Taylor & Francis
Taylor & Francis Group

International Journal of Environmental Analytical Chemistry

ISSN: 0306-7319 (Print) 1029-0397 (Online) Journal homepage: https://www.tandfonline.com/loi/geac20

High adsorption of methylene blue from aqueous solutions using leaf-shaped ZIF-8

Abdolazim Alinejad, Shahram Sadeghi, Mansour Ghaderpoori, Soleyman Sahebi, Afshin Ghaderpoury, Ali Akbar Mohammadi, Mohammad Hossien Saghi, Yousef Gholampour & Ali Khani Jeihooni

To cite this article: Abdolazim Alinejad, Shahram Sadeghi, Mansour Ghaderpoori, Soleyman Sahebi, Afshin Ghaderpoury, Ali Akbar Mohammadi, Mohammad Hossien Saghi, Yousef Gholampour & Ali Khani Jeihooni (2019): High adsorption of methylene blue from aqueous solutions using leaf-shaped ZIF-8, International Journal of Environmental Analytical Chemistry, DOI: 10.1080/03067319.2019.1702170

To link to this article: https://doi.org/10.1080/03067319.2019.1702170

Published online: 20 Dec 2019.

INTERNATIONAL JOURNAL OF ENVIRONMENTAL ANALYTICAL CHEMISTRY
https://doi.org/10.1080/03067319.2019.1702170

ARTICLE

High adsorption of methylene blue from aqueous solutions using leaf-shaped ZIF-8

Abdolazim Alinejad[a], Shahram Sadeghi[b], Mansour Ghaderpoori[c,d], Soleyman Sahebi[e,f], Afshin Ghaderpoury[g], Ali Akbar Mohammadi[h], Mohammad Hossien Saghi[i], Yousef Gholampour[j] and Ali Khani Jeihooni[k]

[a]Department of Public Health, Fasa University of Medical Sciences, Fasa, Iran; [b]Environmental Health Research Center, Research Institute for Health Development, Kurdistan University of Medical Sciences, Sanandaj, Iran; [c]Department of Environmental Health Engineering, School of Health and Nutrition, Lorestan University of Medical Sciences, Khorramabad, Iran; [d]Nutrition Health Research Center, Lorestan University of Medical Sciences, Khorramabad, Iran; [e]Department for Management of Science and Technology Development, Ton Duc Thang University, Ho Chi Minh City, Vietnam; [f]Faculty of Environment and Labour Safety, Ton Duc Thang University, Ho Chi Minh City, Vietnam; [g]Student Research Committee, Department of Environmental Health Engineering, Shahid Beheshti University of Medical Sciences, Tehran, Iran; [h]Department of Environmental Health Engineering, Neyshabur University of Medical Sciences, Neyshabur, Iran; [i]Student Research Committee, Sabzevar University of Medical Sciences, Sabzevar, Iran; [j]Department of Internal Medicine, School of Medicine, Fasa University of Medical Sciences, Fasa, Iran; [k]Department of Public Health, School of Health, Fasa University of Medical Sciences, Fasa, Iran

ABSTRACT
Dyes are one of the most important environmental pollutants that have a significant impact on the environment, especially water resources. Dyes are toxic compounds that have severe effects on the environment. Methylene blue dye (MBD) causes problems like nausea, profuse sweating, vomiting, mental confusion, and methemoglobinemia. In this study, ZIF-8 with leaf-shaped morphology was used for MBD adsorption. All experiments were performed in batch conditions. The Leaf-shaped ZIF-8 is obtained at the molar ratio of 2-methylimidazole/Zn = 8. The prepared leaf-shaped ZIF-8 was white powder. The as-synthesis adsorbent is in the form of the leaves of a tree. The thickness of Leaf-shaped ZIF-8 is about 6–98 nm. Alkaline conditions were much more favourable than acidic to MBD adsorption. By increasing the dosage of Leaf-shaped ZIF-8, MBD adsorption increased until reaching an equilibrium dose at 0.5 g/L. the kinetic model of pseudo-first-order and the isotherm model of Langmuir have the highest coefficient of determination (R-square). Based on the Langmuir model, the maximum capacity of MBD adsorption on the Leaf-shaped ZIF-8 was 205 mg/g. In this study, the R_L was less than one which indicates MBD adsorption is favourable. Also, based on the Freundlich model, 1/n was 0.26, favourable adsorption condition was favourable.

ARTICLE HISTORY
Received 17 October 2019
Accepted 24 November 2019

KEYWORDS
Methylene blue; leaf-shaped ZIF-8; metal-organic frameworks; zeolitic imidazolate frameworks

1. Introduction

Dyes are one of the most important environmental pollutants that have a significant impact on the environment, especially water resources [1–3]. Because of the increasing population and increasing demand, new colours are being introduced to the

CONTACT Soleyman Sahebi soleyman.sahebi@tdtu.edu.vn

environment. Estimates show that there are more than 100,000 commercial dyes (and are growing in number) and produce approximately 700,000 tons per year [4]. Textile industries are one of the most important sources that significant amounts of coloured effluents into the environment [4–6]. Industries such as textiles have always had problems with the removal of dye and organic matter. These industries are important industries in the field of diversity in raw material consumption and high pollution load. Dyes are toxic compounds which have severe effects on the environment, plants, and animals such as reduce light transmission in water, reduce dissolved oxygen (DO) levels, and increase chemical oxygen demand (COD) [4,7]. Dyes are detectable even at very low concentrations (less than 1 mg/L) in water and have undesirable effects [4]. Without adequate and proper treatment, these compounds are able to persist in the environment for a very long time [3,8]. One of the colours widely used in the textile industry, leather, paper, and plastic industries that can eventually enter the environment through manufacturing wastewater is methylene blue [3,9,10].

Methylene blue dye (MBD) is one of the most important compounds used for dying silk, wood, and cotton [4]. The MBD is a polycyclic aromatic compound (PAC). The aromatic methylene blue portion contains sulphur and nitrogen atoms. In the aromatic unit, the dimethylamine group ($(CH_3)_2NH$ or C_2H_7N) is attached to it. The dimensions of the methylene blue molecule in length, width and thickness are 16.9, 7.4, and 3.8 angstrom (Å), respectively. The previous studies show that MBD can cause eye burns which may be responsible for permanent injury to the eyes of humans and animals [4,11]. If inhaled, this dye can cause breathing problems quickly. It also causes problems like nausea, profuse sweating, vomiting, mental confusion, and methemoglobinemia (MetHb), If MBD is eaten [4].

