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Removal of Methylene Blue Dye from Waste Water Using Ionic Liquid Modified Aluminium Isopropoxide Under Ultrasonic Irradiations

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ABSTRACT

In this paper, Methyltrioctylammonium Chloride modified Aluminium isopropoxide researched as adsorbent for the removal of Methylene Blue (MB) dye from waste water through a novel and efficient adsorption process under ultrasonication. Ultrasonic irradiations remarkably boosted the adsorption rate comparative to conventional shaking while maintaining the same adsorption capacity. In addition, the effects of initial MB concentration, Adsorbent dosage, pH, reaction time and temperature on the adsorption were studied. It was found that the isotherm data had a good correlation with the Langmuir isotherm through analysing the experimental data by various models. The results showed that Methyltrioctylammonium chloride modified Aluminium isopropoxide was four times effective for the adsorption of MB dye under ultrasonication.

Key words : *Methyltrioctylammonium Chloride, Adsorption, Methylene blue, Ultrasound irradiations.*

Introduction

Water contamination is a very significant problem for human society due to tens of thousands of dyes being ubiquitous in sewage waters from multiple industries such as textiles, rubbers, cosmetics, food, printing, paper, carpets, leather, etc. (Zhao *et al*., 2014). Textile is one of the largest waters consuming and water body polluter industries that produce coloured wastewater with different quantitative and qualitative chemical properties containing substantial amount of coloured substances (Neill *et al.*, 2000). Methylene blue is cationic dye ($C_{16}H_{18}ClN_3S$) which is widely used as chemical indicators, dyes and biological dyes. A large amount of organic dye wastewater is produced in the processes of the dyeing and printing in industries. Most of these dyes are toxic and even carcinogenic and make a serious hazard to aquatic living organisms (Saeidi *et al.,* 1999). The waste water has characteristics such as large discharge, high chromaticity, high organic matter concentration, poor biodegradability and it greatly effects the water body health and the photosynthesis of microorganisms in water environment (Wong *et al.,* 2004; Tan *et al.* 2008). When this water gets mixed up to different sources of water it makes water fatal for both human beings and other living organisms. The existence of very small amount of dyes in water (less than 1 mg/l) is even extremely unacceptable (Kyzas *et al.,* 2016). When Methylene blue is present in large amount i.e. (≥ 7 mg/kg), it can cause methaemoglobin (Garza *et al.,* 2007), resulting lack of oxygen throughout the body. At present, many researchers have used different methods to treat the dye waste water (Pavithra *et al*., 2019). Typical treatment methods include physical, chemical and biological methods, such as flocculation (Verma *et al.* 2012), membrane filtration (Yu *et al*., 2010; Delara *et al.,* 2012), advanced oxidation (Asghar *et al.,* 2015), ozonation, photocatalytic degradation (Kordouli *et al*., 2015), and biodegradation. These traditional methods have inherent limitations (Yagub *et al*., 2015), such as the complex and uneconomical nature of the technology and thus it is necessary to seek efficient and simple dye wastewater treatment methods (Sun *et al*., 2010). Among these technologies, the adsorption technique is considered to be one of the most straightforward and promising approaches, due to its ease of operation, simple unit assembly, low cost and high efficiency (Fan *et al*., 2017), adsorption capacity is an important index to evaluate the adsorption effect of adsorbent. Various low-cost alternative adsorbents from agricultural solid waste, industrial solid waste, agricultural by-product and biomass are used in waste water treatment. For example, Sludge (Wang *et al*., 2017); Montmorillonite (Wang *et al*., 2018); Flax fiber (Hailu *et al*., 2017); Zeolite (Castaneda *et al*., 2017; Leng *et al*., 2015); Biochar (Rice Husk), Pinewood (Mohammed *et al*., 2004; Abdel-Fattah *et al*., 2015); Wheat (Mubarik *et al*., 2016); Sugarcane bagasse (Mahmoud *et al*., 2016), Switch grass (Pathania *et al*., 2017), *Ficus carica* bast (Li *et al*., 2015) as adsorbents that have been used for adsorption treatment of dye waste water. Investigations on the low-cost adsorbents with high adsorption capacities are still under development to reduce the adsorbent dose and minimize disposal problems (Repo *et al*., 2013). However, IL-Al Porous materials have large number of active sites for excellent adsorption of adsorbate. The purposes of this study were to (1) confirm the adsorption rate and capacity through the adsorption model; (2) determine the various parameters that effect the adsorption. In the present investigation we have used ionic liquid (IL) Methyltrioctylammonium Chloride modified Aluminium isopropoxide as an adsorbent due to its low cost, meek procedure, environmentally safe and relatively good adsorption performance.

