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Methyl Orange, An Organic Dye: Its Health Impact And Sorptive Removal From Waste Water

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Abstract – Methyl Orange (MO) a member of Azo dyes are commonly used as synthetic dyes in textile, food, paper and cosmetics. Their use is easy and cost-effective, compared with natural dyes. However, azo bonds are hardly removed because of their high water solubility as well as low exhaustion with the potential for persistence and accumulation in the environment, therefore aqueous solution of MO is toxic and irritating. Thus, the removal of them from industrial wastewaters is capital with regard to protect public health, environment, and aquatic life.

Keywords – Methyl Orange, Health impact, Wastewater, Sorption, Azo dyes.

I. Introduction

In textile dyeing processes, a large volume of dye contaminated effluent is discharged and about 15 % of the dyes used are lost in the effluent Kaushik *et al.,* 2008. This effluent is discharged to the nearby land or channeled into rivers without any prior treatment because the conventional treatment methods are very expensive (Verma and Mishra, 2010).

These industries emit amounts of dye wastes caused water pollution by dyes has become a environmental issue because most of their toxicity to human health and aquatic plant and animal life. The presence of even a small amount of dye in water is undesirable as it is highly visible, and may be toxic and carcinogenic (Sun and Yung, 2003). Hence, the dye wastewaters has to be treated before the eventual discharge of wastewater into the environment (Regine and Volesky, 2000; Dionysiou et al., 2004). Most dyes are stable to light and oxidizing agents and non-biodegradable in nature .The colour in water resources poses aesthetic problem and they also cause serious ecological problems like significantly affecting photosynthetic activity of aquatic plants due to reduced light penetration and may be toxic to some aquatic organism Dizge *et al.,* 2008.

II. Different Adsorbents For Dye Adsorption

Haque and co-workers suggested the potential applications of MOFs for the adsorptive removal of methyl orange (MO) especially MOFs having a positive charge such as protonated ethylenediamine-grafted Crterephthalate (MIL-101) which gave high adsorption capacity, rapid uptake and ready regeneration for the MO (Haque et al. 2010). Also, Bello et al., 2012 worked on the removal of Congo Red dye from aqueous solutions using imperatacylindrica leaf powder activated carbon. Ahmad et al., 2017 reported the adsorption of malachite green dye removal using lime peel activated carbon. Hameed *et al*., 2008 studied batch adsorption of methylene blue on activated carbon prepared from coconut husk. Ong *et al.,* (2010) reported the use of sunflower seed husk for the removal of methylene blue from aqueous solution.

Abdulsalam et al., 2017 reported the adsorption of Malachite green from quaternary dye mixture using modified sawdust of Locust bean tree. Giwa *et al*., (2013) worked on the removal of basic dyes from aqueous solution by adsorption onto melon husk. Damiyine *et al*., (2017) reported the removal of Rhodamine B from simulated wastewater using Expanded Perlite as an adsorbent

III. Health Impact Of Methyl Orange Use

Methyl orange (MO) is a type of p-aminoazobenzene dyes. The Azo dyes class, with MO as a member, is assumed to be the major group of the industrial dyes production (60–70 %). They are commonly used as synthetic dyes in textile, food, paper and cosmetics because of their ease and cost-effectiveness, compared with natural dyes (Ong *et al*., 2010). It is usually used in the textile stain industry and chemical as well as an acid-base indicator in research and experimental laboratories. However, release of residual azo dye into the industrial effluents deteriorates the water quality with hazard impact on public health based on the azo dye structures, toxicity and carcinogenic potentiality (Heiss *et al*., 1992). The structural similarity that characterizes azo dyes is the presence of at least one R–N=N-R' group. The R and R' components of the azo functional group can be either aryl or alkyl groups (Daneshvar *et al*., 2007). The azo bonds are hardly removed because of their high water solubility as well as low exhaustion with the potential for persistence and accumulation in the environment (Pinheiro *et al*., 2004). However, the aqueous solution of MO is toxic and irritating *El Gamal et al*.., 2020. Thus, the removal of them from industrial wastewaters is capital with regard to protect public health, environment, and aquatic life **(Hussein *et al*.**, 2018)