The main methods used to remove these compounds are photo-catalytic degradation [12–14], Sono-chemical process [15], adsorption [3,16], H_2O_2 [17], TiO_2 [18], biological [19], photo-Fenton oxidation [20], and electro-Fenton degradation [21]. Different physical, chemical, and biological methods have been used to remove dyes. Each of these methods has its advantages and disadvantages. These methods may be costly, produce secondary pollutants, may not be able to purify large volumes of effluent or have high efficiencies to remove dye. Among the methods, the adsorption processes have received more attention. The most important advantages of the adsorption process are economical, not sensitive to contaminants, and easy to use which gives these advantages more attention [8,22]. Before now, the previous studies show that different adsorbents have been used to remove MBD like mesoporous carbon [9], biopolymer oak sawdust composite [23], activated carbon and water hyacinth [24], waste cotton-activated carbon [25], can papyrus [26], natural Illitic clay [10], zeolite material [27], modified pumice stone [28], carbon nanotubes [29], NaOH-modified dead leaves [30], blast furnace sludge [31], bentonite [32], wool fibre and cotton fibre [33], etc.

Metal-organic frameworks (MOFs) are a new class of porous compounds that have significant properties compared to conventional adsorbents [34,35]. These features include very high surface area (up to 12,000 m^2/g), large pore volume, tunable pore structures, adjustable size by temperature changes, high crystallinity, and designable organic ligands [36–38]. Actually, MOFs are a new class of porous compounds composed of two-part of organic (as linker) and inorganic (as metalcore) [39]. Environmental researchers have used this category of emerging adsorbents to remove environmental pollutants [40] and have so far used various pollutants such as p-nitrophenol (HKUST-1) [41], fluoride (Uio-66) [34,42], diethyl phthalate and phthalic acid (ZIF-8) [43], Arsenate (ZIF-8, MIL-53 and F-BTC) [44–47], etc. These compounds have also been used as catalysts in advanced oxidation processes (AOPs) process (MIL-100 (Fe), MIL-53, and Fe^{II}@MIL-100(Fe) [48,49]. So far, several MOFs are used to adsorption of various dyes such as magnetic $CU_3(BTC)_2$ [50,51], MIL-125 (Ti) [52], MOF (Co/Ni) [1], Fe (BTC) [53], iron terephthalate (MOF-235) [54], MIL-100 (Fe) [37]. Zeolite imidazole frameworks (ZIFs) are a subclass of MOFs with topologies of zeolite or zeolite-like [47,55]. Among deferent ZIFs, ZIF-8 is the most extensively studied, which is a tetrahedral structure formed by zinc (Zn) ions and imidazole ligands with sodality topology [38]. ZIF-8 itself has three different morphologies: cubic, dodecahedral, and leaf-shaped [35,47]. The production of different morphologies of this compound is strongly dependent on the reaction conditions during its synthesis. The innovation of this work was to use porous adsorbent of the ZIF-8 with leaf-shaped morphology (Leaf-shaped-ZIF-8), to enhance its adsorption performance towards MBD. There is no research on the use of Leaf-shaped ZIF-8 (LZIF-8) in the MBD adsorption from textile effluents. So, the aim of this work was to synthesis leaf-shaped ZIF-8 and use it to MBD adsorption. Also, Organic dyes (OD) are one of the most important dyes widely used in the industry. MBD is usually used as an indicator dye for this group. The choice of MBD was because it is an indicator of organic dyes and if the dye was removed by the selective adsorbent (Leaf-shaped ZIF-8), other organic dyes would be removed as well. Also, it was also introduced to remove organic dyes from industrial wastewater.

2. Materials and methods

2.1. Used materials

2-methylimidazole or 2-Hmim (with the chemical formula $CH_3C_3H_2N_2H$), zinc nitrate hexahydrate (with the chemical formula Zn $(NO_3)_2.6H_2O$), methanol (with the chemical formula CH_3 OH) sodium hydroxide (with the chemical NaOH), sulphuric acid (with the chemical H_2SO_4), methylene blue (with the chemical $C_{16}H_{18}N_3ClS$) were supplied by Sigma-Aldrich and Merck Co. All chemicals were used in the experiments without further purification. All solvents and reagents were used as received from commercial suppliers without further purification.

2.2. Preparation of leaf-shaped ZIF-8

Leaf-shaped ZIF-8 was synthesis by reported procedure [35]. Zn $(NO_3)_2 \cdot 6H_2O$ (1.18 g) and 2-methylimidazole (2.60 g) were dissolved in deionised water (80 mL), respectively. The two solutions, also, were mixed under magnetic stirring for 4 h. The final products, white powder, were collected by centrifugation (5000 rpm, 1 min) and washed with double distilled water (also abbreviated ddH_2O) five times. The obtained products were dried in an oven (at 60 ◦C for 24 h). Finally, the obtained products kept in a polyethylene (PE) bottle for the next use.

2.3. Analytical methods and MBD adsorption experiments

The synthesised Leaf-shaped ZIF-8 was characterised by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX) spectroscopy and Brunauer-Emmett-Teller (BET) surface area and total pore volumes of the samples were determined from N_2 adsorption isotherms at 77 K. All experiments were performed MBD adsorption by Leaf-shaped ZIF-8 in batch conditions. According to the literature review, the most important variables affecting the dye adsorption process over an adsorbent were pH, initial dye concentration, contact time, and adsorbent dose. In this study, all the factors affecting the adsorption process were kept constant and only one variable was changed at each stage, then its effect was evaluated to achieve the best conditions. The performance of each variable in this method must be independent of the other and not affect each other. To prepare different concentrations of dye, a stock MBD solution (1000 mg/L) was prepared. To prepare the stock solution, 1 g of pure MBD was dissolved in one litre of ddH_2O.

All experiments were performed in a fixed solution volume (100 mL). The solution pH of MBD was adjusted using NaOH and H_2SO_4 (0.1 N). After experiments of MBD adsorption, the used adsorbent was separated from solution by centrifugation procedure (5,000 rpm, 1 min). Then, the concentration of the residual MBD was determined by ultraviolet–visible spectroscopy (UV/Vis spectrophotometer) (λ = 624 nm) [56]. The calibration curve was prepared to measure initial and residual MBD concentration. For calibration curves, concentrations of 5, 10, 15, 20, 25, and 30 mg/L were used (R^2 = 0.9997). All the adsorption experiments were done at laboratory temperature [57]. Finally, the amount of adsorbed MBD on the leaf-shaped ZIF-8 and the removal efficiency was calculated according to Equations (1) and (2), respectively [58,59]:

$$q_e = \frac{V(C_o - C_e)}{m} \tag{1}$$

$$R, \% = \frac{(C_0 - C_t)}{C_0} \tag{2}$$

where C_o and C_e are the initial and final concentration of MBD in solution (mg/L), respectively. V and m are the volume of MBD solution (mL) and the leaf-shaped ZIF-8 weight (g), respectively. Also, C_o and C_t represent the initial and final concentration of MBD (mg/L), respectively. All experiments were repeated three times and the results were reported as the mean and standard deviation (mean ± SD)

