Efficient removal of methylene blue dye from aqueous media using Fe/Si, Cr/Si, Ni/Si, and Zn/Si amorphous novel adsorbents

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Abstract

In this paper, non-crystalline novel adsorbents composed of sodium, oxygen, silicon, and other metals such as iron, nickel, chromium, or zinc were produced using the gelation method. The amorphous products were characterized using various instruments, for example, XRD, FT-IR, FE-SEM, EDS, and BET. The BET affirmed that the amorphous products contain mesopores, micropores, and macropores. Broad XRD peak in the range 2θ = 20–40 was gotten for every one of the synthesized products. Thus, the synthesized products were non-crystalline. The FE-SEM images showed that every one of the synthesized products consists of irregular shapes. FT-IR confirmed the presence of T–O–T bending, T–O–T symmetric, and T–O–T asymmetric vibrations (T = Si, M) (M = Fe, Ni, Cr, or Zn). Also, methylene blue dye was proficiently removed from aqueous media utilizing the amorphous products. Besides, the removal of methylene blue dye from aqueous media was assessed via studying some variables, for example, the concentration of dye, time, adsorption pH, temperature of dye solution, and reusability of amorphous products. In addition, the removal processes were physical, exothermic, spontaneous, and follow both of the pseudo-first-order kinetic model and Freundlich isotherm. Moreover, the amorphous products have adsorption capacity values in the range from 36.51 to 53.79 mg/g. Finally, the amorphous products were regenerated then reused without changing their efficiency.

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1. Introduction

World Economic Forum report elucidated that the water shortage occupies extremely importance [1]. Reports demonstrated that almost 40% of the total populace will live in zones with constrained water sources. Unsustainable industrial and massive population growth increase water consumption and...
opportunities for pollution. An extensive number of undesired products such as dyes, heavy metals, pharmaceuticals, chlorinated compounds, pesticides, surfactants, and personal care products contaminate water resources. Some industries such as printing, textiles, paper, leather, food, and pharmaceuticals need pigments and dyes for coloring their products. Hence, the presence of highly colored waste effluents in the water causes problems for humans and the environment. Therefore, water treatment occupies extraordinary importance due to the water shortage. Methylene blue dye, which was needed by the textile industry, is one of the most famous water contaminants that cause many health problems such as abdominal disorders, respiratory distress, skin sensitization, and blindness [2,3]. Also, methylene blue dye adversely affects the environment and damages the balance of the ecosystem. It blocks light permeation for aquatic organisms and thus threatens their life. Thus, the removal of this dye from water is foremost for keeping up the environment. Various techniques were utilized for removing methylene blue dye, for example, ultrafiltration, ozonation, reverse osmosis, ion exchange, chemical oxidation, photodegradation, solvent extraction, electrochemical degradation, and adsorption [4–7]. But, the adsorption method is simple, easy, efficient, and economical. Materials, which were utilized for the adsorption technique, such as zeolite, activated carbon, multiwalled carbon nanotubes, and polymers are characterized by high cost due to the consumption of energy and expensive chemicals during their preparation [8–12]. Recently, non-crystalline substances such as geopolymers (i.e., amorphous aluminum silicates) form extraordinary importance for water treatment due to their simple cost, easy production, and excellent porosity [13–21]. These materials were utilized successfully for removing many dyes such as methyl violet, methylene blue, methyl orange, and Congo red from wastewater. It is known that the production of geopolymers by the gelation method takes in three stages. The first stage is the dissolving of silicon and aluminum precursors. The second stage is the condensation for forming a \(-SiO\_2-AlO\_2\) monomer. The third stage is gel production through polycondensation for forming repeating units of \(-SiO\_2-AlO\_2\). So, our research team produced amorphous materials similar to geopolymers through the replacement of aluminum with other metals such as iron, nickel, chromium, and zinc. The repeating unit in our products is \(-Si\_O\_2-MO\_2\) (M = Fe, Ni, Cr, or Zn). Also, the amorphous products were characterized using various instruments, for example, XRD, FT-IR, FE-SEM, EDS, and BET. Besides, the synthesized amorphous materials were tested as adsorbents for removing methylene blue dye from aqueous media. Moreover, several factors were studied for evaluating the removing processes, for example, the concentration of dye, time, adsorption pH, temperature of dye solution, and reusability of adsorbents.

