Adsorption and kinetic study of Cr(VI) on ZIF-8 based composites

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Abstract

In this study, adsorption of hexavalent chromium has been examined on ZIF-8 and its various composites. ZIF-8 was modified by using amine groups, GO and Mg(OH)₂/GO. ZIF-8, Mg(OH)₂/GO, ZIF-8/NH₂, ZIF-8/Mg(OH)₂/GO, ZIF-8/NH₂/GO and ZIF-8/NH₂/Mg(OH)₂/GO was studied for Cr(VI) adsorption Several characterization techniques were used for the structural and surface characterization such as Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller ( BET) surface area analyzer. The impact of various adsorption parameters (contact time, pH, initial concentration of Cr(VI) and absorbent dosage) was studied in batch experiments. Different kinetic and isotherm models were applied on equilibrium data. The adsorption process of ZIF-8 and its composites was explained by pseudo-second-order kinetic model as well as Langmuir isotherm, with maximum removal efficiency of 98% for Cr(VI) by ZIF-8/NH₂/Mg(OH)₂/GO.

1. Introduction

Water pollution is the prime ecological complication encountered today, which give rise to ecological instability causing destructive influences on flora and fauna fatalities of the biosphere. As reported by the WHO, 1.2 million people use water without health assurance, resulting in almost 30,000 deaths every day and diseases worldwide [1, 2]. Quick development and expansion of industries have caused heavy environmental pollution. Heavy metal injection in potable water is the most dangerous impact of this waste [3]. Among several heavy metals in the aquatic environment, Cr(VI) due to its toxicity and water solubility [4] has the most astounding hurtful impact on the surroundings, particularly water assets [5]. The wide usage of chromium in tanning, metallurgy, electroplating and related industries has caused the release of chromium at numerous sites [6]. Hexavalent chromium is a substantial metals which is broadly utilized in industries e.g. tanning, dyeing, pigments, photography, textiles and electroplating [7]. In this manner, the wastewater released from the specified sources may contain Cr(VI) higher than the allowed limit. High accumulation of Cr(VI) can be a reason for significant dangers to living organisms. Chromium oxidation states are Cr(III) and Cr(VI) [8]. Cr (VI) is comparatively more toxic and carcinogenic to humans [9, 10]. As exhibited by the US environmental protection agency (EPA), the best reasonable degree of chromium is 0.1 mg l⁻¹ and the best acceptable degree of Cr(III) and Cr(VI) in drinking water is 5 mg/l and 0.05 mg l⁻¹, separately [3]. Therefore, Cr(VI) is considered as the most indispensable contaminant require to be controlled [11]. In Pakistan, chromium concentration found to be exceeded the WHO limit of 0.05 mg l⁻¹. Water analysis of different residential zones of Pakistan such as Kasur, Lahore, Gujarut, Karachi and Khyber Pakhtoonkwa has shown chromium concentration higher than the permissible levels. These elevated levels are due to industrial proximity to the residential zones [12, 13].

