ON METHYL ORANGE SORPTION VIA LAYERED DOUBLE HYDROXIDES

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A variety of strategies were used to study the best ways to remove pollutants from water, whereupon it turned out that sorption techniques are among the most effective and economically viable processes. Due to numerous applications, including the removal of dyes from wastewater by sorption method, layered double hydroxides (LDHs) have been extensively investigated in recent times. Several features of LDHs, such as the ability of anion exchange, tunable structure and high specific surface area make them highly efficient sorption materials and suggest LDHs for water purification. Methyl orange has been used as a model pollutant in most studies of the sorption properties of LDH, as a result of its widespread use. The influence of several factors including pH, contact time and initial dye concentration on methyl orange removal by various LDH materials have been reviewed in detail.

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Introduction

Water pollution is a significant problem on Earth that affects both humans and aquatic life [1]. According to reports, 80% to 95% of not treated wastewater is discharged into the environment in some underdeveloped countries [2]. Wastewater contains many different emerging contaminants (ECs) such as synthetic hormones, pesticides, pharmaceuticals and dyes [3]. Up to 10% of dyes used in textile, food, leather, cosmetic, paper and ink industries are lost during production and processing and released into the ecosystem [4]. Azo dyes, aromatic compounds, consist of azo bonds (-N=N-) and sulfonic, amino or hydroxyl ionic groups. About 70% of the annual worldwide manufacturing of dye is made up of azo dyes [5, 6]. Harmful, persistent, and mutagenic azo dyes and their metabolites can have an adverse effect on the environment [7]. A significant threat to aquatic life and people is posed by the fact that azo dyes, even at very low concentrations, can generate extremely strong colouring, decrease water-gas solubility, and decrease light penetration causing an increase in biochemical oxygen demand, which in turn hinders aquatic flora's photosynthetic activities and negatively affects aquatic species primary food supply [8-12]. Methyl orange, an azo dye that is frequently used, can cause serious health problems such as cyanosis, tissue necrosis, vomiting, increased heart rate and quadriplegia [13,14]. The development of techniques for dye removal from water has been going on for over thirty years and they are based on biological, physical, and chemical processes [15]. Many different effluent treatments have been reported for the elimination of dyes from aqueous medium such as sorption, ozonation, membrane filtration,

biological treatment, chemical oxidation, ion exchange, photo-catalysis, coagulation/ flocculation, depending on the nature and amount of contaminants [16, 17]. Sorption is considered to be a very efficient and superior separation process and provides several advantages over other processes, including ease of operation, low cost, adaptability to a wide range of sorbates, lack of a need for pretreatment, and absence of the formation of harmful byproducts [18, 19]. To achieve the best sorption performance, it is crucial to select the appropriate sorbents that are more effective in removing contaminants, more sustainable, and capable of capturing a variety of effluents. The research on methyl orange dye removal from wastewater by sorption has been conducted using a variety of materials, such as activated carbon [20], biochar [21], chitosan [22], fly ash [23], carbon nanotubes [24], zeolite [25] and wheat bran [26]. Layered double hydroxides (LDHs) have attracted considerable attention lately due to their efficiency in environmental remediation processes, especially in removing various dyes [15]. The two-dimensional structured LDHs have drawn a lot of interest as a result of their application in a variety of sectors including energy storage, biomedical applications, electrocatalysts, photochemistry, environmental applications, and flame retardants. Recent studies have shown that the utilization of LDHs is regarded as an effective, affordable, widely accessible, and environmentally friendly alternative sorbent for the removal of methyl orange [27].

In this review methyl orange (MO), $C_{14}H_{14}N_3NaO_3S$ (C.I. 13025), was chosen as a model sorbate since it is a typical azo-based dye with a variety of applications, its

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chemistry is well understood and there are several references about sorption of MO dye on the surface of LDH to compare.