2. Experimental

2.1. Chemicals

The used chemicals are sodium metasilicate pentahydrate (Na\(_2\)SiO\(_3\)·5H\(_2\)O), nickel(II) sulfate heptahydrate (NiSO\(_4\)·7H\(_2\)O), chromium(III) sulfate (Cr\(_2\)(SO\(_4\))\(_3\)), iron(III) sulfate (Fe\(_2\)(SO\(_4\))\(_3\)), zinc sulfate heptahydrate (ZnSO\(_4\)·7H\(_2\)O), hydrochloric acid (HCl), sodium hydroxide (NaOH), and potassium chloride (KCl). These chemicals were bought from Sigma-Aldrich Company.

2.2. Synthesis of amorphous products

6 g of sodium metasilicate pentahydrate (28.28 mmole) was dissolved in 50 mL of distilled water to obtain a solution named S. Also, 4.27 g of iron(III) sulfate (10.68 mmole) was dissolved in 50 mL of distilled water to obtain a solution named M. Other M solutions, which have the same number of mmoles, were prepared by dissolving 3.00, 4.19, and 3.07 g of nickel(II) sulfate heptahydrate, chromium(III) sulfate, and zinc sulfate heptahydrate in 50 mL of distilled water, respectively. Solution M was added to solution S drop by drop with continuous stirring for 1 h. Finally, the precipitate was filtered utilizing a centrifuge fixed at speed equals 2500 rpm, washed a few times utilizing distilled water, and dried at 100°C for 15 h. The samples, which were produced using iron(III) sulfate, nickel(II) sulfate heptahydrate, chromium(III) sulfate, and zinc sulfate heptahydrate, were labeled as AFe, ANi, ACr, and AZn, respectively.

2.3. Removal of methylene blue dye from aqueous media

The contact time effect was studied as follows; 0.1 g of the amorphous product (AFe, ANi, ACr, or AZn) and 50 mL of 80 mg/L methylene blue dye solution were mixed using 250 mL beaker then stirred at 600 rpm for different times (5–220 min). The pH effect was studied as follows; 50 mL of 80 mg/L methylene blue dye solutions was adjusted using 0.1 M hydrochloric acid or sodium hydroxide to obtain different pH values (2–9). After that, the adjusted methylene blue dye solutions and 0.1 g of the amorphous product (AFe, ANi, ACr, or AZn) were mixed using 250 mL beaker then stirred at 600 rpm for 80, 100, 80, and 100 min in the case of AFe, ANi, ACr, and AZn, respectively. The methylene blue concentration effect was studied as follows; different concentrations (20–100 mg/L) of methylene blue dye were adjusted to obtain pH equals 9. After that, 50 mL of the adjusted methylene blue dye solutions and 0.1 g of the amorphous product (AFe, ANi, ACr, or AZn) were mixed using 250 mL beaker then stirred at 600 rpm for 80, 100, 80, and 100 min in the case of AFe, ANi, ACr, and AZn, respectively. The adsorption temperature effect was studied as follows; 0.1 g of the amorphous product (AFe, ANi, ACr, or AZn) and 50 mL of 80 mg/L methylene blue dye (pH = 9) were mixed using 250 mL beaker at different temperatures (298-328 K) then stirred at 600 rpm for 80, 100, 80, and 100 min in the case of AFe, ANi, ACr, and AZn, respectively. The amorphous products were regenerated by heating them at 300 °C for degrading the adsorbed dye. After that, 0.1 g of the regenerated amorphous product (AFe, ANi, ACr, or AZn) and 50 mL of 80 mg/L methylene blue dye (pH = 9) were mixed using 250 mL beaker then stirred at 600 rpm for 80, 100, 80, and 100 min in the case of AFe, ANi, ACr, and AZn, respectively. The previous recovery and reusing steps were repeated three times. After examining any of the above variables, the methylene blue dye was separated by centrifugation at 3000 rpm. The concentration of the separated dye was estimated from a previously constructed calibration curve using UV-V is spectrophotometer. The point of zero
charge (pH_{pzc}) of the amorphous products was studied as follows: 50 mL of potassium chloride solutions were adjusted to obtain different initial pH values (pH_i = 2.5-11.5). After that, the adjusted potassium chloride solutions and 0.5 g of the amorphous product (AFe, ANi, ACr, or AZn) were mixed using 250 mL beaker then stirred at 600 rpm for 24 h. The final pH value (pH_f) was recorded utilizing a pH meter. Finally, pH_f values are presented as a function of pH_i values. The pH_{pzc} is the pH_f level where a common plateau was obtained [22].