Experimental

Chemicals

Chemicals used in the work was procured from various companies, such as Methylene Blue used as an adsorbate is purchased from MERK. Methyltrioctylammonium Chloride ≥ 97.0 % (extra pure) was purchased from Sigma Aldrich. Aluminium isopropoxide ≥ 98% and Ethanol 99.8% were purchased from Merk. Methyltrioctylammonium Chloride was used after purification. Aluminium isopropoxide was used as such without any purification.

Analytical Instruments

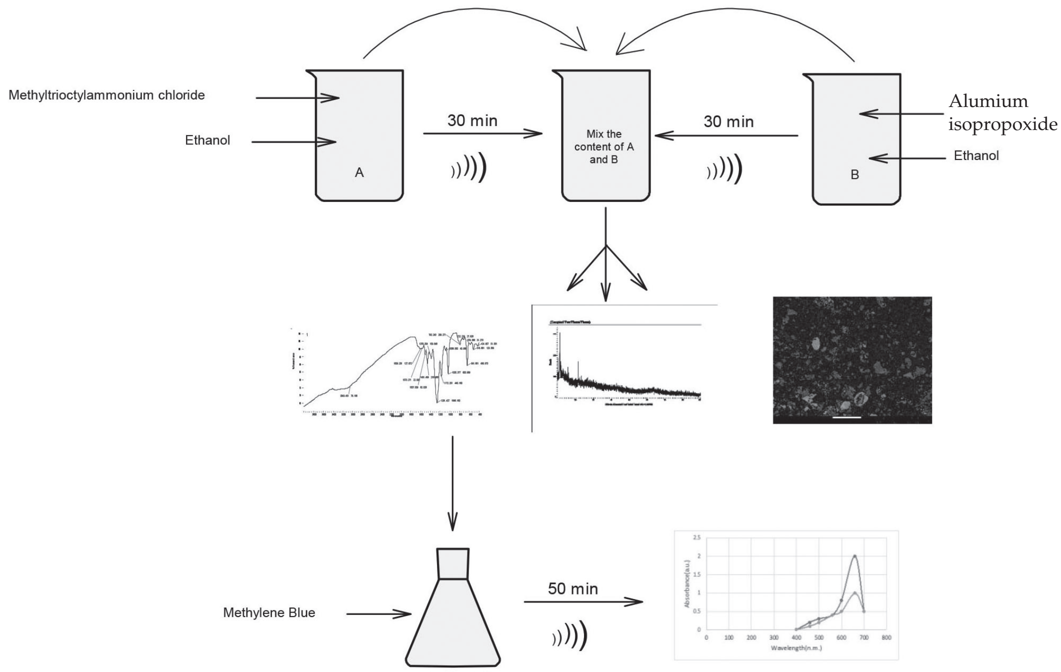
According to the standard method of water and waste water monitoring and analysis methods, the absorbance of MB solution was measured by UV-Visible spectrophotometer UV-260 (UV-260, Shimadzu). Fourier transform infrared spectra of the samples were obtained by using FT-IR Spectrometer. Sonicator used in this study was of Microsil model no. GB2500B ultrasonic bath cleaner (with a frequency of 40 KHz and capacity of 2500 ml). The phases of the synthesized adsorbent were determined by an X-Ray diffractometer (XRD) (Maker: Broker, Model: D8 Advance) and characterization was done by IR (FTLA 2000 spectrophotometer using KBr disc method). To study the surface of adsorbent, Ultra-high resolution schottky field emission scanning electron microscope (SEM) (JSM-7610F) was used. The pH of solution is monitored by FZS-706 multi-parameter.

