Abstract—Dye wastewater produced in textile industries is a warning issue that threatens the environment due to discharge into the waterway. This study reviewed the adsorption of Methylene Blue (MB), as a toxic dye, onto diatomite adsorbent. A series of chemical modifications were examined by impregnating diatomite into various acidic and basic solutions to obtain the most active sample with the highest capacity. Both raw diatomite (RD) and modified diatomite (MD) were analyzed under different experimental conditions, such as PH, contact time, the dose of adsorbent to attain the optimum quantities of each in which adsorption capacity and removal percentage were in their highest amount. FESEM analysis indicated the surface characterization and the morphology of both adsorbents. The results of batch experiments showed that the equilibration removal capacities of MB under the optimum condition were 72 mg/g for RD and 127 mg/g for MD. Overall results suggested that due to the low-cost, naturally available, simple treatment methods and materials, and sustainability, the modified adsorbent has the potential for dye removal in the practical process.

Index Terms—Adsorption, chemical modification, diatomite, methylene blue, textile wastewater.

I. INTRODUCTION

Water has a unique place amongst the other natural sources, and human life depends intensively on it; nevertheless, the amount of freshwater accessible globally to use is not sufficient. Additionally, the availability of water per capita in the world is continuously shrinking due to the expanding growth of the population [1]. Providing fresh water is necessary for domestic usages, agriculture, and other sectors. With the rapid growth in industries, the water pollution caused by industries has increased in the past decades. These sectors release large amounts of wastewater throughout their production processing, which can make severe problems for human, plant, and aquatic life [2]. Hence, there are significant limitations worldwide on clean water to set proper water consumption plans and conservation management strategies [3].

The textile industries are one of the largest consumers of water that produce a large amount of effluents daily in various steps of textile processing [4]. Approximately 72 types of toxic chemicals have been identified thus far in textile wastewater with an averagely daily discharging of 200 L per each kilogram of fabric [5], [6]. Some of the textile dyes can cause adverse, permanent effects on ecosystems when they directly release into the environment and water [7]. Hence, removing these dyes from industrial effluents before discharge to the environment is of high importance. Methylene blue (MB) is a type of cationic dye using commonly in the textile industry since it is quite inexpensive and easy to provide, and its long term, constant exposure and large doses (>7.0 mg/kg) can induce vomiting, anemia, and high blood pressure. MB can produce a reactive singlet atom (\( O_2 \)), which mainly at higher concentrations, can destruct DNA structures and spread into the food chain [8], [9], only around 5% of this dye is utilized in the coloring process and the rest is discharged as waste [10].

During the years, many approaches have been examined in order to find out a sustainable way of textile wastewater treatment. The choice of an appropriate method depends on some factors such as the production process, the scale and constituent of the effluents, the limitation in discharging dosage, operation costs, available land, and more [11]. Some of these technologies investigated in the literature are: coagulation/ flocculation [12], membrane reactors or bioreactors [13], [14], biological treatment [15], oxidation [16], or a combination of some techniques [17], [18]; however, each method, along with its efficiency, has also its own drawback. For instance, in a low concentration of the contaminant, the chemical precipitation and biological oxidation might not be economical and applicable enough. Besides, the biodegradation processes are slow in some cases and not suitable when the time of treatment is crucial, some synthetic organic dyes are even non-bio degradable which makes it difficult to remove from the wastewater [19]. Another example is membranes, which are efficient equipment with a high removal percentage in many cases, but it has a limited lifetime owing to the possibility of clogging and fouling [20]. Comparatively, the adsorption method is an effective method and a more reliable alternative for wastewater treatment due to the low initial cost, ease of operation, non-sensitive to toxic pollutants, and simplicity of design [21]. Activated carbon has been considered a common adsorbent, suitable for removing many pollutants because of its high capacity and versatility; nevertheless, the cost of this adsorbent sometimes restrict its widespread use and make it commercially unattractive [22]. This problem has motivated scholars to search for low-priced, natural and efficient alternative adsorbents such as, biochar [23], graphene oxide [24], cellulose [25], chitosan [26], clay [27], fly ash [28] and more. An ideal adsorbent should have an adequate capacity with a large surface area, both thermally and chemically stable, abundantly available, selective, low cost, sustainable and easily regeneratable [29].