2.3.1. Adsorption equations

Eq. (1): The adsorption capacity (O_i, mg/g) of the amorphous products at time t

\[ O_i = (A_i - A_{f})V/m \]

Eq. (2): % removal of methylene blue dye (% R_i) at time t

\[ %R_i = \frac{(A_i - A_{f})100}{A_i} \]

Eq. (3): The adsorption capacity (O_{ph}, mg/g) of the amorphous products at varied pH values

\[ O_{ph} = (A_i - A_{ph})V/m \]

Eq. (4): % removal of methylene blue dye (% R_{ph}) at varied pH values

\[ %R_{ph} = \frac{(A_i - A_{ph})100}{A_i} \]

Eq. (5): The adsorption capacity (O_e, mg/g) at equilibrium

\[ O_e = (A_i - A_e)V/m \]

Eq. (6): % removal of methylene blue dye (% R_e) at equilibrium

\[ %R_e = \frac{(A_i - A_e)100}{A_i} \]

Eq. (7): The adsorption capacity (O_T, mg/g) at varied temperature values

\[ O_T = (A_i - A_T)V/m \]

Eq. (8): % removal of methylene blue dye (% R_T) at varied temperature values

\[ %R_T = \frac{(A_i - A_T)100}{A_i} \]

Eq. (9): Pseudo-first-order kinetic model

\[ \log(O_e - O_t) = \log(O_e - K_{1}t/2.303) \]

Eq. (10): Pseudo-second-order kinetic model

\[ t/O_t = (1/K_2O_e^2) + (1/O_e)t \]

Eq. (11): Intra-particle diffusion Kinetic model

\[ O_t = K_3t^{0.5} + C \]

Eq. (12): Langmuir adsorption isotherm

\[ A_e/O_e = (1/K_4O_m) + (A_e/O_m) \]

Eq. (13): Freundlich adsorption isotherm

\[ \ln O_e = \ln K_f + (1/n)\ln A_e \]

Eq. (14): Freundlich maximum adsorption capacity (O_{mf}, mg/g)

\[ O_{mf} = K_5(A_i)^{1/n} \]

Eq. (15): Distribution co-efficient (K_d, L/g)

\[ K_d = [%R_T/(100-%R_T)]V/m \]

Eq. (16): Distribution co-efficient (K_d, L/g)

\[ K_d = O_T/A_T \]

Eq. (17): Relation between ln K_d and 1/T

\[ \ln K_d = (\Delta S^o/R) - (\Delta H^o/RT) \]

