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# UIO-66 (Zr)-Metal Organic Frameworks for oil orange SS adsorption from aqueous effluent towards eco-friendly wastewater management

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**Abstract.** Wastewater treatment is essential for efficient removal of harmful substances such as dyes and organic contaminants from aqueous streams. In this regard, metal-organic frameworks (MOFs) are introduced by academia owing to their superior properties that including efficient adsorbents as well as reliable semi-permeability. Thus, such characteristics are making them attractive for wastewater treatment applications. The experimental results revealed that the modified MOF structures namely, UIO-66 (Zr) possess a superior adsorption capacity for orange SS dye. The influence of pH value, the temperature, adsorption isotherm time, initial pollutant load, as well as coexisting ions is highlighted. Initially, 30-minutes of reaction contact time is monitored as the isotherm time. The experimental results demonstrate a maximum dye removal efficiency of 100% and an adsorption capacity of 2062.175 mg/g is investigated. Such outcomes confirm the efficient adsorption capacity of UIO-66 (Zr) based MOF material for dye elimination.

**Keywords:** Metal-organic frameworks; Adsorption; Wastewater; Textile dye.

## 1. Introduction

Clean water is essential for human beings, sustainable development as well as industrial purposes. However, globally, there is water challenges like scarcity, contamination and inadequate sanitation infrastructure threaten public health and ecosystem integrity [1]. Addressing these issues requires sustainable water management practices, severe regulations, improved industrial wastewater treatment and exploration of advanced technologies and eco-friendly dyes [2]. Massive efforts from industrial sectors, policymakers and academic researchers are required for sustainable practices [3]. The disposal of synthetic dyes into water sources is the leading cause of dye pollution hence posing a major environmental problem. Such dyes are widely used in industries like printing, leather works and textiles industry which heavily rely on them due to their bright colors [4]. Dyes might be an issue to the environment because they have toxicity levels and can be stored in organisms, remain for long durations, interfere with light harvesting processes in plants and also have impacts on ecosystems. Additionally, they decrease the supply of oxygen in water bodies consequently disrupting aquatic food webs as well as being potentially carcinogenic, mutagenic and hazardous to human health [5]. A holistic approach that combines advanced wastewater treatment technologies; tougher discharge thresholds for industries; new treatment methods and combinations; as well as adoption of green dyes and sustainable dyeing practices must be taken into account in addressing concerns attributed to dye pollution [6].

Waters contamination is one of the widespread environmental problems that leads to loss if the aquatic habitat, release of pathogens, and injuries to the ecological system. A vital component in the water preservation journey is getting the adequate water treatment technology to ensure the safety and cleanliness of the resources. Such facilities will necessitate advanced options such as membrane filtration, activated carbon adsorption, and oxidation process to contend with recently emerged contaminants such hazardous chemicals and micro plastic. Partly decomposed wastewater could still be received and treated via old but still applied treatment methods like coagulation-flocculation, sedimentation, and disinfection. Substantial improvement in water treatment quality can be achieved with due attention to the safeguarding of water, correct and well-established operation practices, wastes management and nature-based solutions like bio filtration and wetlands. Such a guarantee that the present and future generations will have to be healthy is what nature-based solutions provide.

The multistage wastewater treatment process entails physical, chemical, and biological stages. The aim is to raise water quality and eliminate all impurities. As it is very flexible, it can operate for long time, the cost of the process of treatment is not very high, and large amount of contaminants can be eliminated from the water, the common water treatment process is adsorption. Adsorption refers to a water treatment technique that not only organic but also inorganic pollutants, including pesticides, medicines, organic dyes, and heavy metals, are easily removed from water [10]. With its higher surface areas and hydraulic performance, it is the most effective among all. Absorption contributes a large part in the removal of any type of pollutants. The contaminants which range from trace to emerging can be removed down to very minute concentrations also. It upgrades the overall productivity through its ease-of-use feature and built-in display system that requires minimal maintenance operations and are compatible with filtration systems.

For Zr as it stores its components, as the UiO-66 type of MOF with a particular structure, the big area of surface and capacity for regulation have been selected as the prospective materials. Studies were concentrated in the question of the removal of effluent coloring and determination of ability to absorb and from the results it was clear that this dirty water can be reused fully with good absorbency capacity [12]. The main goal of the most recent studies is to maximize the ability of the dye sorbent by dopant additions at the surface of the nan adsorbent and its functionalization. Due to using UiO-66 (Zr) along with hybrid systems and polymer-based materials, enhances the absorption of dyes and is highly promising [13]. Two Zr and other active components were tested and showed good synergistic effects with fast kinetics and also efficient adsorption.