Diatomite is a kind of siliceous rock with high porosity and lightweight available abundantly worldwide at a low cost. The different physiochemical characteristics of diatomite make it an attractive material for
the adsorption process [30]. Many studies have proved that
diatomite has a remarkable capability in removing a wide
range of pollutants [31], [32] and even its waste used in
adsorption process [33]. The adsorption capacity of this
adsorbent can be improved through modifications processes
and the removal percentage can be enhanced [34], [35].

Using chemicals for diatomite activation is advantageous
since it is a simple method compared to the other complicated
treatment techniques. Besides, the present method is an
economical alternative method to remove the impurities on
the diatomite surface and activate it with a low price, both in
terms of materials and the process costs, and can be employed
as a pre-treatment option for industrial effluent. Hence, in the
first part of this work, a comparative study on diatomite
chemical modification with different acids and bases is
provided to remove MB from model textile effluent, and the
results of testing the modified diatomite (MD) compared with
the raw diatomite (RD) sample. Besides, different adsorption
parameters were studied to find the optimum amounts for
enhancing adsorption capacity and removal percentage. At
the end, the thermodynamic parameters were also calculated
to find out the possibility and spontaneous of the process.

II. MATERIALS AND METHODS

A. Material

Diatomite was provided from the Binalod region in Iran,
the MB and acidic/basic solution using in this study were
supplied from Merck, Germany. The chemical composition
of the diatomite analyzed by XRF and also the main
characteristics of MB are provided in Table I, II, respectively.

| Chemical composition (XRF) | wt. % |
|---------------------------|-------|
| SiO₂                      | 87.36 |
| Al₂O₃                     | 2.35  |
| Fe₂O₃                     | 1.07  |
| CaO                       | 0.65  |
| K₂O                       | 0.31  |
| Na₂O                      | 0.27  |
| MgO                       | 0.30  |
| TiO₂                      | 0.119 |
| MnO                       | 0.003 |
| Loss on ignition (L.O.I.)  | 7.36  |

| TABLE II: METHYLENE BLUE CHARACTERISTICS [36]. |
|-----------------------------------------------|
| Color Name           | Methylene Blue (MB) |
| C.I. Number          | 52015               |
| Type                 | Cationic            |
| λmax (nm)            | 665                 |
| Molecular Formula    | C₂₂H₂₄N₂SCl         |
| Molecular Weight     | 319.85 g/mol        |
| Chemical Structure   |                    |

B. Apparatus

The final concentrations of the residual solution after the
adsorption process were determined using UV2100/VISIBLE UNICO-US spectrophotometer by using

the maximum wavelength (λmax) of MB. The pH of the
solutions was measured by the AZ-8686 Taiwan pH meter.
Moreover, the morphology of the adsorbent was
characterized by FESEM (Sigma Zeiss-Germany), XRD (D8 ADVANCE Bruker-Germany), and FTIR (Shimadzu-IR
solution 8400 S).

C. Diatomite Preparation

The raw diatomite was modified by chemical treatments
with various types of acids and alkalis, as it is listed in Table
III, in order to choose the best chemical with the highest
removal percentage and adsorption capacity to proceed with
the experiments. After a certain mixing time of diatomite
with the chemicals, the solutions were filtered and dried in
the oven at 100°C for 18h. Finally, all modified diatomite
samples were kept in zip lock bags to use in the adsorption
processes.

| TABLE III: THE CHEMICALS USED TO MODIFY DIATOMITE AT 25°C AND SOLID:LIQUID=1:10 |
|-----------------------------------------------|
| Material | Molarity | Contact time (hr) |
|----------|----------|------------------|
| NaOH     | 1.35     | 3                |
| KOH      | 1.35     | 3                |
| H₂SO₄    | 1.3      | 1                |
| HCl      | 1.3      | 1                |
| H₃PO₄    | 1.3      | 1                |

D. Adsorption Experiment

The adsorption process was carried out with 100 ml of MB
with a concentrate of 20 mg/L and 0.03 g of diatomite, both
with raw and modified samples, stirring for half an hour at
room temperature in 250 ml volume beaker flask. Then, the
solution was filtered to measure the final dye concentration
with UV spectrophotometry. The parameters affected the
adsorption process were also studied through the same
procedure as described earlier to find out the optimum
quantity of each factor. The amount of MB adsorbed onto
each adsorbent sample was calculated with the following
expressions [37]:

\[
q = \frac{(C_i - C_f)V}{m} \quad (1)
\]

\[
%R = \frac{C_i - C_f}{C_i} \times 100 \quad (2)
\]

where \(q\) is the adsorption capacity (mg/g), \(C_i\) and \(C_f\) are,
respectively, the dye concentration (mg/L) in initially and in
residual solution after adsorption, \(V\) is the volume of MB
solution (L), \(m\) is the mass of sorbent (g) and \(%R\) is the dye
removal percentage.