Eq. (18): Relation between thermodynamic parameters

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

where, A_i (mg/L) is the methylene blue dye concentration before adsorption, A_e (mg/L) is the methylene blue dye concentration after adsorption at time t, A_{ph} (mg/L) is the methylene blue dye concentration at equilibrium, A_{ph} is the methylene
blue dye concentration at varied pH values, $A_T$ is the methylene blue dye concentration at varied temperature values, $m$ (g) is the mass of the amorphous product, $V$ (L) is the volume of methylene blue dye solution, $K_1$ (1/min) is the pseudo-first-order rate constant, $K_2$ (mg/g.min$^{0.5}$) is internal diffusion constant, $K_3$ (g/mg.min) is the pseudo-second-order rate constant, $C$ (mg/g) is the thickness of boundary layer, $O_m$ (mg/g) is the Langmuir maximum adsorption capacity, $K_s$ (mg/g) is the Freundlich constant, $K_4$ (L/mg) is the Langmuir constant, $1/n$ is the heterogeneity factor, $K_5$ (L/g) is distribution co-efficient, $R$ (KJ/mol K) is gas constant, $T$ (K) is temperature, $\Delta S^o$ (KJ/mol K) is change in the entropy, $\Delta H^o$ (KJ/mol) is change in enthalpy, and $\Delta G^o$ (KJ/mol) is change in free energy [23-40].

2.4. Physicochemical measurements

The XRD patterns of amorphous products were gotten using an X-ray diffraction apparatus (18 kW diffractometer; Bruker; model D8 Advance) outfitted with monochromated Cu $K_a$ radiation with wavelength equals 1.54178 Å. The FT-IR spectra of amorphous products were gotten using an FT-IR spectrophotometer (Perkin Elmer) in the 4000-400 cm$^{-1}$ region. After coating the amorphous samples with gold on K550X sputter coater, the elemental analysis and morphology were investigated with an ultra-high-resolution FE-SEM microscope (Model Quanta 250 FEG) outfitted with an energy-dispersive X-ray spectrometer SEM-EDX. Calculation of surface textures of the amorphous samples such as BET surface area, average pore radius, and total pore volume were gotten from nitrogen isotherms at $-196$ °C using a Quantachrome analyzer (Nova 2000 series).

3. Results and discussion

3.1. Characterization of amorphous samples

Fig. 1A–D illustrates XRD of AFe, ANi, ACr, and AZn samples, respectively. Broad peak in the range $2\theta=20–40$ was gotten for every one of the synthesized samples. Thus, the synthesized products were non-crystalline. Fig. 2A–D illustrates EDS of AFe, ANi, ACr, and AZn samples, respectively. The results affirmed that all the amorphous products were composed of silicon, sodium, and oxygen as well as iron, nickel, chromium, and zinc in the case of AFe, ANi, ACr, and AZn, respectively, as shown in Table 1. Fig. 3A–D illustrates FT-IR of AFe, ANi, ACr, and AZn samples, respectively. The results affirmed that the peaks which appeared in the range 459–523 cm$^{-1}$ are the
result of T–O–T bending vibrations (T = Si, M) (M = Fe, Ni, Cr, or Zn). Besides, the peaks which were appeared in the range 688–767 cm$^{-1}$ are the result of external symmetric stretching vibrations of T–O–T. In addition, the peaks which were appeared in the range 1000–1022 cm$^{-1}$ are the result of internal asymmetric stretching vibrations of T–O–T. Moreover,
the peaks which were appeared in the range 1470–1486 cm$^{-1}$ are the result of external asymmetric stretching vibrations of T–O–T. The peaks which were appeared in the range 1642–1650 cm$^{-1}$ and 3364–3522 cm$^{-1}$ are the results of bending and stretching vibrations of adsorbed water, respectively [22]. Fig. 4A–D illustrates FE-SEM images of AFe, ANi, ACr, and AZn samples, respectively. The results affirmed that every one of the synthesized products consists of irregular shapes. Fig. 5A–D illustrates the N$_2$ adsorption/desorption isotherms of AFe, ANi, ACr, and AZn samples, respectively. The results affirmed that isotherms of type IV were obtained. Average pore diameter, BET surface area, and total pore volume were estimated in Table 2. Fig. 6A–D illustrates the BJH pore size distribution of AFe, ANi, ACr, and AZn samples, respectively. The results affirmed that every one of the synthesized products possesses three types of pores; micropores (0 nm < pore diameter < 2 nm), mesopores (2 nm < pore diameter < 50 nm), and macropores (pore diameter > 50 nm).