This investigation is centered an around use of MOFs to remove common orange SS dye, which belong to new prohibited colors category. The OOSS dye most likely surpasses the UiO-66 (Zr) of one of the modifications of UiO-66 which incorporates positive kinetics and rate of removal efficiency. The presented research covers a variety of the effects areas, for example, the temperature, pH, and the strength of the textile dyes, the volume of the MOF-adsorbent, and the dye removal efficiency value starting from. These outcomes, understandable and appealing, lie at the crossroads of our concrete perception of the capabilities of MOF for wastewater cleaning. This knowledge and appreciation enjoy very deep levels of sharing and understanding. Due to their large coordination number of MOF nodes and strong node-linker connections, zirconium-based MOFs, such as UiO-66, have better mechanical stability. UiO-66 can improve catalytic performance and preserve thermal stability by introducing metal ions and organic ligands. Its high connection stops further disintegration and allows for speedier defect restoration.

## 2. Experimental section:

### *2.1. Batch adsorption investigation*

The first model pollution chosen was orange SS dye, which is extensively applied in textile manufacturing (see properties in Table 1 [14]). This is done by dissolving the dye in distilled water to make a stock solution, which is then diluted to obtain numerous dye solutions for experimentation. The dye solution (20ml) is placed into airtight containers, and adjusted to the required pH levels. Thereafter, the MOF dose is added to the stirred sealed containers to measure isotherm time. In between runs, the MOF material is filtered out using a micro filter prior to analysis. The aim of this work was to explore the spectrophotometric removal of Orange SS (OSS) dye by using modified Metal-Organic Framework (MOF). This approach gives simple guidance for the execution of adsorption experiments and assists in understanding the effect of operating variables on adsorption process. Factors considered were dye solution concentration, contact time, solution pH, adsorbent dosage as well as temperature.

Remaining concentration of dye after adsorption was determined by measuring absorbance at λmax = 410 nm for orange SS dye. To compute the removal efficiency (R, %) and the quantity of orange SS dye adsorbed at equilibrium (Qe, in mg/g), the following equations were investigated according to the following:

$$R = (Co - Ce) \times 100 / Co \quad (1)$$

$$Qe = (Co - Ce) \times V / m \quad (2)$$

where V is the volume of the solution (mL), m is the weight of the adsorbent (g), and Co and Ce are the initial and final dye concentrations (mg/L).

**Table 1.** Physical-chemical characteristics of the orange SS dye

| **Parameters** | Values |
|---|---|
| *Molecular weight* | 264.32 g/mol |
| *Molecular formula* | $C_{17}H_{14}N_2O$ |
| *Synonyms* | Solvent Orange |
| *IUPAC name* | 1-[(E)-(2-Methylphenyl) diazenyl]-2-naphthol |
| *λ max* | 330-490 nm. |

## 3. Results and Discussions:

### *3.1 Morphological analysis of UiO-66(Zr) MOF*

Figure 1. Illustrates the scanning electron microscopy (SEM) images of UiO-66(Zr)-green sample. UiO-66(Zr)-green exhibits a thin brick-like image is shape. Furthermore, the average particle size is investigated and the recorded size is approximately 200 nm.

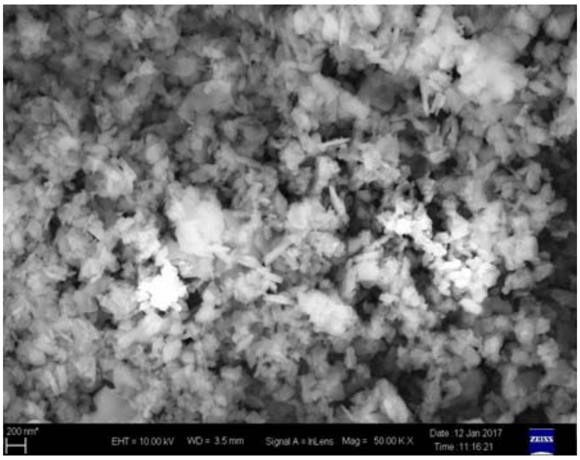

**Figure 1.** SEM image of UiO-66(Zr)-Metal Organic Framework

*3.2. Applying UiO-66(Zr) MOF on Orange SS removal*

*3.2.1. Determination of equilibrium isotherm time:* At first, the isotherm equilibrium time must be determined before designing the adsorption matrix. The time-profile of oil orange SS dye sorption through UiO-66(Zr) MOF was investigated at room temperature while keeping other parameters constant (pollutant load 100 mg $L^{-1}$ and adsorbent dose 1 g $L^{-1}$) and the data is exhibited in Fig. 2. The results revealed that additional dye uptake with the extension of the reaction time is achieved until the 30 minutes of contact time. But, the prolonged contact time results in a decline in the adsorption capacity. This behaviour may be explained to the availability of active sites on the MOF surface for dye molecule adsorption. However, further time, the occupation of the available active sites on the MOF surface is attained. There is no further dye uptake after the saturation of UiO-66(Zr) MOF [13, 17]. Initially, the orange SS dye is rapidly adsorbed, but the rate of removal gradually slows down over time. This phenomenon may be clarified by the abundance of vacant sites on the surface for dye adsorption initially. As dye molecules occupy these sites, the remaining vacant sites become harder to access owing to repulsion between dye molecules at the solid-liquid interface [18].