3. Results and discussion

3.1. Characterisation of leaf-shaped ZIF-8

The prepared leaf-shaped ZIF-8 was white powder. The crystal structure of prepared leaf-shaped ZIF-8 was studied by XRD. The XRD pattern of the prepared leaf-shaped ZIF-8 presents Figure 1. The XRD spectrum is very consistent with the spectrum presented in Liu et al. [35]. The XRD spectrum presented for leaf-shaped morphology is different from the spectra of cubic [47] and dodecahedral [60] morphology. The main cause of this difference is attributed to the magnitude of its differences compared to other morphologies. Liu et al. reported Leaf-shaped ZIF-8 is obtained at the molar ratio of 2-methylimidazole/Zn = 8, which this ratio is the key factor to make a unique structure [35,61]. If this ratio is greater than 35, ZIF-8 will be formed by dodecahedral morphology (dodecahedral-ZIF-8). Also, if this ratio is equal to 2, ZIF-8 will be formed by cubic morphology (cubic-ZIF-8). Figure 2(a,

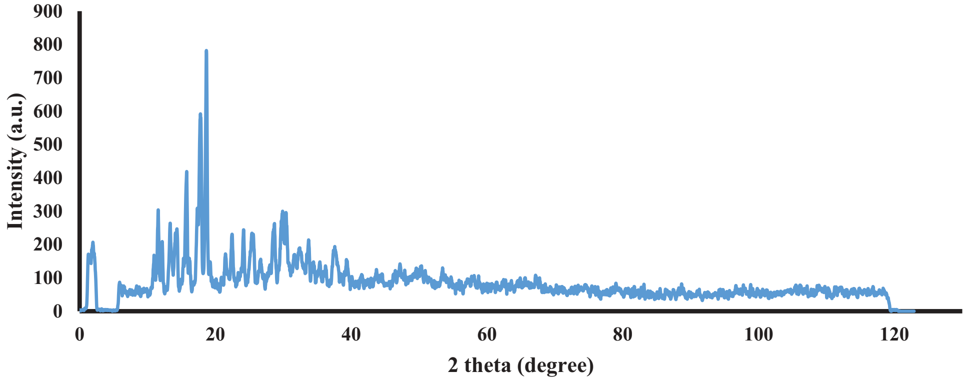

Figure 1. XRD pattern of prepared Leaf-shaped ZIF-8.

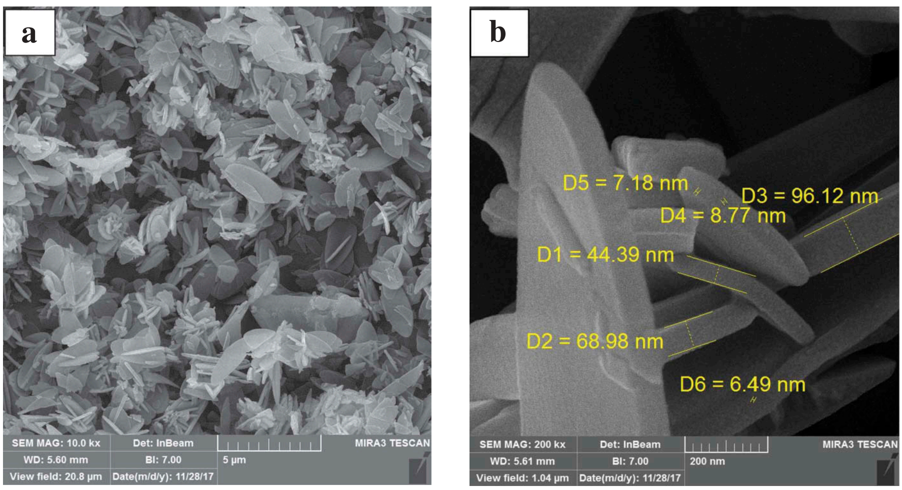

Figure 2. Field Emission-SEM image of prepared Leaf-shaped ZIF-8.

b) present the FESEM morphology of Leaf-shaped ZIF-8. Based on Figure 2(a), the as-synthesis adsorbent is in the form of the leaves of a tree. The same morphology was the reason why it was named. According to Figure 2(b), Leaf-shaped ZIF-8 is large in size (more than several microns) but slightly thick. The thickness of Leaf-shaped ZIF-8 is about 6 nm to 98 nm. Liu et al. reported synthesis of the Leaf-shaped ZIF-8 have very large dimension, but its thickness was only 150 nm [35]. Based on Figure 2(b), it is clear that the Leaf-shaped ZIF-8 has a significant number of heterogeneous pores, morphology of uneven and rough surface, where there is a good possibility for MBD adsorption [62]. Nitrogen (N_2) adsorption-desorption isotherms of the Leaf-shaped ZIF-8 were explored to analyse the specific surface area and the pore structure. N_2 desorption-adsorption curve for the Leaf-shaped ZIF-8 is an almost straight line indicating low N_2 adsorption quantities and poor pore structure [35]. These results might because of the bigger size and higher density (Figure 2(a,b)). Based on BET, the surface area and pore volume of leaf-shaped ZIF-8 was 20 m^2/g and 0.16 cm^3/g. If one examines the literature, it can be concluded that this surface area is very low compared to other morphologies. Liu et al. reported the surface area of leaf-shaped ZIF-8, cubic ZIF-8, and dodecahedral ZIF-8 are of 12.7, 958.4, and 1151.2 m^2/g, respectively [35]. One of the important results of this study was that the BET surface area of morphology (leaf-shaped) is lower than others (cubic and dodecahedral), which is because of the large size of this species compared to other species.