Layered double hydroxides (LDHs) Structure of LDHs

LDHs are a two-dimensional, widespread group of inorganic nanostructured materials. Due to its talc-like structure and high-water content, the first naturally occurring LDH, found in Sweden in 1842, was named Hydrotalcite [15]. The majority of LDHs share structural characteristics with the naturally occurring magnesiumaluminum hydroxyl carbonate (Mg $_{\rm 6}$ Al $_{\rm 2}$ (OH) $_{\rm 16}$ CO $_{\rm 3}$ \cdot 4H $_{\rm 2}$ O), mineral hydrotalcite [28]. The LDH's formula is commonly represented as: $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+} [A_{x/n}^{n+}mH_2O]$. M^{2+} and M^{3+} represent bivalent and trivalent cations respectively, and An− represents the anions in the interlayer. A molar ratio of $M^{3+}/(M^{2+} + M^{3+})$ is given as X, and its values are generally between 0.17 and 0.33 [29]. A large number of cations can be utilized to prepare LDHs and the most common bivalent cations are Mg^{2+} , Mn^{2+} , Co^{2+} , Ni²⁺, Fe²⁺, Cu^{2+} , Ca²⁺ and Zn²⁺, while trivalent cations are Cr³⁺, Mn³⁺, Fe^{3+} , A $13+$, Co³⁺ and N $13+$. Anions between the layers neutralize the positive residual charges of the layers created by the exchange of M^{2+} with M^{3+} cations in LDH materials, and the hydroxide layer and/or anions in the interlayer are linked to water molecules by hydrogen bonds [30, 31]. Nonetheless, the size/charge ratio of anion is significant because large anions with a low charge can't distribute evenly between the layers of positive charge. There are numerous arrangements in the interlayer that are feasible for non-spherical anions or anions that contain long chains, including parallel or tilted monolayers or bilayers. Due to the functional diversity that results from compositional variety in the layers, there are numerous applications of LDH [28].

Properties of LDHs

LDHs exhibit a unique combination of chemical and physical properties due to their structural arrangements

and various preparation methods. LDH materials have high anion exchange capacity, adjustable composition, considerable specific surface area (up to 200 m^2/g) [32] and functionalization according to target pollutant, which makes them potentially excellent materials for sorption [33]. Another important property of LDHs is the memory effect. Despite its high thermal stability, LDH calcination at about 500 °C breaks down a layered structure and forms layered double oxides (LDOs), a type of metal oxide. LDOs have a high surface area and exhibit well in catalysis and sorption [34]. LDOs can recapture the interlayer anions and be converted back to the original structure of LDHs, by contacting with an aqueous solution or humidity. Hence, the memory effect can improve decontamination or performance by enhancing the captured capacity to target matter [35]. Figure 1 shows LDH's sorption mechanism which is based on an anion exchangeability of LDHs and is enabled by weak electrostatic interactions with layers, which makes it simple to substitute anions [36]. The predisposition for replacing inter-lamellar anion varies according to an array of factors such as the ratio of cationic metals, the applied anion's capacity to stabilize the layer formation, and the cation and anion molecular masses [37, 38]. Interlayered anions may be substituted with other anions depending on the anion's charge density and the intensity of the ensuing interaction between LDH's layers and anions, as in the following hierarchy: NO_3^- < Br $^-$ < Cl $^-$ < OH $^-$ < SO₄² \leq HPO $_4^2$ \leq CO $_3^2$. Anion exchange is less likely when carbonate ions are present in the interlayer because they interact with the LDH's metallic layers most strongly [32, 39]. Understanding how LDH properties such as pore structure and surface area control the morphology and affect how organic pollutants like dyes sorb, is crucial for adjusting active sites for highly effective sorbents. An improved comprehension of the basic connection between both the capacity of sorption and physiochemical characteristics would allow the designing of more effective sorbent materials [40].

Figure 1. Mechanism of sorption by LDH

Sorption of MO

Sorbent dosage, the pH of the solution, contact time, temperature, ionic strength, and initial concentration are only a few examples of variables that might have an impact on the sorption of dyes. A significant increase in the sorption of dyes onto the surface of the sorbent may be achieved by optimizing and retaining the optimal parameters during the process. In this review, the effect of initial pH, initial MO concentration and contact time will be discussed.