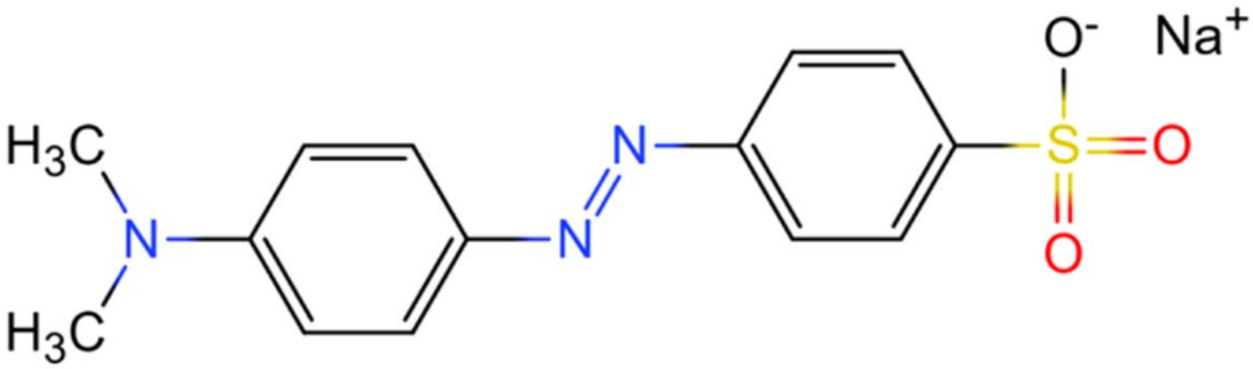

Figure 1. Schematic diagram of molecular structural formula of methyl orange (Source: **Lijuan et al., 2021)**

IV. Review Of Methyl Orange Sorption

Abdulsalam *et al*., 2020 discussed the Optimized Sorption of Methyl Orange using Functionalized Carob Plant Pod. The adsorbent was prepared by functionalizing the pod of carob with concentrated H_3PO_4. The effects of operational parameters such as adsorbent dosage, contact time, initial concentration of dye and temperature were studied and optimized using central composite design of design of experiment (DOE). The effects of process parameters (contact time, concentration, adsorbent dosage and temperature) on the dye adsorption were determined and optimized. It was observed that the colour removal efficiency increased with an increase in adsorbent mass and contact time. The adsorption process is endothermic as the percentage removal increases with temperature. The optimum contact time, concentration, adsorbent dosage and temperature were found to be 60^0C, 9.74hr, 10ppm, and 5g respectively for the maximum decolorization.

Chakkrit and Songsak, 2012 reported the removal of methyl orange from aqueous solutions by adsorption using chitosan intercalated montmorillonite. The characteristics of montmorillonite and chitosan intercalated montmorillonite (CTS/MMT) were examined by means of SEM and BET-analysis. The effects of operating parameters such as contact time, initial solution pH, initial dye concentration, and temperature on the adsorption of MO were also studied. The results revealed that adsorption of MO was initially rapid and the equilibrium time was reached after 1 hr. Adsorption kinetics were best described by the pseudo-second order model. An aqueous solution with a pH of 2.0 was favorable for the adsorption. The equilibrium data were better fitted by Langmuir isotherm compared to the Freundlich isotherm. The adsorption of MO increased with operating temperatures indicating anendothermic process. Reutilization of the bio-composite was feasible. These results suggested that the CTS/MMT can beused as an adsorbent for removal of MO from aqueous solutions.

Dhafir et al.,2012 reported the removal of methyl orange from aqueous solution by Iraqi Bentonite adsorbent. The effects of various parameters such as initial concentration of methyl orange, amount of adsorbent, ionic strength and temperature on the adsorption capacity has been

studied. The percentage removal of methyl orange increased with the decrease of initial concentration of methyl orange and it increased with the increase of dose of adsorbent. The adsorbed amount of methyl orange decrease with increasing ionic strength and an increase in temperature. The equilibrium adsorption isotherms have been analysed by the linear, Langmuir and Temkin models. The Langmuir isotherms have the highest correlation coefficients. Thermodynamic parameters such as ΔG, ΔH and ΔS for the adsorption process were calculated. The adsorption process was found to be exothermic and spontaneous.

Yujin et al., 2012 investigated the removal of methyl orange from aqueous solution by Calcium Alginate/Multi-walled Carbon Nanotubes Composite Fibers. Calcium alginate/multi-walled carbon nanotubes (CA/MWCNTs) composite fiber was prepared by wet spinning. And the initial pH is one of the most important factors that affect the adsorption capacity of MO onto CA/MWCNTs composite fiber. The novel CA/MWCNTs composite fiber can be utilized as environment friendly adsorbent for the removal of MO from aqueous solution due to the efficient and fast adsorption process.