3.2. Influence of operation parameters on the efficiency of the adsorption process

pH variations in a solution can affect the distribution of the charge on the adsorbent and the solution, which can have a significant effect on the MBD adsorption. pH changes the surface charge of adsorbent and the degree of ionisation of the target pollutants [51,52,63]. In other words, the soluble pH will have a great influence on the adsorption performance [64,65]. In the present study, MBD adsorption by Leaf-shaped ZIF-8 was studied at different pH and at the laboratory temperature. To study the effect of pH on MBD adsorption, the different pH were used in the range of 3–11. To better understand the effect of pH on the performance of the adsorption process, first, the isoelectric point (pH_{IEP}) was determined. pH_{IEP} was nine (9) for leaf-shaped ZIF-8. The concept of pH_{IEP} is that at a higher and lower pH this point (pH_{IEP} = 9), the adsorbent surface is negative and positive, respectively [5]. In the adsorption experiments, a 0.5 g of leaf-shaped ZIF-8 was added to 100 mL volume of MBD solution with an initial concentration of 50 mg/L. Figure 3 presents MBD adsorption at different pH. As seen in Figure 3, by increasing solution pH, from 3 to 11, MBD adsorption increased. In solution pH of 3 and 11, the removal efficiency of MBD was 40% and 94%, respectively. The q_e also increased with increasing solution pH. In solution pH of 3 and 11, the q_e for MBD adsorption was 100 mg/g and 200 mg/g, respectively. MBD is a cationic dye (Positive charge). At acidic pH (↓), the concentration of H^+ radicals is high, so, Leaf-shaped ZIF-8 surface charge is positive which, in turn, reduces the MBD adsorption. By increasing pH (↑), gradually the concentration of hydroxyl (OH°) radicals increased, so MBD adsorption on Leaf-shaped ZIF-8 increased [6,66]. It is reported that the adsorption reaction with cationic dyes is mainly through the interaction between hydrogen bonds and Van der Waals forces [67]. Jian et al. have also reported that at acidic pH, ZIF-8 is an unstable compound. Therefore, the efficiency of this compound in the removal of pollutants can be significantly reduced [38]. In 2019, Khoshnamvand et al. used

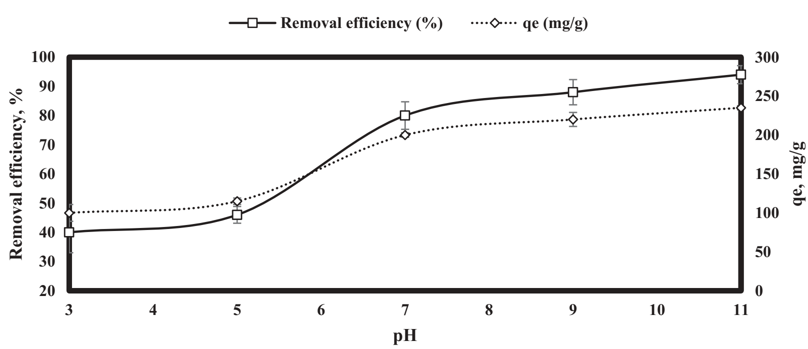

Figure 3. The effect of solution pH over MBD adsorption by Leaf-shaped ZIF-8 (Contact time = 30 min, initial MBD concentration = 50 mg/L, adsorbent dosage = 0.4 g/L).

Zeolitic Imidazole Framework-8 to remove malachite green dye [68]. Pavan et al. reported that by increasing the solution pH to 12, the MBD removal efficiency increased by up to 96% [69]. The reason for the increase in removal efficiency with increasing solution pH in cationic base dyes (like MBD) is shown in Equations (3) and (4) [62]:

$$S - OH + OH^{-} \Rightarrow SO^{-} + H_2O \tag{3}$$

$$SO^{-} + Dye^{+}(\text{like MBD}) \Rightarrow S - O - Dye \tag{4}$$

The results of the study showed that the removal of this dye in alkaline conditions is better than acidic. In Lin et al. study, the adsorption of the methylene blue dye increased with increasing pH [51]. As mentioned earlier, pH_{IEP} of Leaf-shaped ZIF-8 was equal to 9. As a result, at solution pH above this point, MBD adsorption over Leaf-shaped ZIF-8 was favourable. At higher pH, the adsorbent surface becomes negatively charged, which increases the electrostatic force between the MBD cation and the adsorbent surface. Maximum MBD adsorption has been achieved at pH = 11. Because the MBD removal efficiency was not significantly different at pH 9 to 11, pH = 9 was chosen for the next experiments. Mohammadi et al. used Uio-66 to adsorption of the methylene blue dye from aqueous solutions [67]. The maximum adsorption of this dye was reported to be 91 mg/g.

To investigate the effect of MBD concentration changes, the concentration of 20 mg/L to 150 mg/L at the contact time of 45 min was used. Figure 4 presents the effect of initial concentration on MBD adsorption over Leaf-shaped ZIF-8. As seen in Figure 4, by increasing solution pH, from 3 to 11, MBD adsorption increased. In 2014, García et al. used Iron-Benzenetricarboxylate to adsorption of azo-dye orange II. In lower MBD concentration, MBD molecules are adsorbed on the Uio-66 adsorbent surface, rapidly, but with the increasing of MBD concentration, gradually Uio-66 surface becomes saturated. Finally, the adsorption decreased because of the repulsion among MBD molecules [53].

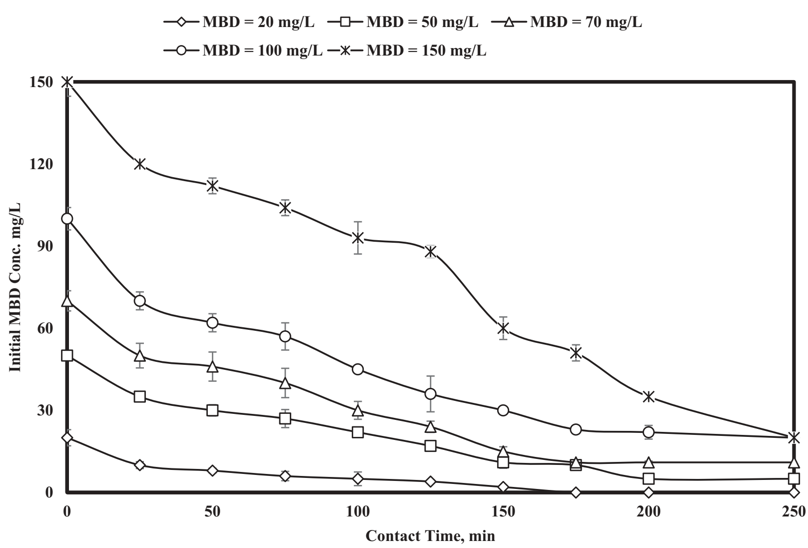

Figure 4. The effect of initial MBD concentration vs. contact time over MBD adsorption by Leaf-shaped ZIF-8 (pH = 9, adsorbent dosage = 0.4 g/L).

Figure 4 demonstrates the more rates of MBD adsorption were observed at the beginning. The MBD adsorption rate may be more for an increase in the number of vacant sites initially available. As a result, the concentration gradient between MBD in the solution and that at the sorbent surface increased. At this time, the concentration gradient is decreased owing to the dye molecules adsorption onto the vacant sites, leading to decreased MBD adsorption during the next steps. The removal MBD by adsorption on Leaf-shaped ZIF-8 was found to increase with contact time and attained a maximum capacity at 150 min (Figure 4). With changing the initial MBD concentration in solution from 20 mg/L to 150 mg/L, the concentration of dye adsorbed increased from 15 mg/g to 170 mg/g and removal efficiency decreased from 85% to 45%. This phenomenon is because of the fact that at lower concentrations almost all the dye molecules were adsorbed very rapidly on the outer surface of the adsorbent, but further increase in initial dye concentrations led to quick saturation, and thus most of the dye adsorption took place slowly inside the pores [62].