The effect of initial pH

The effects of solution pH on the sorption process is a crucial parameter to be researched because of the direct influence of the sorbent's surface charge, along with the degree of ionization and chemical structure of the studied organic dyes. The ability of sorption depends on the pH point of zero charge (pHpzc) which represents the solution's pH needed to achieve a net zero charge on the sorbent surface. Cationic dye sorption is preferred at pH values above pHpzc on the negatively charged sorbent, whereas anionic dye sorption is preferred on the positively charged sorbent surface at pH values below pHpzc [41, 42]. Since MO's pKa dissociation value is 3.46, at pH above 3.46 MO ions typically appear as monovalent anions which enhances attaching of positively charged layered compounds by electrostatic forces [43].

Zaghouane-Boudiaf et al. [44] studied the influence of the solution's pH from 2 to 12 on the sorption of MO dye by two prepared samples, calcined (MgNiAl–C) and uncalcined (MgNiAl–CO $_3$) LDHs. Their results showed that sorption of MO was reduced at pH values of less than 4, and greater than 10. One of the reasons was the increase of hydroxide concentration above pH 9 which leads to competition between MO anions and excess hydroxide ions in the solution. The lack of this material is the decrease in MO sorption which is influenced by the dissolving of magnesium at pH below 10, and aluminum and nickel at pH below 4 and above 10 [45, 46]. Since in both of the prepared LDHs samples, with a pH decrease the amount of dissolved magnesium rises, it was concluded that the most optimal value for performing experiments is pH 8. Furthermore, the calcined form of the material showed a higher sorption capacity towards MO than the uncalcined form.

Mahjoubi et al. [47] reported that the pHpzc of synthesized Zn/Al LDHs containing carbonate (Zn–AlCO $_{\scriptscriptstyle 3}$) and sodium dodecyl sulfate (SDS) (Zn–AlDs) are respectively 7.63 and 8.20. A rise in the percentage of dye removed in an acidic solution is related to the possible exchange between MO anions and carbonate anions in the interlayer as well as attraction forces among dye anions and the positive surface of LDH. On the contrary, with the rise of pH solution significant repelling forces between more negatively charged LDHs and dye ions increase. Organic LDH (Zn–AlDs) showed that the MO sorption behavior was not significantly influenced by pHpzc and it is probably connected to the stabilization buffering properties of Zn–AlDs LDH. This sorption process can be explained by the MO dissolving into the structure of the hydrophobic interlayer generated by dodecyl sulfate anions, instead of its uptake on the Zn–AlDs LDH external surface. Therefore, Zn–AlDs LDH performed better as a material that can be used for dye effluent treatment without further pH adjustment and with a higher removal efficiency. On the other hand, $Zn-AlCO₃$ is affected by pH and has the best removal efficiency in the range of 3 to 7.

The effect of pH variation on the sorption of MO onto NiAl conventional LDH (c–LDH) and LDH with a morphology resembling flowers (f–LDH) has been studied by El Hassani et al. [48]. It has been reported [49] that by replacing magnesium ions with nickel ions, the solubility of LDH material decreases. Likewise, Monash and Pugazhenthi [50] confirmed the structural stability of Ni–LDH at pH 2. Both sorbents, c–LDH and f–LDH, showed similar results with the highest capacity of sorption at pH values from 3 to 5 which is connected to attraction among the protonated surface of NiAl–LDH and negatively charged MO anion.

Yadav and Dasgupta [51] synthesized MgAl–NO₃ LDH and studied the influence of initial pH in the range of 1 to 11 at 25 °C for 60 min on the removal of MO. The results showed an increase in sorption capacity from 89% to 98% with an increase in pH from 2 to 5. The maximum sorption capacity at pH 5 can be explained by electrostatic attraction forces and phase stability of LDH with a reduced chance of carbonate intercalation in the interlayer space. As a result of its dissolution and subsequent phase change at pH 2 and 3, LDH's sorption capacity slightly diminished. Above pH 7 with a further increase to pH 11, the percentage of sorbed dye reduced from 90.14% to 26% due to the repelling of negative sorbent surfaces and dye anion along with the competition among carbonate and dye anion. MgAl–NO $_3^{}$ LDH material exhibits a great sorption activity in the narrow range of pH.