Tapan *et al*., 2010, studied the kinetics and adsorption mechanism of methyl orange (MO) onto chitosan. Chitosan was utilized as adsorbent to remove methyl orange (MO) from aqueous solution by adsorption. Batch experiments were conducted to study the effects of pH, initial concentration of adsorbate and temperature on dye adsorption. The kinetic data obtained from different batch experiments were analyzed using both pseudo first-order and pseudo second-order equations. The equilibrium adsorption data were analyzed by using the Freundlich and Langmuir models. The best results were achieved with the pseudo second-order kinetic model and with the Langmuir isotherm equilibrium model. The equilibrium adsorption capacity (q_e) increases with increasing the initial concentration of dye and with decreasing pH. The values of q_e were found to be slightly increased with increasing solution temperatures. The activation energy (E_a) of sorption kinetics was found to be 10.41 kJ/mol. Thermodynamic parameters such as change in free energy (Δ*G*), enthalpy (ΔH) and entropy (Δ*S*) were also discussed.

Yujin *et al.,* 2012, A commercial activated carbon fiber (ACF) was applied as efficient adsorbents for adsorption of methyl orange (MO) dye in aqueous solution. The results showed that ACF had good adsorption capacity on MO dye due to the large surface area and excellent pore size structure. In addition, the adsorption property of MO dye in aqueous solution onto ACF was investigated as a function of the initial dye concentration, pH value and temperature of solution. It is observed that the adsorption capacity of ACF for MO dye increased with the increases in the initial dye concentration and the temperature of solution, but the pH value had no significant effect on ACF adsorption performance.

Lijuan Wu and co-workers reported in 2021 that halloysite nanotubes (HNTs) and chrysotile nanotubes (ChNTs) that are natural one-dimensional nano-mineral materials were used as adsorbents for the removal of MO dyes from water. In the near-neutral aqueous solution, the average maximum adsorption capacity of HNTs and ChNTs to MO dyes are 13.56 mg/g and 31.46 mg/g, respectively, and the latter is about twice as much as the former. Further adsorption isotherm model fitting study shows that the process of HNTs adsorption of MO dyes is more consistent with the Temkin model, which belongs to multi-molecular layer adsorption. The analysis results of BET adsorption–desorption curve also show that multi-molecular layer adsorption is easy to take place on the surface of HNTs. The adsorption of MO dyes by ChNTs is most consistent with the Langmuir model, so monolayer adsorption is the main adsorption process. Although ChNTs also have a fibrous tubular structure, because of their small inner diameter, it is difficult for macromolecular dyes to enter the channel with the effect of capillaries, so ChNTs mainly absorb MO dyes by electrostatic gravity. In the condition that the specific surface area, average pore size and pore capacity of ChNTs are far lower than that of HNTs, the adsorption amount of MO dyes by ChNTs is still much higher than that of HNTs, which shows that the positive surface charge of ChNTs plays a major role in the adsorption process. The infrared test results also confirmed indirectly that there was a difference in the adsorption capacity. The above results show that HNTs and ChNTs, the one-dimensional nanotube materials with similar morphology, can obtain different surface charges due to the different curling forms that form the crystal structure, which leads to significant differences in their adsorption effects on MO anionic dyes.

