Comparison between nano zero valent iron supporting onto activated carbon collected via two types of reagents statistically: Carbon for cationic dye removal

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Abstract. One of the important substances was the carbon which was used to prepare adsorbents like, Nano zero-valent iron on carbon as supporting materials by sodium borohydride as a reducing agent. Nitric acid was used with heating at a temperature of 90 °C and stirring for two hours to generate active groups on the surface of the activated carbon. The new zero-valent iron adsorbent was loaded on the surface of the functionalized activated carbon (NZVI/AC) and characterized using X-ray diffraction (XRD), the surface area measurement (SBET), and the Field emission scanning electron microscopy (FESEM). The synthesized (NZVI/AC) was applied for the removal of cationic dye as methylene blue (MB) from simulated wastewater. On the other hand, the adsorption and the kinetic studies for the MB removal were investigated via both kinetic models as the pseudo-first and the pseudo-second-order kinetic models. Also, the initial concentration of the MB adsorption studies was with a concentration of 20 mg/L, the adsorbent dosage of 0.1 g, the contact time of 60 minutes with high uptake value at natural pH solution. It was found that the removal efficiency of the adsorbent NZVI/AC was higher than the AC without Nanomaterial’s with values of 96.70% and 84.16% respectively. It is noted that the removal rate increased almost 12 times in comparison between AC and NZVI/AC. In the kinetic studies; the second-order kinetic model was more favorable than the first-order kinetic model in the adsorption mechanism. Thermodynamically, the Gibbs free energy (∆Gf) was found to be with a negative value indicating the spontaneity of the process, while the change in the entropy ∆S and the enthalpy ∆Hf with positive values indicating the adsorption of MB was an endothermic process. It could conclude that the new adsorbent NZVI/AC had significant potential for the cationic dye removal than the activated carbon AC in the environmental application.
1. Introduction

Naturally, the activated carbon may be found as powdered charcoal or granular black solid substance. This material has different pore structures and a huge internal surface area. The preparation of activated carbons with different pore sizes could be carried out by the physical and chemical processes. To prepare highly porous carbon, which is used in selective removal processes, hydrogen gas is used in this process at a constant temperature [1]. On the other hand, the chemical activation process was achieved after mixing the precursor with chemical reagent as salts like sodium chloride or chemical reagents such as sodium hydroxide (a strong base), acid, potassium hydroxides, zinc chloride, and phosphoric acid can be used in the chemical reactivity processes [2]. The next important step is the decomposition of the precursor by exposing the carbonized material to carbon dioxide, nitrogen, or steam at high temperatures. In this step, the chemical reagents react with the surface of the carbon precursor inhibit the particle shrinking, and reduce the evaluation of the volatile matter. Finally, the chemical reagent was removed and leave behind very high porosity [3]. The chemical activation was more favorable than the physical activation because it was achieved in lower temperatures and shorter times [4].

The methylene blue (MB) was selected as a heterocyclic compound which has a lot of industrial application such as in printing, textual, and painting. On the other hand, the chemicals have harmful and carcinogen effects [5]. Different techniques were used for removing MB from the aqueous solution, for instant coagulation and foliation, advanced oxidation process, ion-exchange, reverse osmoses, and adsorption [6]. Recently, the Nano zero-valent iron was proven as an effective material in the removal of a high range of a contaminated compound in an aqueous solution [7]. The aim of this study is the preparation of the new adsorbents and the characterization of Nano zero-valent iron supported onto activated carbon. Finally, two kinetic models first order and second-order kinetic models were tested to those of batch equilibration process via sampling taken at different time intervals. The thermodynamic parameters such as entropy ($\Delta S^\circ$), Gibb’s free energy ($\Delta G^\circ$), and the enthalpy ($\Delta H^\circ$) were evaluated to study the spontaneity of the process.