### Table 2 – Surface textures of the AFe, ANi, ACr, and AZn samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>Total pore volume (cc/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFe</td>
<td>334.40</td>
<td>4.423E-1</td>
<td>5.291</td>
</tr>
<tr>
<td>ANi</td>
<td>211.70</td>
<td>1.688E-1</td>
<td>3.190</td>
</tr>
<tr>
<td>ACr</td>
<td>119.60</td>
<td>7.268E-1</td>
<td>24.300</td>
</tr>
<tr>
<td>AZn</td>
<td>19.73</td>
<td>7.401E-2</td>
<td>15.000</td>
</tr>
</tbody>
</table>

### 3.2. Removal of methylene blue dye from aqueous media

#### 3.2.1. Effect of contact time

Fig. 7A,B illustrates the relationship between contact time and both of the % removal ($\%R_0$) which was estimated using Eq. (2) and amount of adsorbed methylene blue dye ($O_t$) which was estimated using Eq. (1), respectively. In the case of increasing contact time, the % removal of dye using AFe, ANi, ACr,
Fig. 5 – N\textsubscript{2} adsorption/desorption isotherms of the AFe (A), ANi (B), ACr (C), and AZn (D) samples.

Fig. 6 – BJH pore size distribution of the AFe (A), ANi (B), ACr (C), and AZn (D) samples.
Parameters affecting on the adsorption processes; time (A&B), pH(C&D), concentration (E&F), and temperature (G&H).

and A\text{Zn} samples increases until it reached ca. 74.38, 70.28, 63.50, and 59.38 at equilibrium times equal ca. 80, 100, 80, and 100 min, respectively. Also, the amount of adsorbed dye using A\text{Fe}, A\text{Ni}, A\text{Cr}, and A\text{Zn} samples increases until it reached ca. 29.75, 28.11, 25.40, and 23.75 mg/g at equilibrium times equal 80, 100, 80, and 100 min, respectively. Kinetic models, for exam-
ple, pseudo-first-order which was described utilizing Eq. (9), pseudo-second-order which was described utilizing Eq. (10), and intra-particle diffusion which was described utilizing Eq. (11) were presented as clarified in Fig. 8A–C, respectively. The results affirmed that the removal processes of methylene blue from aqueous media fitted well with the pseudo-first-order rather than the pseudo-second-order. This is clarified on the basis that the correlation coefficient of the pseudo-second-order is lower than that of the pseudo-first-order. Also, plotting $O_t$ against $t^{0.5}$ produces straight lines have strong correlation
coefficients but they do not pass through the origin. Hence, the intra-particle diffusion model is not the only mechanism that controls the removal processes. Every one of the constants, which were estimated utilizing the previously kinetic models, was clarified in Table 3.

3.2.2. Effect of pH

Fig. 7CD illustrates the relationship between pH and both of the % removal (%R_{pH}) which was estimated using Eq. (4) and amount of adsorbed dye (O_{ads}) which was estimated using Eq. (3), respectively. In the case of increasing pH, the % removal of dye using AFe, ANi, ACr, and AZn samples increases until it reached ca.80.49, 77.99, 70.51, and 68.75 at pH 9, respectively. Also, the amount of adsorbed dye using AFe, ANi, ACr, and AZn samples increases until it reached ca. 32.12, 31.12, 28.21, and 27.75 mg/g at pH 9, respectively. This is explained because the surface of the amorphous products is surrounded by positive hydrogen ions at pH values less than pH_{ZPC}. Hence, repulsion established between the surface of amorphous products and positive dye ions. The net result is a decrease in the value of the amount of adsorbed dye and % removal. Also, the surface of the amorphous products is surrounded by negative hydroxide ions at pH values greater than pH_{ZPC}. Hence, attraction established between the surface of amorphous products and negative dye ions. The net result is an increase in the value of the amount of adsorbed dye and % removal. pH_{ZPC} values of AFe, ANi, ACr, and AZn products were ca. 7.65, 8.01, 6.58, and 6.09, respectively as clarified in Fig. 8F.