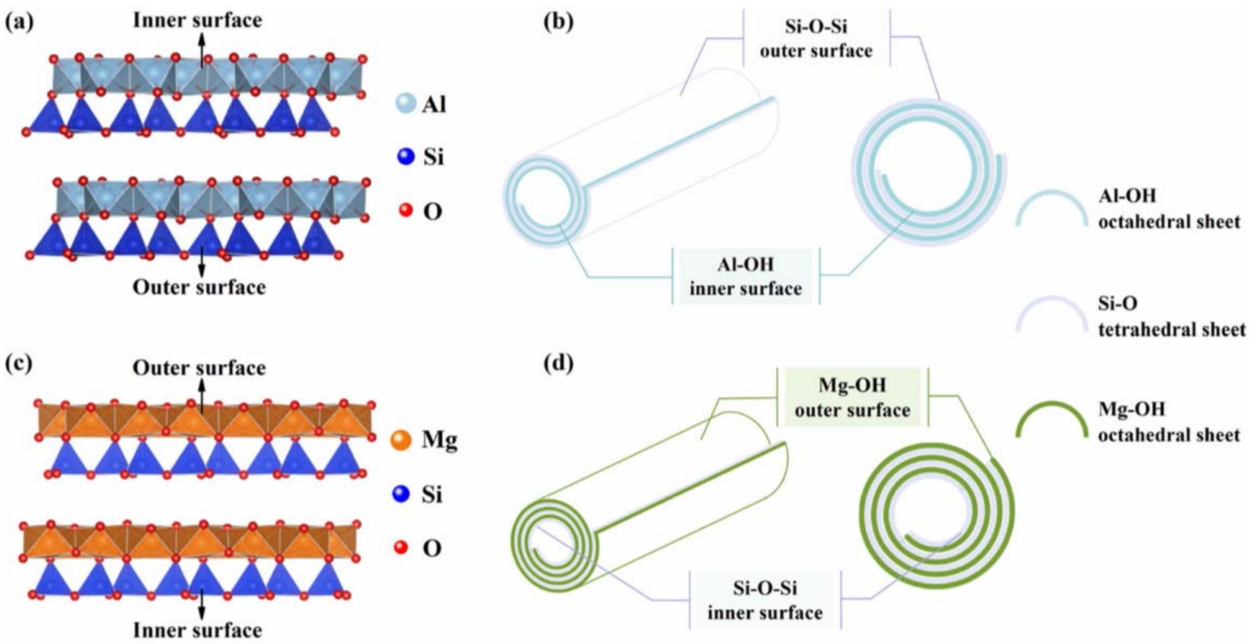

Figure 2. The crystal structure of (a) kaolinite (**b**) the morphological diagrams of HNTs and (**c**) ChNT (**d**) ChNTs (Source: **Lijuan *et al*., 2021).**

Adsorption Properties of Methyl Orange in Water by Sheep Manure Biochar was reported by Yixin *et al*., 2018. The sheep manure was used to prepare biochar under pyrolysis temperature of 600ºC. The structural features of biochar were characterized by elemental analysis, BET analysis and scanning electron microscopy. The effects of pH, biochar dosage, adsorption time, temperature on adsorption of methyl orange (MO) in water by sheep manure biochar, as well as its adsorption mechanism, were investigated via batch experiments. The results showed that the sheep manure biochar had large specific surface area, abundant hole structure and high aromaticity and polarity. When temperature was 25ºC, MO concentration was 20 mg/L, initial pH was 4.0, and biochar dosage was 0.6 g/L, the adsorption achieved balance at about 250min, and the MO removal rate reached to 92.55%. Pseudo second-order kinetic model and Langmuir model could more accurately describe the adsorption behavior of MO onto sheep manure biochar, and the theoretical maximum adsorption capacity was 42.513 to 45.563 mg/g as shown in Table 1. Besides, the process is a favorable adsorption. Thermodynamic studies showed that the adsorption was a spontaneous, endothermic and entropy-increasing process. Sheep manure biochar could be used as a good adsorption material for MO in water, which achieved the goal of controlling waste by waste.

Table 1. Fitting parameters of adsorption kinetic model.

Pseudo first order kinetic model			Pseudo second order kinetic model			Particle diffusion model		
q_e	k_1	R^2	q_e	k_2	R^2	C	k_3	R^2
30.674	0.0179	0.9587	34.758	0.0007	0.9922	1.2614	8.7873	0.8022

Mohamed *et al*., 2020 reported Manganese–containingmica (Mn–mica) was synthesized at 200 ^oC/96 h using Mn–carbonate, Al–nitrate, silicic acid, and high KOH concentration under hydrothermal conditions. Mn–mica was characterized and tested as a new adsorbent for the removal of methyl orange (MO) dye from aqueous solutions. Compared to naturally occurring mica, the Mn–mica with manganese in the octahedral sheet resulted in enhanced MO uptake by four times at pH 3.0 and 25 ^oC. The pseudo-second order equation for kinetics and Freundlich equation for adsorption isotherm fitted well to the experimental data at all adsorption temperatures (i.e., 25, 40 and 55 ^oC). The decrease of Langmuir uptake capacity from 107.3 to 92.76 mgg^{-1} within the temperature range of 25–55 ^oC suggested that MO adsorption is an exothermic process. The role of manganese in MO selectivity and the adsorption mechanism was analyzed via the physicochemical parameters of a multilayer adsorption model. The aggregated number of MO ions per Mn–mica active site (n) was superior to unity at all temperatures signifying a vertical geometry and a mechanism of multi-interactions. The active sites number (DM) of Mn–mica and the total removed MO layers (Nt) slightly changed with temperature. The decrease in the MO adsorption capacities (Qsat = n_DM_Nt) from 190.44 to 140.33 mgg^{-1} in the temperature range of 25–55 °C was mainly controlled by the n parameter. The results of adsorption energies revealed that MO uptake was an exothermic (i.e., negative DE values) and a physisorption process (DE < 40 kJ mol^{-1}). Accordingly, the adsorption of MO onto Mn–mica was governed by the number of active sites and the adsorption energy.