Preparation of Methyltrioctylammonium Chloride modified Aluminium isopropoxide

4 mmol of Methyltrioctylammonium Chloride was dissolved in 15 ml of Ethanol and was sonicated for 30 min. at room temperature. Then 10 ml of Ethanol was mixed with 10 mmol of Aluminium isopropoxide and sonicated for 30 min. at room temperature. After this, solutions of ionic liquid (IL) and Aluminium isopropoxide were mixed and sonicated for 4 hr at 40 ^{o}C to form a colloid. Temperature of reaction mixture was controlled by adding cold water in ultrasonicator bath after every 15 minutes. Reaction was monitored by TLC. After the completion of reaction, colloid was put into oven to undergo solvent evaporation process. The final product will be obtained after grinding with pestle mortar.

Adsorption experiments

In an experiment, a desired amount of adsorbent (0.5 g/l) was added to a beaker containing 10 mL solution of 20 ppm Methylene blue. Then the beaker was placed in ultrasonicator at 40 ^{o}C for 50 minutes. The initial pH 8 of the Methylene blue solutions was adjusted by adding 0.01 M HCl or NaOH solution.



Schematic Diagram

The adsorption percentage (Q) and adsorption capacity values at equilibrium and t time (q_e and q_t mg g^{-1} respectively) were calculated using the following equations:

$$Q = C_o\text{-}C_e / C_o \times 100$$

$$q_e = C_o\text{-}C_e / mV,\ q_t = C_o\text{-}C_t / mV$$

C_o, C_e and C_t (mgL^{-1}) are the Methylene blue dye concentrations at initial, equilibrium and t time respectively, V(L) is the solution volume and m(g) is the mass of used adsorbent. The Methylene blue dye concentrations (C) were obtained through Beer-Lambert law in which absorbance value (k_{max} = 664 nm) for Methylene blue versus concentration obeys a linear relationship.

Results and Discussion

Characterisation of modified adsorbent

After synthesis of adsorbent, its characterization was done by XRD and IR. The FT-IR spectra of the activated Aluminium isopropoxide was recorded by Perkin Elmer 100 spectrometer using potassium bromide (KBr) disc method.

The Peak at 1378.304 cm^{-1} is due to aromatic overtones. The C=C stretch appear at 1461.484 cm^{-1}. The Peak at 3043.451 cm^{-1} due to OH stretch. XRD spectra of unmodified Aluminium isopropoxide and modified Aluminium isopropoxide were recorded. The different phases of the Aluminium isopropoxide and ionic liquid modified Aluminium isopropoxide were examined by an X-Ray diffractometer (XRD). Comparison of both spectra was done and it was analyzed that no characteristic peak of unmodified Aluminium isopropoxide appeared although crystalline phase appeared in the IL-Aluminium isopropoxide from the three peaks at position 20, 100 and 200. However, rest of peaks were broad indicating amorphous nature of modified adsorbent. The surface of the adsorbent was observed with SEM. Figure 4a, 4b show the detailed surface characteristics of the adsorbent. SEM micrograph of IL-Al showed a lumped material with the distribution of intra-agglomerate pore composites. The porosity of Al_2O_3 has been increased. The presence of these pores gives the composites superior chemical performance and could improve the adsorption capacity of adsorbate.

The scanning electron microscopic images (SEM) of IL-Aluminium isopropoxide

Adsorption properties of IL-Aluminium isopropoxide for the removal of Methylene blue