Another parameter which has a great impact on the performance of the adsorption process is the adsorbent dosage. Figure 5 presents the effect of changes on Leaf-shaped ZIF-8 dosage to MBD adsorption. As seen in Figure 5, by increasing the dosage of Leaf-shaped ZIF-8, MBD adsorption increased until reaching an equilibrium dose at 0.5 g/L. Further, by increasing the adsorbent dosage (from 0.5 g/L to 0.9 g/L), the MBD adsorption rate is not significant. At first, the MBD adsorption increases with increasing adsorbent dosage and this is natural because the active sites for adsorption increase. After adding adsorbent more than 0.5 g/L, there is little change in adsorption efficiency and the main cause is the saturation of the active sites on adsorbent. q_e in dosages of 0.5 g/L, 0.7 g/L, and 0.5 g/L was 112.5 mg/g, 115 mg/g, and 117.5 mg/g, respectively. Other findings by the researchers show that at a constant concentration of a pollutant, initially, as the adsorbent dosage increases, the adsorption rate increases. Up to the optimum dosage, this increase in adsorption continues. This increase in adsorption has many reasons, such as high adsorbent surface and availability of more adsorption sites [47,67,70]. At a higher

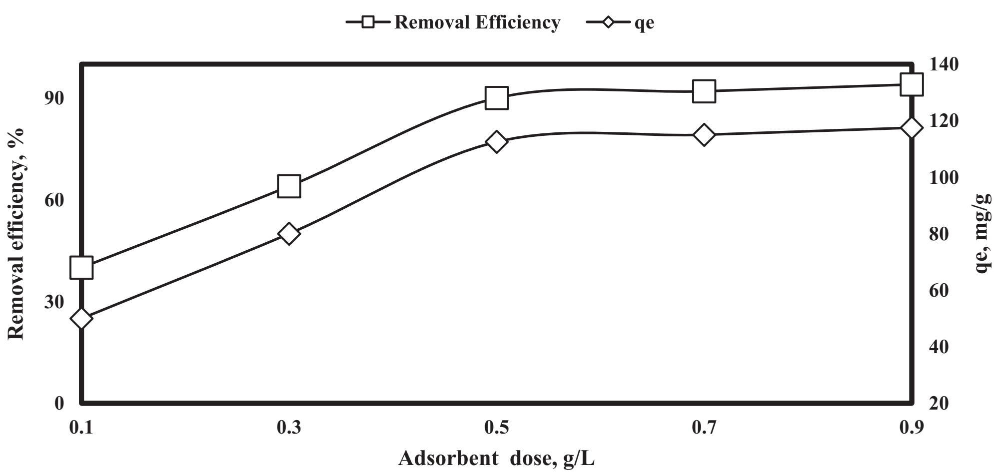

Figure 5. The effect of dose changes on Leaf-shaped ZIF-8 to MBD adsorption.

dose than optimum (0.5 g/L) by increasing Leaf-shaped ZIF-8, MBD adsorption capacity on adsorbent was almost constant (minor increase or decrease). The main reason for the phenomenon may be because of overlapping or aggregation of adsorption active sites of adsorbent which finally can lead to decrease in total surface area [70,71]. As a result, the optimum dosage of Leaf-shaped ZIF-8 to MBD adsorption was 0.5 g/L.

4. Kinetics and isotherms of MBD adsorption

Kinetic models, like pseudo-first-order and pseudo-second-order kinetic, used to investigate the adsorption mechanism of MBD on Leaf-shaped ZIF-8 [66,72]. The pseudo-first and pseudo-second-order kinetic model are expressed as Equations (5) and (6), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{6}$$

where q_e and q_t are the MBD adsorption on the Leaf-shaped ZIF-8 at equilibrium and at any contact time (min) of adsorption t, respectively. The k_1 and k_2 are the rate constant (1/min) and the constant of pseudo-second-order sorption of MBD (g/mg. min), respectively. k_1 and q_e are calculated from the slope and intercept of the linear plots of log (q_e-q_t) vs. contact time, respectively. Also, k_2 and q_e are obtained from the slope and intercept of the linear plots of log (q_e-q_t) vs. contact time, respectively [73]. To do kinetic, 0.5 g of the adsorbent was added to 100 mL of solution at initial MBD concentration of 10 to 50 mg/L. In other words, kinetic and isotherm experiments were performed under the optimal conditions of the variables (pH, contact time, initial concentration, and adsorbent dosage). Table 1 shows the calculated kinetic parameters of kinetics and isotherms model. Based on Table 1, pseudo-first-order kinetic model has the highest coefficient of determination (R-square or R^2). As a result, the kinetic model of pseudo-second-order reaction was a fit model to describe the MBD adsorption over the Leaf-shaped ZIF-8. The results showed that MBD adsorption on the Leaf-shaped ZIF-8 was very fast and more than 90% of the equilibrium adsorption capacity was achieved in the first 45 min. The equilibrium time of the Leaf-shaped ZIF-8 for MBD adsorption was approximately 3 h.

The adsorption isotherms used to study the MBD adsorption and adsorption mechanisms over the Leaf-shaped ZIF-8. In other words, adsorption isotherms are important for the description of how adsorbate (MBD) molecules of reacting with adsorbent surface (Leaf-shaped ZIF-8) [74]. The MBD adsorption over the adsorbent was investigated for five concentration (20, 50, 70, 100, and 150 mg/L), at various contact times (30–250 min) at the laboratory temperature and stirring speed of 250 rpm, respectively. To calculate adsorption isotherms, the equilibrium data of Leaf-shaped ZIF-8 was fitted to the isotherms of Langmuir and Freundlich. The linear isotherm of Langmuir and Freundlich are expressed in Equations (7) and (8) [75–77]:

$$\log qe = \frac{1}{n}\log C_e + \log K_f \tag{7}$$

$$\frac{C_e}{q} = \frac{1}{q_\circ b} + \frac{C_e}{q_e} \tag{8}$$

where q_e and C_e are the amounts of MBD adsorbed at equilibrium (mg/g) and the equilibrium concentration of MBD in solution (mg/L), respectively. n and K_f are the Freundlich constants. 1/n and K_F are the Freundlich constants referring to adsorption intensity or surface heterogeneity and adsorption capacity, respectively. In this study, 1/n was equal to 0.26. If the ratio is in the range of 0.1 to 1, favourable adsorption condition is favourable [51,78]. q_o is the Langmuir monolayer adsorption capacity and b is the Langmuir constant (l/g). Table 1 shows the calculated isotherm parameters. As seen in Table 1, the isotherm model Langmuir has the highest coefficient of determination. As a result, the isotherm model of Langmuir was fit model to describe the MBD adsorption over the Leaf-shaped ZIF-8. Based on the Langmuir model, the maximum capacity of MBD adsorption on the Leaf-shaped ZIF-8 was 205 mg/g. b is Langmuir constant. b, in other words, depends on the adsorption energy. This constant is used to estimate separation factor or equilibrium parameter (R_L). The R_L determined (R_L = 1)/(1 + b.C_o) the adsorption nature: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [79]. In this study, the value of R_L was less than one which indicates the MBD adsorption on the Leaf-shaped ZIF-8 is favourable. Table 2 presents a comparison of the adsorption MBD capacity on the Leaf-shaped ZIF-8 with other adsorbents. As seen in Table 2, the adsorption MBD capacity on the Leaf-shaped ZIF-8 is significantly higher than that of other adsorbents. If the adsorption capacity in some adsorbents was more reported it was because the initial concentration was not the same for comparison. In two separate studies, Haque et al. used two adsorbents MIL-101 and amino-MIL-101 (Al), which the adsorption capacity of the two adsorbents reported 21 mg/g and 380 mg/g, respectively [80,81]. Haque et al. have used the amine group to increase the adsorption capacity and the adsorption capacity has been greatly expanded (from 27 mg/g to 380 mg/g). Therefore, one of the suggested methods for future studies is to use the amine group to enhance the adsorption capacity of the Leaf-shaped ZIF-8 for MBD.

5. Conclusions

All experiments were performed MBD adsorption by Leaf-shaped ZIF-8 in the batch conditions. The most important variables affecting the dye adsorption process over an adsorbent were pH, initial dye concentration, contact time, and adsorbent dose. The concentration of the residual MBD was determined by the DR-5000 spectrophotometer. The prepared leaf-shaped ZIF-8 was white powder. The thickness of Leaf-shaped ZIF-8 is about 6 nm to 98 nm. Nitrogen desorption-adsorption curve for the Leaf-shaped ZIF-8 is

Table 1. Calculated constants of kinetic and isotherm for the MBD adsorption the Leaf-shaped ZIF-8.

	pseudo-second-order			pseudo-first-order		
Kinetics	$q_{e(mg\ g^{-1})}$	k_1	R^2	$q_{e(mg\ g^{-1})}$	k_2	R^2
	60.45	0.0345	0.9886	71.34	0.0156	0.775
	Freundlich			Langmuir		
Isotherms	n	K_f	R^2	$q_{m(mg\ g^{-1})}$	b	R^2
	3.8	16.5	0.665	205	5	0.898

Table 2. Comparison of the capacity adsorption of MBD on the Leaf-shaped ZIF-8 with other adsorbents.

The type of adsorbent	C_o (mg/L)	qe (mg/g)	Reference
Uio-66	20	91.1	[67]
Iron terephthalate (MOF-235)	30	100	[54]
MFCs or $Fe_3O_4/Cu_3(BTC)_2$	30	84	[50]
	300	245	
MIL-101	30	21	[80]
Amino-MIL-101(Al)	30	380	[81]
Leaf-shaped ZIF-8	50	205	the present study

an almost straight line indicating low N_2 adsorption quantities and poor pore structure. pH_{IEP} was observed 9 for leaf-shaped ZIF-8. By increasing solution pH, from 3 to 11, MBD adsorption increased. By increasing the dosage of Leaf-shaped ZIF-8, MBD adsorption increased until reaching an equilibrium dose. According to the coefficient of determination, the kinetic model of pseudo-first-order reaction was a fit model to describe the MBD adsorption over the Leaf-shaped ZIF-8. Also, the isotherm model of Langmuir was fit model to describe the MBD adsorption.

Acknowledgments

The authors of this project thanks Fasa University of Medical Sciences to support (grant NO. 97217)

Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Soleyman Sahebi http://orcid.org/0000-0002-5901-1084
Mohammad Hossien Saghi http://orcid.org/0000-0003-1802-7546

References

[1] A. Abbasi, M. Soleimani, M. Najafi and S. Geranmayeh, Inorg. Chim. Acta **439**, 18 (2016). doi:10.1016/j.ica.2015.09.028.
[2] A. Dehghan, A.A. Mohammadi, M. Yousefi, A.A. Najafpoor, M. Shams and S. Rezania, Nanomaterials **9**, 1422 (2019). doi:10.3390/nano9101422.
[3] M.A. Akbar, A. Abdolazim, K. Bahram, J. Safora, G. Afshin, A. Mohammad and G. Mansour, Int. J. Environ. Sci. Technol. **14**, 1959 (2017). doi:10.1007/s13762-017-1289-z.
[4] M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, J. Hazard. Mater. **177** (70), 70 (2010). doi:10.1016/j.jhazmat.2009.12.047.
[5] M. Yousefi, R. Nabizadeh, M. Alimohammadi, A.A. Mohammadi and A.H. Mahvi, Desalin. Water Treat. **158**, 209 (2019).
[6] C.-H. Weng and Y.-F. Pan, J. Hazard. Mater. **144**, 355 (2007). doi:10.1016/j.jhazmat.2006.09.097.
[7] A. Ayub, A.A. Mohammadi, M. Yousefi and F. Changani, Desalin. Water Treat. **142**, 293 (2019). doi:10.5004/dwt.2019.23455.