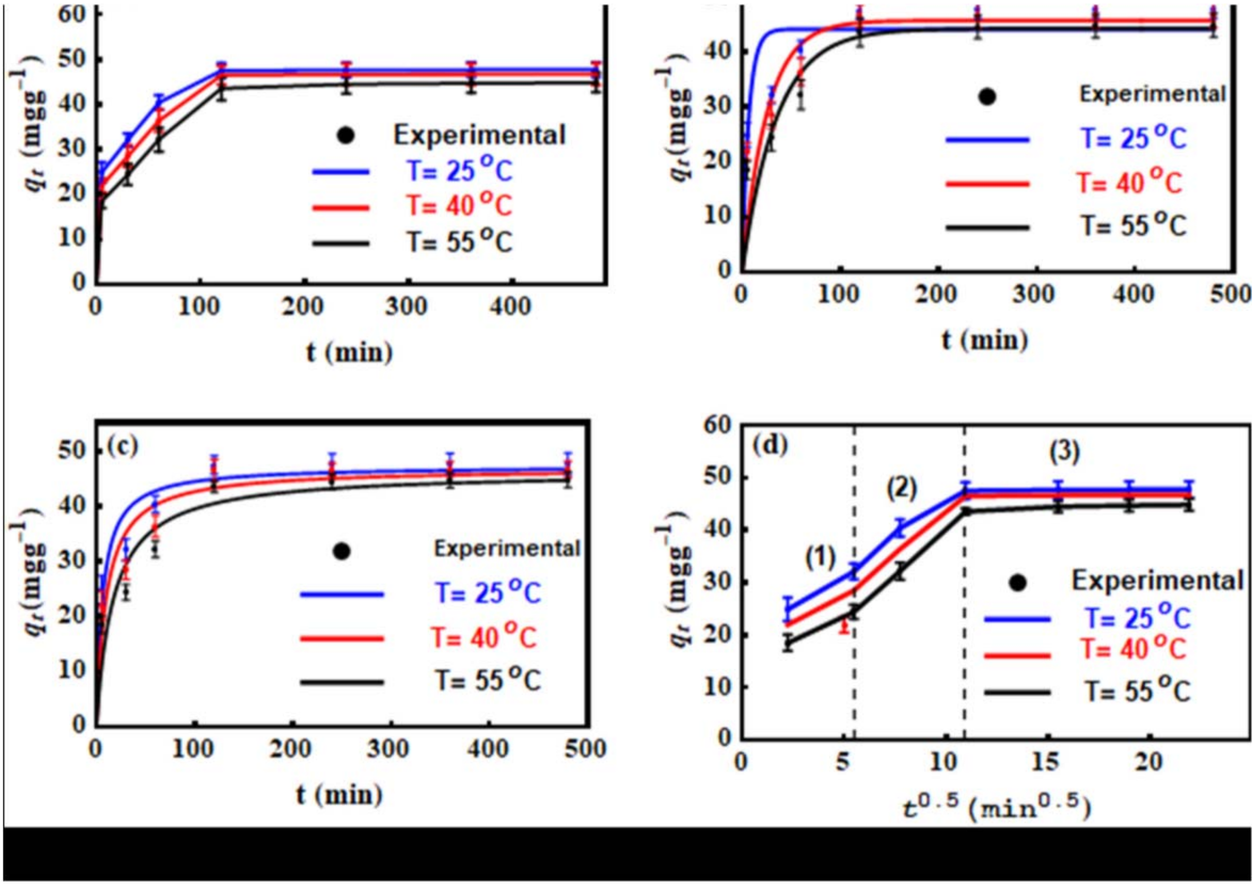

Figure 3. Kinetic studies of MO uptake by the Mn-mica, effect of contact time (**a**), pseudo-first order model (**b**), pseudo-second order model (**c**) and intra-particle diffusion model (**d**) at different

V. Conclusion

The removal of Methyl Orange from industrial wastewaters is essential with regard to protect public health, environment and aquatic life because it is toxic and irritating and have a potential for persistence and accumulation in the environment. The adsorption capacities ranges from 190.44 to 140.33 mgg^{-1} in the temperature range of 25–55 °C for adsorbent like Manganese–containingmica (Mn–mica).

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