III. RESULTS AND DISCUSSION

A. Modification Method Selection

The results of the chemical treatment of meshed diatomite
with 125μm particle size are listed in the Table IV.

According to above table, the best modification method is
acid treatment with H₂SO₄ (1molar). Thus, all the
experiments are performed by using this sample as the
TABLE IV: THE RESULT OF DIATOMITE CHEMICAL TREATMENTS

| Additive       | q (mg/g) | %R   |
|----------------|----------|------|
| Raw            | 24.14    | 36.21|
| NaOH (1molar)  | 46.90    | 70.36|
| NaOH (3molar)  | 52.89    | 79.36|
| NaOH (5molar)  | 48.73    | 73.09|
| KOH (1molar)   | 47.23    | 70.85|
| KOH (3molar)   | 51.48    | 77.22|
| KOH (5molar)   | 44.74    | 67.11|
| H$_2$SO$_4$ (1molar) | 60.83      | 91.24|
| H$_2$SO$_4$ (3molar) | 57.97      | 86.95|
| HCl (1molar)   | 49.64    | 74.46|
| HCl (3molar)   | 49.00    | 73.50|
| H$_2$PO$_4$ (1molar) | 44.49     | 66.73|
| H$_2$PO$_4$ (3molar) | 40.79     | 61.19|

B. Characterizations of the Adsorbents

To study the surface morphology of both adsorbent samples before MB adsorption, FE-SEM analysis was performed as shown in Fig. 1. As it can be seen, the surface morphology of untreated sample was irregular, rough, heterogeneous, and without considerable numbers of pores for adsorbing MB from the solution. The impurities presence on the surface of RD are almost covered the surface and blocked some pores leading to a lower removal percentage. H$_2$SO$_4$ washed diatomite seems to be capable of dissolving the impurities, and the modified sample is altered to a highly porous media with more and bigger cavities resulted in a higher adsorption capacity and MB removal.

XRD analyses were conducted to identify the amorphous nature and the form of crystalline in both RD and the MD, as shown in Fig. 2. According to the figure, the raw sample mainly includes amorphous SiO$_2$ (diatoms) as well as tracks of some minerals e.g., montmorillonite (M), kaolinite (K), hematite (He) and mica (Mic). It seems that phase transformation happened throughout the modification, and some new peaks (S) emerged.

A. Process Optimization

In order to enhance the dye removal percentage and obtaining the highest adsorption capacity of diatomite, some physical properties, such as pH, contact time, dosage of adsorbent, and the initial MB dye concentration in the solution are investigated.

1) Effect of pH

pH is an important parameter that not only changes the adsorbent characteristics, but it also affects the diatomite surface structure in the solution, which could alter properties both physically and chemically [38]. This factor was studied to determine the optimum value of pH by evaluating the capacity of adsorbent samples for dye removal at different pHs levels from 4 to 13. As presented in Fig. 3, increasing pH quantity from 4 to 12 resulted in increasing the adsorption percentage from 29 to 52% for RD and from 61 to around 90% for MD. After pH=12, the dye removal percentage gradually decreased for both adsorbents’ samples. Hence, this pH value was chosen as an optimum amount for further experiments.

2) Effect of contact time

Another critical factor that the adsorption process depends on is the contact time because the equilibrium time of each sample is different in an experiment [39]. The adsorption trend of MB dye onto diatomite samples with time was investigated in a period of 20 to 120 minutes, as shown in Fig. 4. It was observed that from 20 to 90 minutes, the adsorption percentages rise; however, from 40 up to 90 min, the
increases are slow especially for the modified sample. After this time, no remarkable increase was witnessed, and the adsorption rate stayed steady. Thus, 90 minute was chosen as the equilibrium time with 65% and 96.5% dye removal for RD and MD, respectively.