Batch adsorption studies: The adsorption of Methyl-

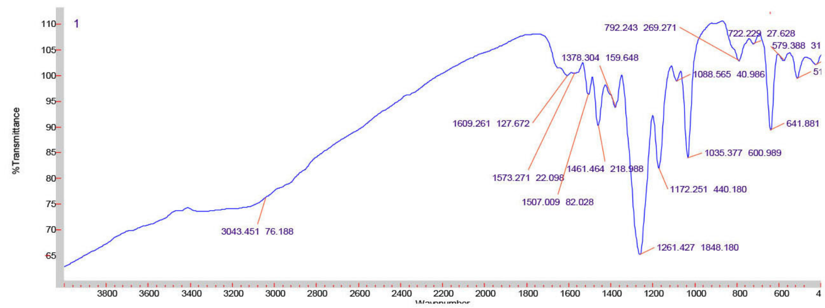


Fig. 1. FT-IR spectra of Methyltrioctylammonium Chloride modified Aluminium isopropoxide

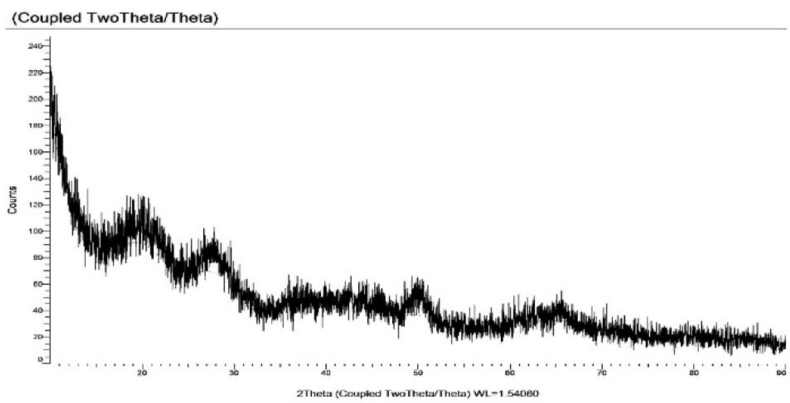


Fig. 2. XRD spectra of unmodified Aluminium isopropoxide

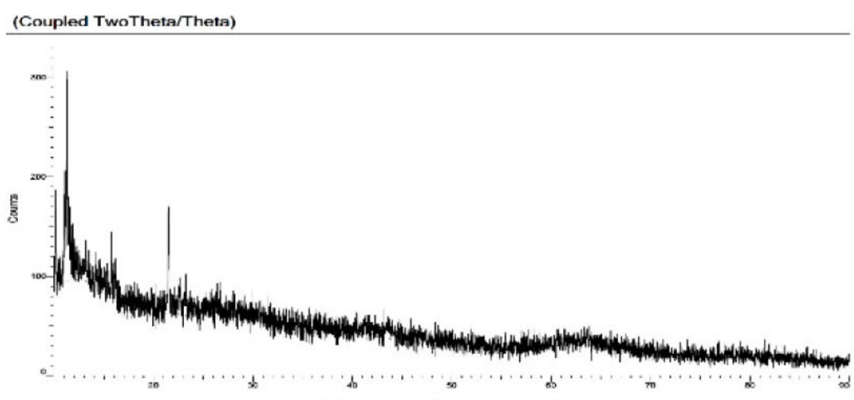


Fig. 3. XRD spectra of Methyltrioctylammonium Chloride modified Aluminium isopropoxide

ene blue on IL-Aluminium isopropoxide was studied in the batch mode and the effect of different parameters, including adsorbent dose (0.1–2.5 g/l), pH of solution (2–10) initial Methylene blue concentration (10–800 mg/l) and Temperature (10 °C-40 °C) of the reaction mixture were assessed.

Effect of initial pH on the adsorption

The pH value is a prime parameter in the adsorption process because of its effect on the active sites of adsorbents during the adsorption process (Figure 6). The experiments were conducted at Methylene blue initial concentration of 20 ppm and 4 mgl^{-1} of IL-Aluminium isopropoxide. pH of solutions was changed in the range of 2–10. Adsorption % of methylene blue by IL-Aluminium isopropoxide was 30% at pH 2, 90% at pH 4, 98% at pH 8 and 30% at pH at 10.