Nazir et al. [52] synthesized three different LDH sorbents, NiAl–LDH, ZnAl–LDH and NiZnAl–LDH. The calculated pHpzc for synthesized NiZnAl–LDH was 7.32, and an effect of different pH values at 2, 6 and 10 for all three materials is explored. The obtained results show a higher sorption capacity in mild acidic and neutral solutions than in strongly acidic or alkaline mediums which is a consequence of the anticipated charge of the dye and the LDH surface. The highest capability to sorb was demonstrated by NiZnAl–LDH and NiAl–LDH.

CoAl–LDH nanosheets were prepared by Chen et al. [53] to investigate its sorption potential for MO dve. It was discovered that the pH point of zero charge was 11.3 and it is expected that the positively charged surface of LDH is below pHpzc and the negatively charged surface of LDH is above pHpzc, which confirms maximum sorption capacity at pH 3 – 10 and decreasing at pH 10 – 11. The presence of a significant concentration of hydrogen ions, which interact with hydroxyl groups from LDHs to break down its crystal structure is attributed to the rise in sorption capacity from 75.15% to 98.28% at pH $2 - 3$. The increasing capacity of sorption in the pH range from 3 to 6 is a result of reacting leftover carbonate and hydronium ions to create bicarbonate ions or carbonic acid. It can be easily substituted by MO molecules and broken down into water and carbon dioxide. The drastic decrease in removal efficiency from 94.16% to 8.43% when the pH is raised from 10 to 11 is a result of the CoAl–LDH dissolving [54]. The main advantage of this material is its high removal capacity in the wide range of pH.

Table 1. Results of the pH effect on the sorption of MO dye in various types of research.

Table 1. shows the data from the mentioned papers and it can be concluded that increasing the value of pH affected the dye removal efficiency of almost all observed sorbents. Optimal pH is a value that is defined as the most suitable with the highest removal efficiency. Overall, MO removal efficiency at medium acidic pH ranges is better than those at base pH ranges, which is related to hydroxide and MO ions competing [53]. Furthermore, a higher positive charge on the sorbent surface caused by a rise in the concentration of hydrogen ions, enhances the electrostatic interactions between the LDHs and the MO ions, even though at strongly acidic pH values sorption percentage decreases due to the dissolution of LDHs. On the other hand, in most cases at high pH conditions, the deprotonated surface of sorbent repels from negatively charged dye and it leads to a lower sorption degree. The effect of pH value on the removal of MO of all mentioned materials was carried out in a wide range of pH values. According to the removal range percentage of the compared LDHs, f-NiAl showed excellent results with the highest range of 76% to 98%. On the contrary, Zn-AlCO $_{\scriptscriptstyle 3}$ performed as the material with the lowest removal range of 0.40% to 10%.

The effect of MO dye initial concentration

Due to its relationship with unoccupied sites on the adsorbent surface, the initial concentration of the sorbate greatly influences the sorption capacity. The saturation of the sorption sites occurs rapidly with higher initial concentrations of dye. Also, the sorption capacity increases with higher initial concentrations of dye because

of the high driving force of mass transfer [55, 56].

Zubair et al. [17] studied the effects of increasing MO dye concentration on sorption by NiFe–LDH and starch– NiFe–layered double hydroxide (S/NiFe-LDH) and reported that when the starting concentration of MO was increased, the efficiency of removal decreased for each sorbent. On the other hand, low dye concentration led to a high MO removal efficiency which was related to the low number of dye molecules present compared to the number of free sorption sites. When the MO's starting concentration is raised from 20 to 200 mg/dm3 , the removal efficiency decreased from 98.55% to 60.80% for S/NiFe–LDH (1:1), from 89.40% to 49.77% for S/NiFe– LDH (2:1) and from 75.80% to 43.25% for NiFe–LDH. This indicated that the intercalation of starch into NiFe– LDH's interlayers significantly increased the elimination effectiveness of MO.

Zaghouane-Boudiaf et al. [44] showed that increasing the initial MO concentration from 20 to 100 mg/dm3 decreases the removal efficiency of dye from 95.00% to 86.80%. A greater probability of collision between free MO molecules and available surface area can explain higher absorption capacity.