Several conservative methods such as electrochemical techniques, membrane filtration, ion exchange and reverse osmosis etc have been applied for the chromium removal but some of these routes are expensive while others are not entirely effective [14–17]. Adsorption is the most useful method for the chromium removal and several studies are focusing on more innovative and effective materials as adsorbents [16]. Adsorption is also a simple and cost efficient technique [18]. Various adsorbents such as clays, activated carbons, chitosan, metal
organic framework (MOFs) and natural zeolites etc have been used and explored for the elimination of heavy metals from aqueous system [19–21]. MOFs consisting of organic linkers attached to metal ions developing a 3D porous structure, are extraordinary materials which have the ability to meet the present heavy metal capture necessities because of high surface area, high porosity, variable pore sizes and various functionalization that can be customize by changing either the metal ions or organic ligands [22]. Zeolitic imidazolate frameworks (ZIFs) is a sub-category of MOFs, have metal ions which are linked by imidazolate ligands, thus developing zeolite like structure [23]. ZIF-8 in particular has Zn$^{2+}$ ions which are in tetrahedral coordination with four imidazolate rings having sodalite (SOD) topology. The high chemical stability, high porosity and surface area, thermal stability and surface functionalization of ZIF-8 make it suitable in adsorption, catalysis and purification [24]. Zeolitic imidazolate frameworks-8 (ZIF-8), with excellent porosity and high surface area, has been widely explored in the removal of pollutants [25–27]. For example, Wang et al [28] proposed ZIF-8/ZnO/P$_2$W$_{18}$ composites for the adsorption of methylene blue and Rhodamine Jiang et al [29] developed Fe$_3$O$_4$ embedded ZIF-8 for the removal of hydroquinone demonstrating adsorption capacity of 2527 mg g$^{-1}$. Sung Hwa Jhung et al [30] used ZIF-8 for the phthalic acid adsorption. Xiong et al [31] showed that ZIF-8 has ultra-high tetracycline adsorption capacity. Furthermore, fast adsorption and removal of benzoic acid by ZIF-8 was reported by Xiu-Ping Yan et al [32]. Similarly adsorption of various heavy metals such as antimony, arsenic, mercury and lead etc has also been studied extensively [33–35]. Furthermore, ZIF-8 has recently been demonstrated as highly efficient material for Cr(VI) removal, with partial reduction process [36]. Particularly, the extremely uniform pore distribution is suitable for entrapping guest molecules and compelling them to participate in chemical coordination in some cases and highly impressive hydrothermal stability grants ZIF-8 with striking adaptability and versatility for chromium adsorption related applications [37].

As a promising carbon material with an exceptional two dimensional highly conjugated chemical structures, graphene and graphene oxide has drawn great attention in these years because of their enhanced conductivity, greater stability, and specific surface area as well as applications in solar cells, super capacitors and catalysis [38, 39]. However, adsorbents comprising graphene for the treatment of wastewater is an emerging field. As graphene is hydrophobic in nature and usually undergoes irreversible agglomeration due to strong van der Waals interactions causing decrease in surface area. This behavior is of course not suitable for water treatment. However, in the last few years, graphene oxide has become a promising adsorbent material [40]. It is not only hydrophilic but also maintains a basic framework having various oxygen containing functional groups such as epoxy, carbonyl, hydroxyl and carboxylic groups etc [41]. High surface area, bonding sites offered by functional groups, high chemical activities etc are those qualities which make GO a suitable candidate for waste water treatment [42, 43] for removing water pollutants because of its charged surface that enables electrostatic interactions. Additionally, magnesium hydroxide (Mg(OH)$_2$), has also drawn significant consideration because of its various uses such as antacid, absorbent and flame retardant. It has the ability to adsorb toxic pollutants from aqueous solutions but its adsorption properties have rarely been studied [44, 45].

Therefore, in the present study, adsorption of hexavalent chromium has been examined on ZIF-8 and its various composites with GO and Mg(OH)$_2$. ZIF-8 was modified by using amine groups, GO and Mg(OH)$_2$/GO. Trend of pure ZIF-8, Mg(OH)$_2$/GO, ZIF-8/NH$_2$, ZIF-8/Mg(OH)$_2$/GO, ZIF-8/NH$_2$/GO and ZIF-8/NH$_2$/Mg(OH)$_2$/GO for Cr(VI) removal was studied where a maximum removal efficiency of 98% of Cr(VI) has been demonstrated.

2. Experimental

2.1. Materials

Cr(VI) stock solution was prepared by potassium dichromate (purchased from Sigma Aldrich, Germany). Zinc nitrate hexahydrate was purchased from DAEJUNG (Korea) and 2-Methyl imidazole was purchased from MERCK (Germany). Batch adsorption tests were performed in bath sonicator.