2. Materials and methods

Activated carbon (AC), was purchased from china company (Sinopharm Chemical Reagent Co., Ltd.), Iron sulfate heptad water molecules (FeSO$_4$$\cdot$7H$_2$O), with the purity of 98%, Sodium borohydride (NaBH$_4$), with the purity of 97.5%, the cationic dye, methylene blue (MB) were obtained from Thomas Baker, PVT. Ltd. India. Besides, the Hydrochloric acid and the Sodium hydroxide were supplied from Merck, nitric acid, absolute ethanol, and Zinc chloride were supplied from Sigma-Aldrich and used as analytical reagent grade without further purification.

2.1 Method

In the first step, two types of chemical reagents were used as HNO$_3$ and ZncL$_2$ in the activation of the carbon in water and oil bath, depending on the preparation methods. On the other hand, the impregnation of Nano zero-valent iron was investigated via sodium borohydride as the reducing agent was investigated. The parameters of the adsorption process such as temperature and contact time were determined. Finally, the kinetic studies of the MB via both kinetic models as pseudo-first-order and pseudo-second-order, and the thermodynamic studies were carried out to find out the values of $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ to express the spontaneous of the process.
2.1.1 Preparation of New Adsorbent of Nano Zero Valent Iron Supported onto Activated Carbon (NZVI/AC)

New adsorbent was prepared via the co-precipitation method. The activation of carbon was carried out by taking a suitable amount from activated carbon (AC) and functionalized the surface with hydrophilic groups by using nitric acid (HNO₃) as chemical reagents with dilution percentage of (70%), with heating at 90°C and stirring on a magnetic stirrer for 3 h. Then, the activated carbon was dried in furnace at temperature of 650°C with the flow of nitrogen gas for the formation of functionalized activated carbon surface. Finally, 6g from the prepared activated carbon were impregnated with 3g from FeSO₄•7H₂O solution for 45 min at 70°C with stirring on a magnetic stirrer. The prepared adsorbent then filtered, washed with distilled water and dried in an oven at 110°C for 4 hours and kept for further use.

2.1.2 Characterization of the Prepared NanoAdsorbents (NZVI/AC)

The modified adsorbents were characterized using field emission scanning electron microscopy (FESEM) to explain the morphology, Brunner-Emmett-Teller (BET), and X-Ray powder diffraction.

2.1.3 Statistical Studies

To validate the results, each experiment was repeated triplicate times and it was calculated the standard deviation to gate the error bar coefficients.

3. Results and Discussion

The initial concentration of the MB stock solution in all the adsorption studies was 20mg/L. From the experimental data, it is found that 60 min was the suitable contact time which applies for the removal of the MB from the simulated wastewater solution.

3.1 The Adsorbent Characterization (NZVI/AC)

For the improvement of the preparation of the new adsorbents, the characterization methods are carried out as follows.

3.1.1 The X-Ray Diffraction

In Figure 1, the diagram of NZVI/AC was illustrated. The peak diffraction (1 0 1) of the 2θ 43.80° was referred to the NZVI, while the apparent peak in the reflection of (2 2 0) and (1 1 1) referred to the (activated carbon-iron) in the 2θ of 23.89° [8] in a small amount from NZVI Nano adsorbent [9].
3.1.2 The Brunner- Emmett Teller (BET) Measurements

The specific surface area and the pore quantity of the adsorbents are summarized in Table 1. The measured specific surface area activated carbon has been measured before and after activation. The surface area was found to be with values of 175.63 m$^2$/g and 598.43 m$^2$/g with a pore volume of values 0.038 cm$^3$g$^{-1}$ and 0.091 cm$^3$g$^{-1}$ for activated carbon (AC) without activation [10] and with chemical activation via HNO$_3$, respectively. It seems the chemical activation increased the surface area. On the other hand, the NZVI had a surface area with a value of 41.36 m$^2$/g with a pore volume of 0.171 cm$^3$g$^{-1}$ without supporting materials. as a result, after the impregnation of NZVI onto the activated carbon, the surface area was decreased as reported previously [11, 12] with values of 276.36 m$^2$/g and pore value of 0.135 cm$^3$g$^{-1}$ The values of the surface area for the prepared adsorbent were described in Table 1.