[8] S. Golmohammadi, M. Ahmadpour, A. Mohammadi, A. Alinejad, N. Mirzaei, M. Ghaderpoori and A. Ghaderpoori, Environ. Health Eng. Manage. J. **3**, 107 (2016). doi:10.15171/EHEM.2016.08.
[9] S. Álvarez-Torrellas, R. García-Lovera, A. Rodríguez and J. García, Chem. Eng. **43**, 2283 (2015).
[10] O. Amrhar, H. Nassali and M.S. Elyoubi, AMRHAR Mor. J. Chem. **3**, 582 (2015).
[11] V.K. Gupta, J. Environ. Manage. **90**, 2313 (2009). doi:10.1016/j.jenvman.2008.11.017.
[12] M.H. Ehrampoosh, S.G. Moussavi, M.T. Ghaneian, S. Rahimi and H. Fallah Zadeh, Toloo-e-behdasht **1**, 1 (2010).
[13] M.R. Sohrabi and M. Ghavami, J. Hazard. Mater. **153**, 1235 (2008). doi:10.1016/j.jhazmat.2007.09.114.
[14] B. Kamarehie, A. Jafari, M. Ghaderpoori, M. Amin Karami, K. Mousavi and A. Ghaderpoury, Chem. Eng. Commun. **206**, 898 (2019). doi:10.1080/00986445.2018.1537266.
[15] M. Abbasi and N.R. Asl, J. Hazard. Mater. **153**, 942 (2008). doi:10.1016/j.jhazmat.2007.09.045.
[16] S.A. Umoren, U.J. Etim, A.U. Israel and J. Mater, Environ. Sci. **4**, 75 (2013).
[17] H. Masoumbeigi and A. Rezaee, J. Health Policy Sustainable Health **2**, 160 (2015).
[18] M. Deilami and N. Fallah, Biol. Forum **7**, 490 (2015).
[19] M. Cheng, G. Zeng, D. Huang, C. Lai, Z. Wei, N. Li, P. Xu, C. Zhang, Y. Zhu and X. He, Appl. Microbiol. Biotechnol. **99**, 5247 (2015). doi:10.1007/s00253-014-6344-9.
[20] B. Gowtham and S. Pauline, Iranica J. Energy Environ. **6**, 255 (2015).
[21] G. Xia, Y. Lu, X. Gao, C. Gao and H. Xu, Clean Soil Air Water **42**, 1 (2014).
[22] M. Massoudinejad, M. Ghaderpoori and M. Rezazadeh, Int. J. Adv. Sci.Technol. **76**, 35 (2015). doi:10.14257/ijast.2015.76.05.
[23] M.M.A. El-Latif, A.M. Ibrahim and M.F. El-Kady, Am. J. Sci. **6**, 267 (2010).
[24] S.M. Kanawade and R.W. Gaikwad, Int. J. Chem. Eng. Appl. **2**, 317 (2011). doi:10.7763/IJCEA.2011.V2.126.
[25] E. Ekrami, F. Dadashian and M. Arami, Desalin. Water Treat. **57**, 7098 (2016). doi:10.1080/19443994.2015.1015173.
[26] U.A. Saed, M.H.A. Nahrain and A.A. Atshan, J. Babylon Univ. Eng. Sci. **22**, 218 (2014).
[27] D.A. Fungaro, L.C. Grosche, A.S. Pinheiro, J.C. Izidoro and S.I. Borrely, J. Chem. **2**, 235 (2010).
[28] Z. Derakhshan, M.A. Baghapour, M. Ranjbar and M. Faramarzian, Health Scope **2**, 136 (2013). doi:10.5812/jhealthscope.
[29] Z. Shahryari, A.S. Goharrizi and M. Azadi, Int. J. Water Res. Environ. Eng. **2**, 016 (2010).
[30] L. Gong, W. Sun and L. Kong, CWEEE **2**, 13 (2013). doi:10.4236/cweee.2013.22B003.
[31] J. Malina and A. Rađenović, Chem. Biochem. Eng. Q **28**, 491 (2014). doi:10.15255/CABEQ.2014.19366.
[32] S. Hong, C. Wen, J. He, F. Gan and Y.S. Ho, J. Hazard. Mater. **167**, 630 (2009). doi:10.1016/j.jhazmat.2009.01.014.
[33] A.R. Khan, H. Tahir, F. Uddin and U. Hameed, J. Appl. Sci. Environ. Manage. **9**, 29 (2005).
[34] M. Massoudinejad, A. Shahsavani, B. Kamarehie, A. Jafari, M. Ghaderpoori, M.M. Amini and A. Ghaderpoury, Fluoride **51**, 355 (2018).
[35] B. Liu, M. Jian, R. Liu, J. Yao and X. Zhang, Colloids Surf. A **481**, 358 (2015). doi:10.1016/j.colsurfa.2015.06.009.
[36] N. Bakhtiari and S. Azizian, J. Mol. Liq. **206**, 114 (2015). doi:10.1016/j.molliq.2015.02.009.
[37] S.H. Huo and X.P. Yan, J. Mater. Chem. **22**, 7449 (2012). doi:10.1039/c2jm16513a.
[38] M. Jian, B. Liu, G. Zhang, R. Liu and X. Zhang, Colloid Surf. A **465**, 67 (2015). doi:10.1016/j.colsurfa.2014.10.023.
[39] M.J. Katz, Z.J. Brown, Y.J. Colon, P.W. Siu, K.A. Scheidt, R.Q. Snurr, J.T. Hupp and O.K. Farha, Chem. Commun. **49**, 9449 (2013). doi:10.1039/c3cc46105j.
[40] A.A. Adeyemo, I.O. Adeoye and O.S. Bello, Toxicol. Environ. Chem. **94**, 1846 (2012). doi:10.1080/02772248.2012.744023.
[41] K.-Y.A. Lin and Y.-T. Hsieh, J. Taiwan Inst. Chem. E **50**, 223 (2014).
[42] M. Massoudinejad, M. Ghaderpoori, A. Shahsavani and M.M. Amini, J. Mol. Liq. **221**, 279 (2016). doi:10.1016/j.molliq.2016.05.087.