2.2. Synthesis of ZIF-8

Generally ZIF-8 is synthesized by solvothermal methods using various organic solvents. Several other alternatives e.g. microwave, steam assisted and sonochemical routes have also been reported [46]. ZIF-8 can also be synthesized in natural aqueous system, but these syntheses require extremely diluted environment with exceptionally high MeM concentration with respect to Zn$^{2+}$ (1:70) [47–55]. From application point of view, our synthesis scheme was intended to use high metal concentration in order to get high product yield without using excessive amounts of expensive MeM which was essential for green synthesis. These green approaches so far do not seem to satisfy high yield criteria.

ZIF-8 was prepared by using pH adjusted double base method via sonochemical route. Briefly, Zinc nitrate hexahydrate and 2-methylimidazole were taken in 2:2 molar ratios in 50 ml DMF. This solution was sonicated
for 1 h without cooling. After 1 h, 2 ml of TEA and 3 ml of 10 M NaOH were added to the solution resulting in white precipitates which were washed with DMF and collected by centrifugation. Sample was then suspended in methanol by changing the solvent four times in two days and dried at 80 °C for 6 h in vacuum oven [46].

2.3. Synthesis of ZIF-8/NH$_2$
ZIF-8 was modified with amine groups by using ammonium hydroxide. Briefly, 25 ml of NH$_4$OH and 10 ml of H$_2$O was added to 1.0 g of ZIF-8. This mixture was sonicated for 60 min. After sonication, this mixture was stirred for 24 h at 60 °C followed by centrifugation and removal of supernatant and washing of the residual ZIF-8 with water (thrice). After washing, the ZIF-8/NH$_2$ was dried at 80 °C for 6 h in vacuum oven [56].

2.4. Synthesis of GO
Improved Hummers method was used for the synthesis of GO where 3.0 g of graphite flakes and 18.0 g of KMnO$_4$ were mixed together followed by the addition of 9:1 mixture of H$_2$SO$_4$/H$_3$PO$_4$ (360:40 ml) to this mixture. The exothermic reaction was stirred for 12 h at 60 °C followed by the addition of 400 ml ice and 30% H$_2$O$_2$ (3 ml). Reaction mixture was cooled and centrifuged by using 30% HCl at 4000 rpm for 20 min. The supernatant was decanted and the residue was washed with ethanol and water for numerous times until the pH of the dispersion was 7.0. The residual GO was dried at 60 °C for 24 h [57].

2.5. Synthesis of ZIF-8/Mg(OH)$_2$/GO composite
ZIF-8 and Mg(OH)$_2$/GO composite was synthesized by post synthetic modification. GO dispersion was prepared in water and sonicated for 6 h. Subsequently, ZIF-8 was dispersed in methanol and this dispersion was added to Mg(OH)$_2$/GO suspension followed by sonication for additional 3 h. The resultant mixture was centrifuged and supernatant was decanted and residual composite was dried at 60 °C. Different wt% of GO were added (from 5 wt% to 20 wt%).

2.6. Synthesis of ZIF-8/NH$_2$/GO composite
ZIF-8/NH$_2$ and GO composite was synthesized by post synthetic modification. GO dispersion was prepared in water sonicated for 6 h. Subsequently, ZIF-8/NH$_2$ was dispersed in methanol and the dispersion was added to the suspension of GO followed by sonication for additional 3 h. The resultant mixture was centrifuged and supernatant was decanted and residual composite was dried at 60 °C for 6 h in vacuum oven. Different wt% of GO were added (from 5 wt% to 20 wt%) [24].

2.7. Synthesis of ZIF-8/NH$_2$/Mg(OH)$_2$/GO composite
Amine modified ZIF-8 and Mg(OH)$_2$/GO composite was synthesized by post synthetic modification. Mg(OH)$_2$/GO dispersion was prepared in water and sonicated for 6 h. Subsequently, ZIF-8/NH$_2$ was dispersed in methanol and the dispersion was added to Mg(OH)$_2$/GO suspension followed by sonication for additional 3 h. The resultant mixture was centrifuged and supernatant was decanted and residual composite was dried at 60 °C for 6 h. Different wt% of GO were added (from 5 wt% to 20 wt%).