Nazir et al. [52] chose a range of MO concentrations $(5-25 \text{ mg/dm}^3)$ to study the impact of dye concentration on the removal capacity of LDH materials and they found that equilibrium sorption capacities were higher with increasing starting dye concentration which is a result of accelerating the mass transfer and enhancing the driving force between the sorbent and liquid sorbate [57].

Zhang et al. [58] investigated how initial dye concentration affected the MgAl–LDH's ability to sorb dye. The initial MO concentration throughout the batch sorption studies ranged from 25 to 200 mg/dm³. The results indicated increasing MO removal without reaching an equilibrium and maintaining removal efficiency at 84% when the starting concentration was greater than 100 mg/dm³. Therefore, at an initial MO concentration greater than 600 mg dm⁻³. the sorption capacity of MO could achieve an equilibrium with its maximum value of 380 mg/g. This indicates the high efficiency of this LDH material in terms of MO dye removal.

Zaghloul et al. [59] synthesized MgAl–LDH sorbent and investigated the effect of initial dye concentration at constant parameters such as pH, temperature and sorbent dosage. It is reported that when the starting MO concentration was raised from 50 to 800 mg/dm³ sorbed amount of MO on the MgAl-LDH increases without reaching equilibrium. It is possible that the sorbent's ability to collect more dye molecules at greater concentrations explains the further rise in sorption capacity with concentration [60].

Mahjoubi et al. [47] found a notable variability in the sorption capacity of Zn-AlCO $_{\tiny 3}$ layered double hydroxide and layered double-containing dodecyl sulfate (Zn-AlDs) through varying initial MO concentration in the range of 50-900 mg/dm³. Zn-AIDs showed a higher value of removal capacity compared to Zn-AICO₃ LDH. Likewise,

results showed that further increasing MO concentration above the value of 100 mg/dm 3 Zn-AlCO $^3_\mathrm{3}$ LDH, sorption capacity reaches the plateau of its values due to the occupation of most sites. The sorption capacity of Zn-AlDs displayed a linear increase which indicates that sorption was a process of dye dissolving in the three-dimensional hydrophobic phase of dodecyl sulfate intercalated in LDH structure.

As can be seen, the initial dye concentration is a very important factor in describing the efficient sorption of LDHs. At a low initial concentration, it is difficult to establish a state of equilibrium, therefore sorption sites remain unsaturated. On the contrary, an increase in the starting concentration causes a reduction in removal efficiency due to sorbent surface overloading, but an increase in sorption capacity because of the strong driving force for mass transfer. Since the potential interactions of the dye molecules with the accessible active sites of the sorbent depend on the initial dye concentration, for better removal efficiencies it is essential to optimize it. The effect of the initial concentration of dye on the sorption was investigated in the widest range by MgAl-LDH and Zn-AlDs LDHs. They showed a constant increase of the sorption capacity with raising the concentration of MO which may be attributed to their excellent sorption efficiency for large amounts of MO. The other described materials reached equilibrium at significantly lower dye concentrations.

The effect of contact time

 Contact time is one of the crucial factors affecting the mass transfer rate of methyl orange dye during sorption and allows the diffusion and adhesion of sorbate molecules.

The investigation of the sorption rate of MO by S/NiFe–LDH (1:1), S/NiFe–LDH (2:1) and NiFe–LDH was performed at an initial time in the range of 0 - 360 minutes [17]. The results showed very fast sorption at 30, 60 and 30 minutes on S/NiFe–LDH (2:1), S/NiFe– LDH (1:1) and NiFe–LDH respectively, and it is concluded that at initial times of 180, 120 and 80 minutes for S/NiFe–LDH (2:1), S/NiFe–LDH (1:1) and NiFe–LDH respectively, equilibrium was reached and it is an optimum contact time to experiment with the highest percentage of removal efficiency.

Zaghouane-Boudiaf et al. [44] reported that the amounts of sorbed methyl orange increased rapidly in the first 20 minutes and after that became slow until reaching equilibrium in 40 minutes. Similarly, Yao et al. [61] obtained that MO sorption on synthesized glycerol-modified nanocrystalline Mg/Al LDH (G–MgAl-LDH) reached an equilibrium in 30 minutes and then, as contact time increased, the maximum sorption efficiency was maintained.