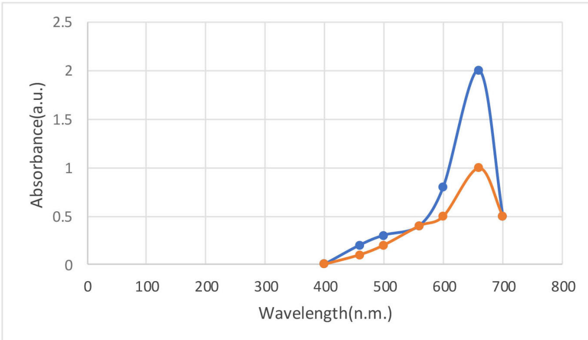


Fig. 5. Adsorption of methylene blue dye on IL-Aluminium isopropoxide under optimized conditions

Effect of adsorbent dose on the adsorption

Adsorbent dose is an important factor that effects the adsorption performance. The influence of adsorbent dose in adsorption of MB dye was studied to obtain the most appropriate amount of adsorbent in Figure 7. The effect of adsorbent dose in adsorption of MB studied to obtain a most appropriate amount of adsorbent at various MB concentration. The effect of adsorbent dose was studied by 100 ml of three different MB concentration (10, 20, 30 mgl^{-1}) and different adsorbent doses (0.1, 0.5, 1.0, 1.5, 2, 2.5 g L^{-1}). Various amounts of IL-Aluminium isopropoxide (0.1–2.5gl^{-1}) were added to 10 mL of dye solution (20 ppm) and ultrasonicated for 24 h. The results show that even though, the removal efficiency is high, already with low amount of adsorbent, the efficiency elevated from 90% to 98% by increasing IL-Aluminium isopropoxide dosage in the range of 0.1–2.5 gl^{-1}, and further increase of IL-Aluminium isopropoxide show only plateau trend. The enhancement in removal efficiency with an increase in adsorbent dosage is due to the availability of larger surface area and greater number of free adsorption sites. Beyond the concentration of 0.5 gl^{-1}, the increase of Methylene blue adsorption turns to be very low as both the surface and solution concentration of Methylene blue settle to equilibrium with each other. Hereby, further increase of IL-Aluminium isopropoxide dosage did not enhance the adsorption percentage.

Effect of contact time on adsorption

The effect of contact time on Methylene blue adsorption was investigated in solutions containing fixed adsorbent amounts (0.5gl^{-1}) at different initial concentrations of Methylene blue (10, 20, 30 and 40 mgl^{-1}). As it can be seen in Figure 8, all the adsorption kinetic curves appear rapid rising and then approaching flattening for Methylene blue initial concentrations of 10, 20, 30 and 40 ppm, respectively and adsorption was maximum after 50 minutes. With further increase in time, it remains stable.

Effect of temperature on adsorption

Temperature of solutions was changed in the range of 10 °C–40 °C in Figure 9. Removal % was 40 % at 10 °C. It was 56 % at 15°C, 67.4 % at 20 °C, 79 % at 25 °C, 90% at 30 °C, 98 % at 35 °C and 98% at 40 °C. Beyond the 35 °C temperature, no increase of Methylene blue adsorption. Thereby, further increase of temperature did not enhance the adsorption percentage.

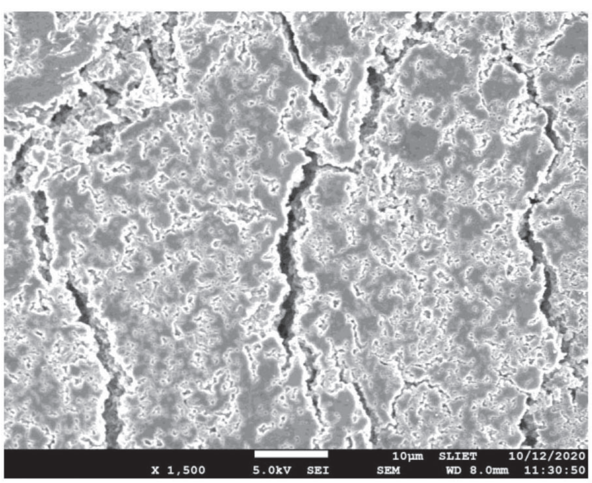


Figure 4(a)