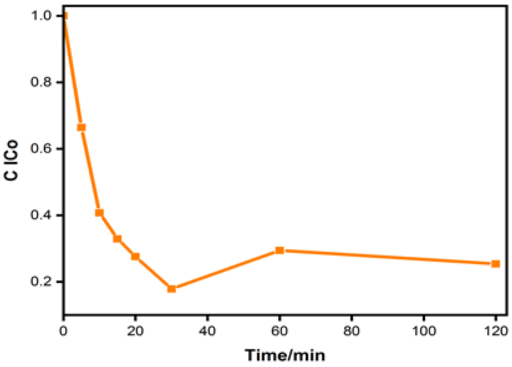

**Figure 2.** Influence of isotherm time of on the orange SS dye adsorption

*3.2.2. Effect of initial dye loading and contact time:* The adsorption capacity of orange SS dye on modified MOF were investigated by varying the initial dye loading of (100, 150, 200, and 300) mg/L at room temperature. The data, shown in Fig. 3(a), explore that an elevation in the initial dye loading of the orange SS dye solution is leading to higher adsorption capacity on the modified MOF adsorbent surface. The uptake of orange SS dye exhibits a nearly linear relationship with the initial concentration, suggesting an enhanced driving force due to the concentration gradient [17].

*3.2.3. Effect of pH of the dye solution:* Batch tests with a constant initial dye loading of 100 mg/L as well as an adsorbent dosage of 1 g/L were carried out, with the pH of the dye solution being varied from 3 to 9. This was done with pH to determine its influence. 30 minutes of adsorption was provided, and since to adjust the pH of dyed solution the diluted HCl and NaOH solutions were used. Figure 3b illustrates the data outlined above. It is shown that acidic conditions favour modification MOF adsorbents because they adsorb more dyes compared to that of the rise in the pH. Orange SS dye's ability to bind readily to the active sites, and the fact that it diffuses faster than GS SS dye; these are the major reasons for its higher adsorption at low pH. In the same experiment Dutta et al. also gained the same data [19].

*3.2.4. Effect of the dose of adsorbent quantity:* By altering the adsorbent dosage from 0.5 to 4 g/L, the influence of the quantity on orange SS adsorption was investigated. The study aimed to determine the minimum amount of adsorbent that would result in maximum adsorption. The adsorptive behavior of the modified MOF was examined at a constant dye concentration of 100 ppm and pH 3. The consequences in Fig. 3**c** demonstrate that the dye removal efficiency of the modified MOF increases with an enhance in the amount of adsorbent from 0.5 to 1 g/L. This may be ascribed to the increased number of available sites for adsorption as the adsorbent concentration increases [20].

*3.2.5. Thermal effect:* The influence of heat on the elimination of orange SS dye was investigated over a temperature range of 40 to70°C. The results, as presented in Fig. 3d, indicate that the adsorption capacity of the dye decreases with higher temperatures. This behavior may be attributed to the exothermic type of the sorption process, resulting in a higher desorption stage. Furthermore, elevated temperature impairs the adsorptive forces among the active sites on the MOF adsorbent as well as the dye molecules, as well as among neighboring orange SS dye species on the adsorbed phase [20].

### *3.3. Desorption and reusability*

The sustainability test of the used MOF material is checked through its reusability and the results is displayed in Fig. 4. After adsorbing of orange SS dye from its aqueous solution, the modified MOF adsorbent was rinsed with distilled water and subsequently dehydrated in a hot-air oven at 40 °C. This cleaned adsorbent was then utilized once again for the elimination of orange SS dye from aqueous solutions within a 30-minute duration. Orange SS dyes in filtrates subsequent each round was quantified by using UV-visible spectrophotometric analysis. The modified MOF adsorbent demonstrated recyclability for orange SS dye adsorption up to six cycles [15].