Table 1. The specific surface area ($S_{BET}$) and the pore volume were described for NZVI, AC without activation, and AC with activation and NZVI/AC.

| Materials                              | Specific surface area ($S_{BET}$) m$^2$/g | Pore volume (BJH) cm$^3$g$^{-1}$ |
|----------------------------------------|------------------------------------------|---------------------------------|
| NZVI                                   | 41.36                                    | 0.171                           |
| Activated carbon without chemical activation via HNO$_3$ | 175.63                                   | 0.038                           |
| Activated carbon with chemical activation via HNO$_3$ | 598.43                                   | 0.091                           |
| Adsorbent (NZVI/AC)                    | 276.36                                   | 0.135                           |
3.1.3 The Field Emission Scanning Electron Microscopy (FESEM) Analysis

In this analysis method, the surface morphology of the prepared (NZVI/AC) adsorbents was characterized. In Figure 2a, the chain-like assembly of the surface of NZVI appears due to the magnetic attraction force as previously demonstrated [13]. On the other hand, the surface structure was explained in Figure 2b, while Figure 2c shows the pore of the activated carbon. Finally, the surface morphology of the activated carbon (AC) was explained in Figure 2e it is clear that different changes will happen after the loading of the NZVI. The suggestion mechanism was the dipole-dipole interaction as reported previously [14].

![Figure 2](image)

Figure 2 The FESEM analysis (a) at x45,000 magnification of (ZVT), (b)The surface structure of the (NZVI/AC) at x10,000 magnification at (c), the pore surface was presented in x20,000 magnification and (d), showed the loaded NZVI/AC surface at x60,000 magnification.
4. Kinetic studies models

The kinetic adsorption was identical via the batch equilibration experiment; however, the aqueous samples were taken with preset time intervals [3]. The kinetic studies were carried out with the initial MB concentration of 20 mg/L. The first-order rate expression established on adsorbent capacity had been generally expressed as uses Equation (1).

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  

Where \( q_e \) and \( q_0 \), the uptake values in equilibrium and initial concentration, respectively. On the other hand, the second-order kinetic model could be described as in Equation (2).

\[ \ln(q_e - q_t)^2 = \ln q_e - k_2 t \]

Figure 3 shows the linear plot of each kinetic model of MB adsorption onto AC as supporting materials as a first-order kinetic model in Fig. 3a and second-order kinetic model as presented in Figure 3b, respectively.

![Figure 3](image)

**Figure 3.** Both kinetic models of MB adsorption onto the activated carbon (AC), (a) pseudo-first-order, and (b) pseudo–second–order kinetic models. The error bars show the stander deviation in length.

On the other hand, the MB adsorption onto NZVI/AC is showed. As clear in Figure 4a that the plot of the first-order kinetic model was not fitted with the experimental data and the second-order kinetic model was more suitable to explain the MB adsorption on the surface.

![Figure 4](image)
Figure 4. Both kinetic models of MB adsorption onto Zero valent iron supported onto activated carbon (NZVI/AC), (a) pseudo-first-order, and (b) pseudo–second–order kinetic models. The error bars show the standard deviation in length.

From the above results, it seems that the second-order-kinetic model was favorable for the methylene blue (MB) adsorption onto the surface of activated carbon (AC) and NZVI/AC, respectively than the first-order kinetic models. The related parameters were summarized in Table 2.