2.8. Synthesis of Mg(OH)$_2$/GO
10 ml suspension of GO (5 mg ml$^{-1}$) was added to 80 ml water followed by ultra-sonication for 2 h and addition of 20 ml of magnesium nitrate hexa hydrate (0.04 M) to this dispersion. After stirring the mixture for 5 min, an aqueous solution of 10 ml of NaOH (0.5 M) was added drop wise following by stirring the mixture for another 10 min. The solid obtained after centrifugation at 4000 rpm was washed and dried at 80 °C (overnight) [44].

2.9. Characterization
X-ray diffraction (XRD) was done on a STOE Powder x-ray diffractometer with Cu ka radiation. The Fourier-transform infrared (FTIR) spectra were attained using a PerkinElmer SpectrumTM100 system. The samples were measured in the wavenumber of 4000 to 450 cm$^{-1}$ at room temperature. Scanning electron microscopy (SEM) images were collected on a JEOL JSM-64900. The samples were degassed at 180 °C for 18 h for BET surface area measurement.

2.10. Adsorption experiment
For adsorption studies, 2.835 g of K$_2$Cr$_2$O$_7$ was dissolved in 1 L of distilled water to prepare 1000ppm stock solution. Several concentrations of chromium were prepared by diluting the chromium solution with appropriate quantity of water. UV–vis spectrophotometer was used for the determination of Cr(VI) concentration while 1, 5-diphenylcarbazide method was used for the chromium spectrophotometric determination. Calibration was done by using various concentrations of chromium (0, 1, 5, 10, 15, 20 and
The phase and crystalline structure of the materials were studied by using powder x-ray diffractometer. In the
3.1. Characterization
3. Results and discussion
30 ppm. A straight line curve was produced which was further used for the determination of chromium concentration. Cr (VI) removal efficiency (R%) was calculated by the following equation (1)

\[ R\% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100. \] (1)

While metal adsorption was calculated the following equation (2)

\[ q = \left( \frac{C_0 - C_e}{m} \right) V. \] (2)

Where
- \( C_0 = \) Cr(VI) concentration before adsorption in mg/L
- \( C_e = \) Cr(VI) concentration at equilibrium in mg/L
- \( V = \) Solution volume
- \( m(g) = \) amount of absorbent per liter

Adsorption experiments were performed by using ultra sonication bath by varying the parameter that can impact the adsorption process of chromium e.g. adsorbent dosage, pH, contact time, initial chromium concentration. 50 ml of chromium solution was taken for the adsorption at room temperature. Adsorption dosage was varied by keeping all other factors constant. Chromium concentration was changed from 1 to 20 ppm while pH was varied from 1 to 14 by employing 0.1 M HCl and 0.1 M NaOH. Contact time was varied from 5 to 120 min. After obtaining fixed time, adsorbent was separated by filtration and chromium concentration was measured by using UV–vis spectrophotometer at 540 nm.

3. Results and discussion

3.1. Characterization
The phase and crystalline structure of the materials were studied by using powder x-ray diffractometer. In the case of GO, spectral data indicated the presence of diffraction peak at \( \sim 10.22 \) due to (002) plane of GO [58], confirming the formation of GO. Furthermore, spectral analysis data for Mg(OH)\(_2\)/GO showed characteristic peaks for brucite phase, peak broadness of (001) plane also confirmed the synthesis of composite and is comparable with the simulated result [44]. Similarly, in the case of ZIF-8, XRD patterns agree with the solidate (SOD) zeolite type structure where all diffraction peaks confirmed the reflection planes of ZIF-8 sodalite (SOD) topology [59].

In the diffraction data for ZIF-8/Mg(OH)\(_2\)/GO composite all characteristic reflections for the individual components can be seen, confirming the successful synthesis.