## 4. Conclusion

In the present exploration, a tailored MOF was effectively employed to eradicate orange SS dye from a water-based solution. The primary aim was to scrutinize the impact of distinct elements on the absorption mechanism. It was observed that the adsorption proved to be exothermic, indicating a predilection for ambient temperature (25°C). Furthermore, the uptake efficacy was noted to be heightened under acidic conditions (pH 3) as opposed to alternative pH states at a pollutant load of 100 mg/L. Notably, the achieved adsorption capacity of 2062.175 mg/g confirmed the superiority of MOF on batch adsorption at 30 minutes with 1 g/L from MOF. Furthermore, through six consecutive cycles, 88% of the dye was effectively removed. These promising results highlight the efficacy of the improved adsorbent in achieving complete removal (100%) of orange SS dye, demonstrated its efficient performance.

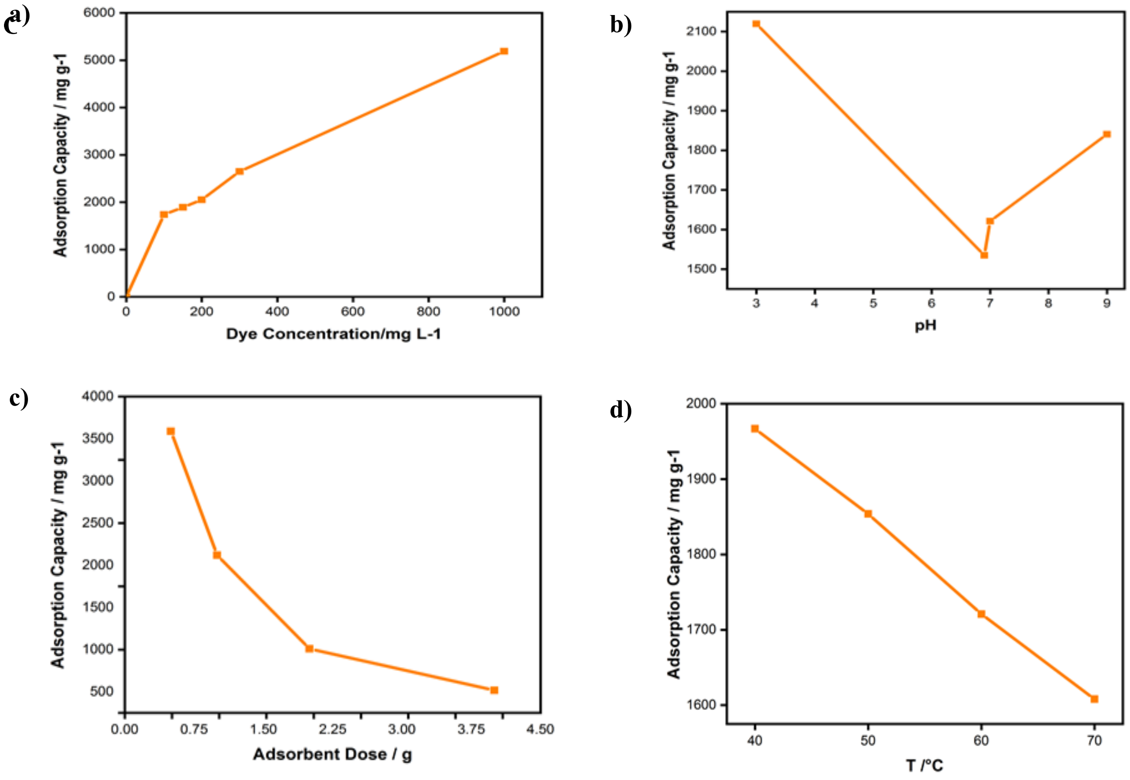

**Figure 3.** Effect of (a) initial dye concentrations (adsorbent dose 1 g/L; pH 6.9 and 298 K), (b) pH adsorbents (Orange SS 100 mg/L; adsorbent dose 1 g/L and 298 K), (c) adsorbent dose (Orange SS 100 mg/L; pH 3 and 298 K) and (d) temperature (Orange SS 100 mg L−1; pH 3 and adsorbent dose 1 g/L).

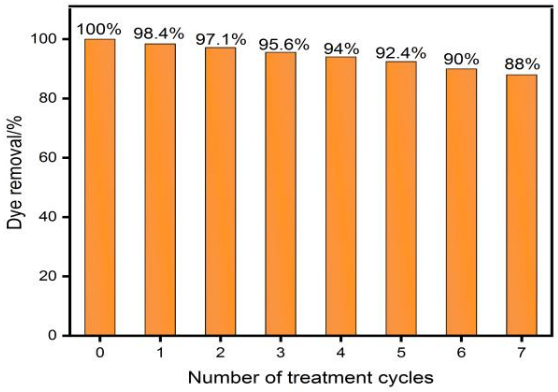

**Figure 4.** Reusability of modified MOF for adsorption of orange SS dye.

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