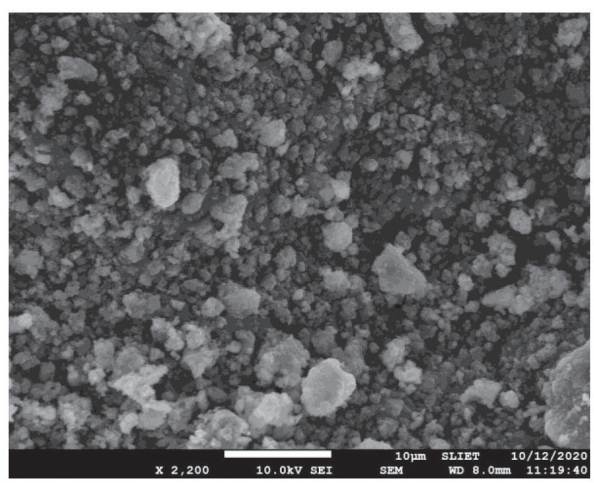


Figure 4(b)

SEM of IL modified IL-Aluminium isopropoxide

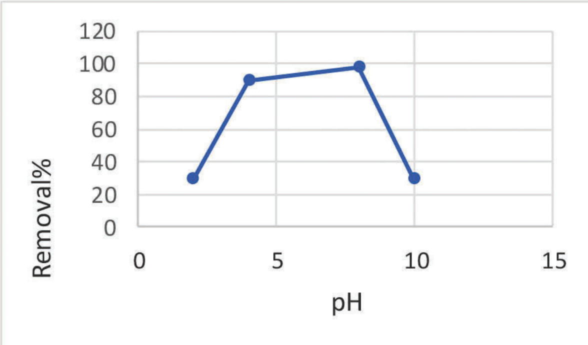


Fig. 6. Effect of pH on the adsorption of MB

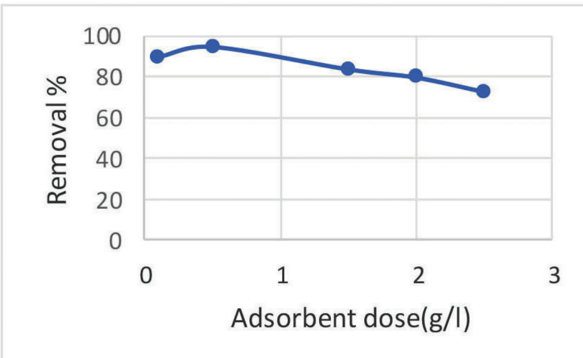


Fig. 7. Effect of dose of IL-Aluminium isopropoxide

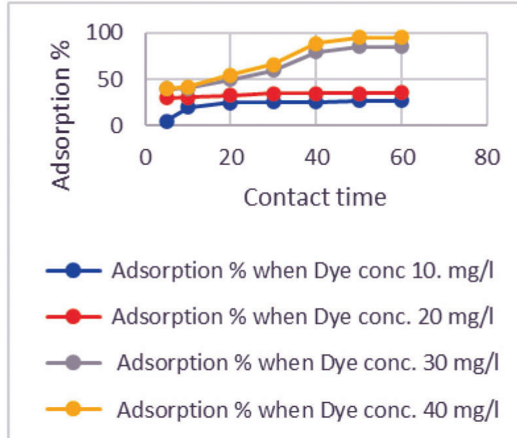


Fig. 8. Effect of contact time on adsorption

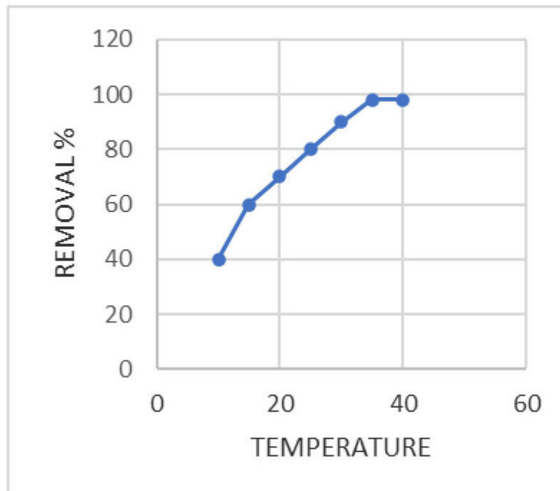


Fig. 9. Effect of temperature on adsorption

Isothermal studies of the adsorption

In this study, the well-known Freundlich and Langmuir isotherm models were employed to simulate the experiment data. For the adsorption systems, the experimental data agreed with Langmuir isotherm.