3.2.3. Effect of concentration

Fig. 7EF illustrates the relationship between initial methylene blue dye concentration and both of the % removal (%R) which was estimated using Eq. (6) and amount of adsorbed dye (O_{ads}) which was estimated using Eq. (5), respectively. It was noticed that when the primary concentration of methylene blue dye increased both of % removal and amount of adsorbed dye decreased and increased, respectively. Adsorption isotherms, for example, Langmuir which was described utilizing Eq. (12) and Freundlich which was described utilizing Eq. (13) were presented as shown in Fig. 8DE, respectively. The removal processes fitted well with the Freundlich rather than the Langmuir. This is clarified on the basis that the correlation coefficient of the Freundlich isotherm is higher than that of the Langmuir. Every one of the constants, which were estimated using the previously adsorption models, was clarified in Table 4. Freundlich maximum adsorption capacities (O_{mf}, mg/g), which was estimated using Eq. (14), of AFe, ANi, ACr, and AZn adsorbents were ca. 53.79, 48.70, 41.41, and 36.51, respectively.

3.2.4. Effect of temperature

Fig. 7G,H shows the relationship between temperature and both of the % removal (%R_{T}) which was estimated using Eq. (8) and amount of adsorbed dye (Q_{2}) which was estimated using Eq. (7), respectively. In the case of increasing temperature, the amount of adsorbed dye or % removal decreased. Fig. 9 illustrates the relationship between ln K_{d} and 1/T (Eqs. 15–18). Table 5 contains the ΔH, ΔG, and ΔS thermodynamic parameters. The results affirmed that the removal processes were spontaneous due to the negative ΔG values. Also, the removal processes were exothermic and physical because the
values of ΔH° are negative and less than 40 KJ/mole, respectively.

3.2.5. Regeneration of amorphous products and comparison with other adsorbents in the literature
The synthesized amorphous products were regenerated and reused up to four cycles as described in the experimental part without changing their efficiency. Table 6 contains the adsorption capacities of AFe, ANi, ACh, and AZn, and other adsorbents in the literature toward methylene blue dye. Many adsorbents were used for removing the organic dyes such as methylene blue dye, for example, kaolin modified with graphene oxide, raw kaolin, magnetic multi-wall carbon nanotube, zeolite, coir pith carbon, silicon dioxide, carbon nanotubes, alginate, poly(styrene-alt-maleic anhydride), poly(3-methylthiophen)e/sawdust, polypyrrole/titanium dioxide, and carbon-based agro-materials [11,41–49]. But, such materials are characterized by the high cost due to the consumption of energy and expensive chemicals during their preparation. Our amorphous products form extraordinary importance for removing methylene blue dye due to their simple cost, easy production, and excellent porosity.

4. Conclusions
Amorphous adsorbents abbreviated as AFe, ANi, ACh, and AZn were synthesized using the gelation method. Broad peak in the range 2θ = 20–40 was gotten for every one of the synthesized samples. Thus, the synthesized products were non-crystalline. The EDS results showed that the AFe, ANi, ACh, and AZn adsorbents were composed of silicon, carbon, and oxygen as well as iron, nickel, chromium, and zinc, respectively. Also, methylene blue dye was efficiently removed from aqueous media utilizing the amorphous products. Besides, the removal of methylene blue dye from aqueous media was assessed via studying some variables, for example, the concentration of dye, time, adsorption pH, temperature of dye solution, and reusability of amorphous products.

Conflict of interest
The authors declare that they have no conflicts of interest.

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