Table 2. The kinetic parameters for the MB adsorption onto AC and NZVI/AC as prepared adsorbents.

| Model of kinetic parameters | AC supporting materials | NZVI/AC adsorbent |
|-----------------------------|-------------------------|------------------|
| Pseudo first-order          | K_1 (min)^{-1}          | 0.0285           | 0.0311          |
| q_e (mg/g)                  | 2.9081                  | 0.5347           |
| R^2                         | 0.8121                  | 0.2532           |
| Pseudo second-order         | K_2 (g/mg. min)         | 0.054            | 1.8426          |
| q_e (mg/g)                  | 14.987                  | 17.245           |
| R^2                         | 0.9879                  | 0.9989           |

5. Thermodynamic studies

Different temperatures were used to understand the MB adsorption onto AC and NZVI/AC, ranged between 30°C to 50°C, respectively. It was found the adsorption capacity of MB onto NZVI/AC increased with increasing the temperature at 60 minutes of contact time via the adsorption capacity of 21.78 mg/g for MB adsorption. It was found that the higher surface energy 127.768 KJ mole^{-1}. This fact indicated the endothermic adsorption process as presented previously [15]. To calculate the thermodynamic parameter such as the chain in the entropy, the enthalpy, and in the Gibbs free energy. Figure 5 shows the Van’t Hoff plots for MB adsorption onto NZVI/AC adsorbents, while the thermodynamic parameters were calculated from the slope using the following equation, Equation 3 as summarizes in Table 3.
From the above results, it seems that the enthalpy calculated value of 125.536 KJ/mole showed the physic-sorption [13], while the spontaneous of the process indicating from the negative value of the $\Delta G^\circ$ which is favorable and applicable for the MB adsorption onto NZVI/AC.

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]  

(3)

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Figure 5. The Van’t Hoff plots for MB adsorption onto NZVI/AC adsorbents.

Table 3. The thermodynamic parameters of the methylene blue (MB) adsorption onto NZVI/AC.

| Enthalpy $\Delta H^\circ$ KJ/mole$^{-1}$ | Entropy $\Delta S^\circ$ KJ/mole$^{-1}$K$^{-1}$ | Temperature $C^\circ$ | $T\Delta S^\circ$ | $\Delta G^\circ$ J mole$^{-1}$ |
|----------------------------------------|-----------------------------------------------|----------------------|-----------------|--------------------------|
| 127.7680                               | 546.243                                       | 30                   | 123119.6        | -7890.51                 |
|                                        |                                               | 35                   | 124521.5        | -97612.4                |
|                                        |                                               | 40                   | 126213.2        | -10897.6                |
|                                        |                                               | 45                   | 127429.3        | -15872.8                |
|                                        |                                               | 50                   | 128945.5        | -16549.4                |

6. Conclusions
The prepared adsorbent was effectively synthesized and characterized simply by several techniques. The chemical activation of activated carbon with nitric acid was better than zinc chloride by penetrating, swelling, and breaking the bonds of lignocelluloses. To conclude, the results showed that which NZVI grafted on the surface of activated carbon lead to decreasing the surface area and the
active surface side of the prepared adsorbents. The size transfer and particles associated with the MB adsorption to NZVI/AC surfaces were authorized. These prevent the clumping of NZVI particles during the adsorption process, which improves the removal efficiency of the MB dye.

Typically, the kinetic data were much better for explained the pseudo-second-order kinetic model for the activated supporting materials via HNO₃ and the NZVI adsorbent. It was found that the high value of 17.87 mg/g for the adsorption capacity of MB adsorption onto the NZVI/AC, while the uptake value for MB adsorption on the AC was lower than the value of 16.81 mg/g in the same experimental condition. Also, the positive value of the entropy ∆S° attributed to increasing the randomly in the interaction system between the adsorbent NZVI/AC and the MB dye. Finally, the negative value of the Gibbs free energy indicated that the prepared adsorbents could be applicable for the MB removal and the adsorption method was an endothermic and automatically acquired process. As a result, the adsorption process via the zero-valent iron supported on activated carbon was found to be an eco-friendly, simple, and cheap effective method for the removal of MB in an aqueous solution.

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