$$C_e/q_e = 1/K_{Lm} + C_e/q_m$$

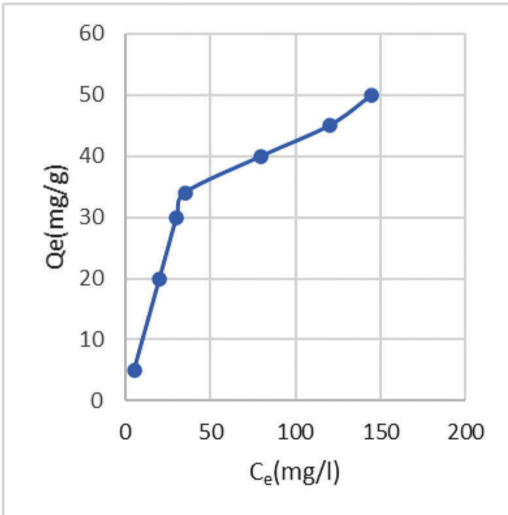
K_L is the Langmuir adsorption constant (Lmg^{-1}), q_m is the maximum monolayer capacity of adsorbent (mgg^{-1}). C_e is the equilibrium concentration. q_e is the adsorption capacity at equilibrium. The well-known logarithmic form of the Freundlich isotherm is given by the following equation.

$$\ln (q_e) = \ln (K_F) + 1/n \ln (C_e)$$

where K_F (Lmg^{-1}) and n are Freundlich constants. K_F is the adsorption capacity of the adsorbent and n gives an indication of how favourable is the adsorption process. Values of $2 < n < 10$, $1 < n < 2$ and <1 show good, difficult and poor adsorption characteristics, respectively.

Conclusion

Methyltrioctylammonium Chloride modified Aluminium isopropoxide used as an adsorbent has the quiescent to remove Methylene blue dye from polluted water. IL-Aluminium isopropoxide is a low-cost good adsorbent for the removal of Methylene blue dye form aqueous solution. Batch adsorption kinetic studies show that the adsorption of Methylene blue dye is strongly affected by initial pH of the solution, adsorbent doses, contact time and temperature of reaction mixture. Adsorption was maximum (98%) at 8 pH, adsorbent dose 0.5 g/l, contact time 50 minutes and temperature 35 ^oC. The amount of Methylene blue dye adsorption on IL-Aluminium isopropoxide initially increases with pH then starts decreasing. With increase in contact time adsorption



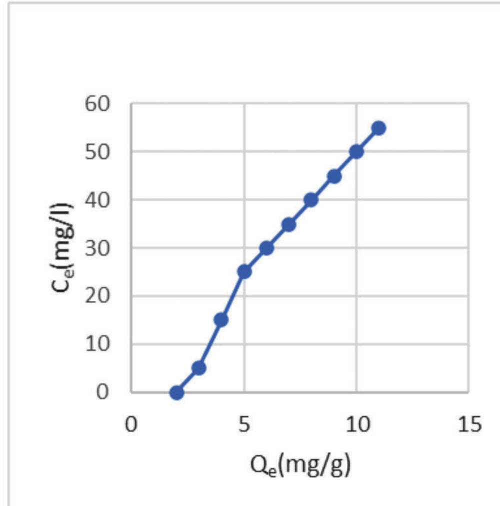


Fig. 10. Langmuir and Freundlich adsorption isotherm for the adsorption of Methylene blue dye by IL-Aluminium isopropoxide

increases then becomes constant and it has found that Methylene blue adsorption increases with increasing dose of IL-Aluminium isopropoxide.

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Conflicts of interest/Competing interests Not applicable

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