In the case of ZIF-8/NH\(_2\) two new small peaks compared to ZIF-8 appear at 13.28° and 15.7° which show possible cage reordering. This cage reordering is possibly due to C=O deprotonation on AIM linker by N–H group during amine modification process [56]. Similarly, ZIF-8/NH\(_2\)/GO composite showed all the characteristics peak of ZIF-8/NH\(_2\) and a small additional reflection for GO [24]. Similarly, ZIF-8/NH\(_2\)/Mg(OH)\(_2\)/GO showed all the characteristic peaks for ZIF-8/NH\(_2\) and Mg(OH)\(_2\)/GO (figures 1(b)–(d)).

Information on the presence of various functional groups and bonding nature of ZIF-8 and its composites were obtained through FTIR. FTIR spectrum of GO shows characteristic peaks at 3433, 2944, 2848, 1736, 1736, 1628, 1389 and 1087 cm\(^{-1}\) which can be credited to O–H, C–H, C=O, C=C and C–O functional groups respectively. Similarly, data for Mg(OH)\(_2\)/GO show peaks at 3433, 2944, 2848, 1736, 1628, 1389, 1087, 861, 671 and 461 cm\(^{-1}\) which can be credited to O–H, C–H, C=O, C=C, C–O and Mg–O vibration respectively. For ZIF-8, peaks at 3423, 3135, 2928, 1605, 1422, 1350, 1139, 990, 770 and 693 cm\(^{-1}\) indicate the existence of O–H, N–H, C–H, C=N, ring stretch, ring bending and aromatic sp\(^2\) CH bending respectively. Regarding FTIR analysis of ZIF-8/NH\(_2\), no major change in the data was found while in the case of ZIF-8/NH\(_2\)/GO, a new peak appear at 1726cm\(^{-1}\) due to C=O of GO. Similarly, composite of ZIF-8/Mg(OH)\(_2\)/GO was found to show all peaks for ZIF-8 with a new peak at 1736 cm\(^{-1}\) for C=O and three new peaks between 400 to 600 cm\(^{-1}\) due to Mg–O vibrations. For ZIF-8/NH\(_2\)/Mg(OH)\(_2\)/GO, again all characteristic peaks of amine ZIF-8 and Mg(OH)\(_2\)/GO could be seen in the FTIR spectrum (figures 2(a)–(c)).

The morphology of ZIF-8 and its composites was studied by using SEM. SEM image of GO shows layered, stacked, well define and interlinked sheets. GO sheets have wrinkled surface texture (figure 3(a)). Similarly, SEM image of Mg(OH)\(_2\)/GO shows irregular Mg(OH)\(_2\) nanoflakes where higher quantity of Mg(OH)\(_2\) on GO sheets causes aggregation (figure 3(b)). SEM image shows dodecahedral crystal of ZIF-8 where sizes of ZIF-8 crystals are between 50 to 80 nm. Due to sonication process employed to synthesize ZIF-8 crystals, crystals are shown to have rough edges (figure 3(c)). As reported for MOFs, sonochemical synthesis causes rapid homogeneous
Figure 1. (a) Simulated XRD pattern of ZIF-8 and Mg(OH)$_2$. (b) XRD patterns of GO and Mg(OH)$_2$/GO (c) ZIF-8 and ZIF-8/NH$_2$ (d) ZIF-8/NH$_2$/GO, ZIF-8/Mg(OH)$_2$/GO and ZIF-8/NH$_2$/Mg(OH)$_2$/GO.

Figure 2. FTIR spectrum of (a) GO and Mg(OH)$_2$/GO (b) ZIF-8 and ZIF-8/NH$_2$ (c) ZIF-8/NH$_2$/Mg(OH)$_2$/GO, ZIF-8/Mg(OH)$_2$/GO and ZIF-8/NH$_2$/GO.
nucleation because of acoustic cavitation produced by ultrasonic waves, which results in a considerable decrease in crystallization time along with significant crystal size reduction \[60\].