3) Effect of adsorbent dosage

Theoretically, the higher the adsorbent quantity is, the higher the removal capability. However, practically, an excessive amount of adsorbent resulted in decreasing efficiency due to wasting adsorbent; so, finding an optimum adsorbent amount that can satisfy both adsorbent capacity and removal percentage is essential. To this aim, various amounts of diatomite from 10mg to 50mg versus both adsorption capacity and removal percentage were plotted in Fig. 5. As can be seen, increasing the adsorbent amount in fixed dye concentration resulted in more free sites for dye adsorption, which means higher removal percentage but lower adsorption capacity. Consequently, to prevent adsorbents loss and make use of the maximum capacity of the adsorbent, the optimum amounts of both samples are the intersection of two diagrams, which is around 16mg for both RD and MD with 58% removal and 72mg/g adsorption capacity and 14.5mg for MD with 92% dye removal and 127mg/g adsorption capacity.

4) Effect of initial dye concentration

The effect of the initial concentration of MB dye was studied at the optimum amounts of adsorbent; 16mg for RD and 14.5mg for MD. at low concentration, the adsorption process attains equilibrium state quicker due to the lower ratio of dye molecules to the adsorption sites [40]. By increasing initial dye concentration, the mass gradient increase which resulted in boosting the adsorption driving force. Different concentrations of MB dye were tested from 10 to 50mg/l as plotted in Fig. 6 to investigate the impact of dye concentration on the removal percentage and adsorption capacity.

IV. THERMODYNAMIC STUDY

The feasibility of the adsorption process is estimated through thermodynamic studies using the following equations:

\[ K_c = \frac{q_e}{C_e} \]  

\[ \Delta G^\circ = -RT \ln K_c \]  

And the Van’t Hoff equation is:

\[ \ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]

where \( q_e \) (mg/g) is the capacity of adsorption at equilibrium state, \( C_e \) (mg/L) is the concentration under equilibrium condition, \( \Delta G^\circ \) (kJ/mol) is the standard free energy change, \( \Delta H^\circ \) (kJ/mol) and \( \Delta S^\circ \) (J/mol.K), which are respectively standard enthalpy and standard entropy are...
The negative values of $\Delta G^\circ$ for both RD and MD confirms the spontaneity of the adsorption processes. Besides, decreasing the $\Delta G^\circ$ amounts with increasing the temperature shows that adsorption of MB dye onto diatomite is more desirable at a lower temperature. $\Delta H^\circ<0$ suggests that energy release during the adsorption process, and it is naturally exothermic. Moreover, negative $\Delta S^\circ$ exhibits that the randomness reduces at the solid-solution interface throughout the adsorption procedure.

### V. CONCLUSION

In the present study, diatomite modified by H$_2$SO$_4$ (1 molar) solution has been used for MB adsorption from model textile wastewater and the results have compared to the natural diatomite. Under optimum conditions, the results confirmed that, the MD was suitable adsorbent with a higher percentage of MB removal (92%) compared to the untreated sample (58%). The comparison of surface morphology through FESEM indicated the development of porosity on diatomite during chemical activation which was the reason for its more adsorption than the unmodified sample. Furthermore, thermodynamic study has been performed, which showed that the MB adsorption onto both diatomite samples were exothermic, spontaneous, and was along with a reduction in the randomness.

### CONFLICT OF INTEREST

The authors declare no conflict of interest.

### AUTHOR CONTRIBUTIONS

Parisa Ebrahimi conducted the data collection, analyzed the results and wrote the first draft; Prof. Anand Kumar reviewed the final draft.

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Parisa Ebrahimi received the BSc in chemical engineering from Persian Gulf University (PGU) University, Iran in 2013 and the MSc in chemical engineering from Semnan University, Iran in 2015. Currently she studies PhD in environmental engineering in Qatar University, Qatar. She used to work as a graduate teaching assistant in Kherad Institute of Higher Education, Iran for three year and also currently work as a graduate assistant in Qatar university, Qatar.

Anand Kumar is an associate professor in the Department of Chemical Engineering at Qatar University. He obtained his Ph.D. in chemical engineering (2011) from the University of Notre Dame, USA, and B. Tech. (2006) from IIT Kharagpur, India. His research interests include heterogeneous catalysis, hydrogen production, nanomaterials synthesis by combustion-based techniques for hydrocarbon reforming, CO2 conversion and environmental applications.