El-Abboubi et al. [62] studied the influence of the contact time of dye solution with MgAl–CO $_{\tiny 3}$ and MgAl–DS on the sorption of MO. It was observed that by increasing the agitation time, sorption capacity increases. In the

first 60 minutes, sorption was fast and then it became slower till reaching equilibrium at 240 minutes.

Likewise, Mahjoubi et al. [47] showed that the sorption of MO at Zn–AlCO $_{\tiny 3}$ LDH increases quickly in the first 60 minutes and almost reached an equilibrium state after 240 minutes for Zn–AlCO $_3$. Zn–AlDs reached equilibrium after more than 300 minutes. They also concluded that the occurrence of a significant number of unoccupied sites on the surface, available for sorption during a short time, may be related to the physical sorption of the MO on LDHs [63].

The MO sorption on NiAl–LDH, ZnAl–LDH and NiZnAl–LDH was examined in the range of 0–180 minutes by Nazir et al. [52] and it was established that the capacity of sorption rises with an increase of the time that the dye solution is in contact with the sorbent. After 180 minutes, sorption didn't attain an equilibrium state.

Based on previously reviewed studies and results in Table 2. it can be concluded that sorption onto LDH starts quickly and subsequently slows down before reaching an equilibrium plateau. This is explained by the higher concentration of pollutants combined with the greater number of initially accessible and available sorption sites. Furthermore, various time ranges for attaining an equilibrium are noted in the literature, according to the type of LDH material. The removal efficiency of MO typically increases with increased contact time until equilibrium is reached. Accordingly, one of the essential features affecting the sorption process is the time of contact between sorbent and sorbate.

Conclusion

Since numerous research has considered MO's removal from aquatic environments, it was selected as a model pollutant for this review. This allowed for a thorough investigation of the influence of LDH characteristics on their capacity for sorption. There are many LDHs that have been employed for the sorption of MO, that vary in both composition and removal effectiveness. Among all mentioned LDH sorbents, some of which have very satisfactory results in terms of sorption capacity, Zn-AlDs

stand out due to their exceedingly high maximum sorption capacities of 2700 mg/g. In order to compare findings from various studies of sorption processes between distinct LDHs and MO dye, it is important to know that effects of pH, initial dye concentration and contact time do have a substantial impact on the sorption capacity of the LDH even though there are overall commonalities in the results and trends. Therefore, it can be said that the removal efficiency of MO is higher at medium acidic pH values, and it increases with the increase of contact time until reaching equilibrium, but the increase in initial MO concentration results in a removal efficiency decrease. More attention should be paid to these factors and finding optimal conditions to achieve the highest removal capacity of the target material.

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Izvod

EFEKTI pH, KONTAKTNOG VREMENA I INICIJALNE KONCENTRACIJE BOJE NA SORPCIJU METIL ORANŽA POMOĆU SLOJEVITIH DVOSTRUKIH HIDROKSIDA

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Primenjivane su različite strategije za proučavanje najboljih načina za uklanjanje zagađujućih supstanci iz vode, nakon čega se pokazalo da su tehnike sorpcije među najefikasnijim i ekonomski isplativijim procesima. Zbog brojnih primena, uključujući uklanjanje boja iz otpadnih voda metodom sorpcije, slojeviti dvostruki hidroksidi (LDH) su opsežno istraživani u poslednje vreme. Pojedine karakteristike LDH, kao što su sposobnost izmene anjona, podesiva struktura i visoka specifična površina, čine ih visoko efikasnim sorpcionim materijalima i predlažu LDH za tretmane prečišćavanja vode. Metil oranž je korišćen kao model zagađivača u većini studija sorpcionih svojstava LDH, kao rezultat njegove široke upotrebe. Detaljno je razmotren uticaj nekoliko faktora uključujući pH vrednost, vreme kontakta i početnu koncentraciju boje na uklanjanje metil oranža pomoću različitih LDH materijala.

- 83

(PREGLEDNI RAD)

Ključne reči: Slojeviti dvostruki hidroksidi, metil oranž, sorpcija, tretman otpadnih voda, uklanjanje boje