumes monolayer adsorption in which the adsorbed layer only one molecule in thickness with no steric hindrance and lateral interaction between the adsorbed molecules [19] and can be presented as shown in Equation 1 [20]:
\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

Where, \( q_m \) is the maximal adsorption capacity and \( K_L \) is the constant related to the free energy of the adsorption.

Meanwhile, Freundlich isotherm describes the reversible and non-ideal adsorption, which can be used for multilayer adsorption, with non-uniform dispersal of adsorption heat and affinities for the heterogeneous surface [21]. This model can be represented as empirical Equation 2 [20]:

\[ q_e = K_F C_e^1/n \]  

Where, \( K_F \) and \( n \) are Freundlich constants, respectively are related to the adsorption capacity and the adsorption intensity.

Both Langmuir and Freundlich linearized equations were used in this study to evaluate the suitability of the model in describing the adsorption mechanism. The equations are expressed as equations (3) and (4), for Langmuir [7] and Freundlich [22], respectively.

\[ \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \]  

\[ \log q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e \]

Based on the correlation coefficient (R²) for the linearized plot of both models (Figure 5), the adsorption of AR onto NiAL can be better explained by the Langmuir model as the R² value is higher (0.939) than Freundlich model (0.102). This indicates that the adsorption was made onto a homogenous adsorbent surface and the formation of monolayer coverage of AR dye onto the NiAL. Subsequent, no adsorption site available for other AR dye molecules once the site is occupied with an AR molecule. The adsorption process favours Langmuir model, may due to the affinity of NiAL surface towards AR dye is low thus the it can only capable to hold a layer of dye molecules.

![Figure 5. Fitting the data into Langmuir (a) and Freundlich (b) isotherms](image-url)
4. Conclusion
The NiAL was successfully synthesized via co-precipitation method and was used as an adsorbent for the AR dye in aqueous solution at different amount of NiAL with the optimum mass of 0.25 g. The experimental data is fitted well with Langmuir isotherm model showing that the process is governed by homogeneous adsorption.

5. References
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