[43] N.A. Khan, B.K. Jung, Z. Hasan and S.H. Jhung, J. Hazard. Mater. **282**, 194 (2015). doi:10.1016/j.jhazmat.2014.03.047.
[44] J. Li, Y.N. Wu, Z. Li, B. Zhang, M. Zhu, X. Hu, Y. Zhang and F. Li, J. Phys. Chem. C **118**, 27382 (2014). doi:10.1021/jp508381m.
[45] T.A. Vu, G.H. Le, C.D. Dao, L.Q. Dang, K.T. Nguyen, Q.K. Nguyen, P.T. Dang, H.T.K. Tran, Q. T. Duong, T.V. Nguyen and G.D. Leed, R. Soc. Chem. **5**, 5261 (2015).
[46] B.J. Zhu, Y. Xin-Yao, Y. Jia, F.M. Peng, B. Sun, M.Y. Zhang, T. Luo, J.H. Liu and X.J. Huang, J. Phys. Chem. C **116**, 8601 (2012). doi:10.1021/jp212514a.
[47] M. Massoudinejad, M. Ghaderpoori, A. Shahsavani, A. Jafari, B. Kamarehie, A. Ghaderpoury and M.M. Amini, J. Mol. Liq. **255**, 263 (2018). doi:10.1016/j.molliq.2018.01.163.
[48] J.J. Du, Y.P. Yuan, J.X. Sun, F.M. Peng, X. Jiang, L.G. Qiu, A.J. Xie, Y.H. Shen and J.F. Zhu, J. Hazard. Mater. **190**, 945 (2011). doi:10.1016/j.jhazmat.2011.04.029.
[49] H. Lv, H. Zhao, T. Cao, L. Qian, Y. Wang and G. Zhao, J. Mol. Catal. A Chem. **400** (81), 81–89 (2015). doi:10.1016/j.molcata.2015.02.007.
[50] X. Zhao, S. Liu, Z. Tang, H. Niu, Y. Cai, W. Meng and F. Wu, J. P. Sci. Rep. UK **5,**1 (2015).
[51] S. Lin, Z. Song, G. Che, A. Ren, P. Li, C. Liu and J. Zhang, Micropor. Mesopor. Mat. **193**, 27 (2014). doi:10.1016/j.micromeso.2014.03.004.
[52] H. Guo, F. Lin, J. Chen, F. Li and W. Weng, Appl. Organomet. Chem. **29**, 12 (2015). doi:10.1002/aoc.v29.1.
[53] E.R. García, R.L. Medina, M.M. Lozano, I.H. Pérez, M.J. Valero and A.M.M. Franco, Materials **7**, 8037 (2014). doi:10.3390/ma7128037.
[54] E. Haque, J.W. Jun and S.H. Jhung, J. Hazard. Mater. **185**, 507 (2011). doi:10.1016/j.jhazmat.2010.09.035.
[55] K.-Y.A. Lin and H.-A. Chang, Water Air Soil Pollut. **226**, 10 (2015). doi:10.1007/s11270-014-2280-7.
[56] A.D. Eaton, L.S. Clesceri and E.W. Rice, *Standard Methods for the Examination of Water and Wastewater* (American Water Works Association, Washington, DC, 2005).
[57] H.M. Cai, G.J. Chen, C.Y. Peng, Z.Z. Zhang, Y.Y. Dong, G.Z. Shang, X.H. Zhu, H.J. Gao and X. C. Wan, Appl. Surf. Sci. **328**, 34 (2015). doi:10.1016/j.apsusc.2014.11.164.
[58] A.A. Mohammadi, A. Zarei, H. Alidadi, M. Afsharnia and M. Shams, Desalin. Water Treat. **129**, 244 (2018). doi:10.5004/dwt.2018.22813.
[59] R. Bhaumik, N.K. Mondal, S. Chattoraj and J.K. Datta, AJAC **4**, 404 (2013). doi:10.4236/ajac.2013.48051.
[60] B. Kamarehie, Z. Noraee, A. Jafari, M. Ghaderpoori, M.A. Karami and A. Ghaderpoury, Data in Brief **20**, 799 (2018). doi:10.1016/j.dib.2018.08.159.
[61] M. He, J. Yao, Q. Liu, K. Wang, F. Chen and H. Wang, Micropor. Mesopor. Mat. **184**, 55 (2014). doi:10.1016/j.micromeso.2013.10.003.
[62] T. Santhi, S. Manonmani, V. Vasantha and Y. Chang, Arab. J. Chem. **9**, S466 (2016). doi:10.1016/j.arabjc.2011.06.004.
[63] M. Qasemi, A. Zarei, M. Afsharnia, R. Salehi, M. Allahdadi and M. Farhang, Data in Brief **20**, 1115 (2018). doi:10.1016/j.dib.2018.08.163.
[64] Q. Qin, Q. Wang, D. Fu and J. Ma, Chem. Eng. J. **172**, 68 (2011). doi:10.1016/j.cej.2011.05.066.
[65] A. Dehghan, A. Zarei, J. Jaafari, M. Shams and A.M. Khaneghah, Chemosphere **217**, 250 (2019). doi:10.1016/j.chemosphere.2018.10.166.
[66] A. G¨urses, C. Do˘gar, M. Yalc¸ın, M. Ac¸ıkyıldız and R.B.S. Karaca, J. Hazard. Mater. **B131**, 217 (2006). doi:10.1016/j.jhazmat.2005.09.036.
[67] A.A. Mohammadi, A. Alinejad, B. Kamarehie, S. Javan, A. Ghaderpoury, M. Ahmadpour and M. Ghaderpoori, Int. J. Environ. Sci. Technol. **14**, 1959 (2017). doi:10.1007/s13762-017-1289-z.
[68] N. Khoshnamvand, A. Jafari, B. Kamarehie, A. Mohammadi and M. Faraji, Environ. Processes **6**, 757 (2019). doi:10.1007/s40710-019-00384-9.
[69] F.A. Pavan, A.C. Mazzocato and Y. Gushikem, Bioresour. Technol. **99**, 3162 (2008). doi:10.1016/j.biortech.2007.05.067.
[70] A. Maleki, B. Hayati, M. Naghizadeh and S.W. Joo, J. Ind. Eng. Chem. **28**, 211 (2015). doi:10.1016/j.jiec.2015.02.016.

[71] N. Zhang, X. Yang, X. Yu, Y. Jia, J. Wang, L. Kong, Z. Jin, B. Sun, T. Luo and J. Liu, Chem. Eng. J. **252**, 220 (2014). doi:10.1016/j.cej.2014.04.090.
[72] B. Kamarehie, A. Jafari, M. Ghaderpoori, M. Amin Karami, K. Mousavi and A. Ghaderpoury, Chem. Eng. Commun. **206**, 898 (2018). doi:10.1080/00986445.2018.1537266.
[73] M. Kragovi´c, A. Dakovi´c, M. Markovi´c, J. Krsti´c, G.D. Gatta and N. Rotiroti, Appl. Surf. Sci. **283**, 764 (2013). doi:10.1016/j.apsusc.2013.07.016.
[74] Y. Bulut and H. Karaer, J. Dispersion Sci. Technol. **36**, 61 (2015). doi:10.1080/01932691.2014.888004.
[75] L.M. Camacho, R.R. Parra and S. Deng, J. Hazard. Mater, **189**, 286 (2011).
[76] M. Qasemi, M. Afsharnia, A. Zarei, A.A. Najafpoor, S. Salari and M. Shams, Data in Brief **18**, 620 (2018). doi:10.1016/j.dib.2018.03.049.
[77] M.H. Dehghani, S. Tajik, A. Panahi, M. Khezri, A. Zarei, Z. Heidarinejad and M. Yousefi, MethodsX **5**, 1148 (2018). doi:10.1016/j.mex.2018.09.010.
[78] M.H. Dehghani, A. Zarei, A. Mesdaghinia, R. Nabizadeh, M. Alimohammadi, M. Afsharnia and G. McKay, Chem. Eng. Res. Des. **140**, 102 (2018). doi:10.1016/j.cherd.2018.10.011.
[79] M. Massoudinejad, A. Asadi, M. Vosoughi, M. Gholami and M.A. Karami, Korean J. Chem. Eng. **32**, 2078 (2015). doi:10.1007/s11814-015-0018-x.
[80] X.X. Huang, L.G. Qiu, W. Zhang, Y.P. Yuan, X. Jiang, A.J. Xie, Y.H. Shen and J.F. Zhu, Cryst. Eng. Commun. **14**, 1613 (2012). doi:10.1039/C1CE06138K.
[81] E. Haque, V. Lo, A.I. Minett, A.T. Harris and T.L. Church, J. Mater. Chem. A **2**, 193 (2014). doi:10.1039/C3TA13589F.