Similarly, SEM image of ZIF-8/NH$_2$ shows hexagonal structures which are well defined and have smooth edges (figure 3(d)). In the SEM images of ZIF-8/NH$_2$/GO, well defined hexagonal ZIF-8/NH$_2$ crystals can be seen on GO sheets (figure 3(e)). Similarly, SEM image of ZIF-8/Mg(OH)$_2$/GO shows ZIF-8 crystals along with irregular Mg(OH)$_2$ nanoflakes distributed on GO sheets (figure 3(f)). In the SEM image ZIF-8/NH$_2$/Mg(OH)$_2$/GO composite, hexagonal ZIF-8/NH$_2$ crystals can be seen decorated with Mg(OH)$_2$ nanoflakes distributed on GO sheets (figure 3(g)).

Porosity and specific surface area of the materials were examined by N$_2$ adsorption at 77 K. For the preparation of sample, pretreatment was carried out in a vacuum oven at 180 $^\circ$C for 18 h followed by degassing at 150 $^\circ$C before placing samples for BET analysis. Surface area measured through BET analysis for all the materials is given in below table 1.

| Sr no | Adsorbent                        | BET surface area m$^2$ g$^{-1}$ |
|-------|----------------------------------|---------------------------------|
| 1     | GO                               | 75.62                           |
| 2     | Mg(OH)$_2$/GO                    | 112.76                          |
| 3     | ZIF-8                            | 719                             |
| 4     | ZIF-8/NH$_2$                     | 515.45                          |
| 5     | ZIF-8/NH$_2$/GO                  | 316.73                          |
| 6     | ZIF-8/Mg(OH)$_2$/GO              | 725.37                          |
| 7     | ZIF-8/NH$_2$/Mg(OH)$_2$/GO       | 712.23                          |

Data show that surface area of ZIF-8/Mg(OH)$_2$/GO and ZIF-8/NH$_2$/Mg(OH)$_2$/GO composite is comparable to ZIF-8 while surface area calculated for all other samples was found to be less than ZIF-8. It is also important to note that due to least surface area of GO is (75.62 m$^2$ g$^{-1}$), its composite has also demonstrated...
decreasing trend e.g. ZIF-8/NH₂ (515 m² g⁻¹) and ZIF-8/NH₂/GO (316.73 m² g⁻¹). This trend could be associated with the partial collapse of the crystals of ZIF-8 in the case of ZIF-8/NH₂/GO composite, also depicted in SEM image (figure 3(f)).

3.2. Adsorption studies

3.2.1. Effect of contact time on adsorption

Effect of time for the adsorption was studied from 5 to 200 min for each adsorbent. It was found that adsorption increased for all adsorbents by increasing time until equilibrium. Once reaching the equilibrium, no further adsorption was observed due to complete surface coverage. Equilibrium time for each adsorbent is given in table 2 while trend of removal efficiency and adsorption capacity with respect to time of ZIF-8 and its composites is given in figures 4(a), 4(b).

3.2.2. Effect of pH on adsorption

The optimum pH for the adsorption was calculated by performing experiments at different pH (2–14) keeping all other parameters as constant. Neutral pH was observed to be the best for the adsorption since ZIF-8 and its composite have positive surface charge at this pH which decreases with increasing the pH. As the pH increases the surface of ZIF-8 becomes negatively charged causing electrostatic repulsion between chromate ions and ZIF-8 and its composites. Negative effect of adsorption at lower pH could be associated with the instability of the ZIF-8 and its composites (figures 5(a), 5(b)).

3.2.3. Effect of adsorbent dosage on adsorption

The optimum adsorbent dosage for ZIF-8 and its composite was determined by performing adsorption experiment at various initial concentrations keeping all other parameters constant. By increasing adsorbent dosage, increase in adsorption was observed. However, it could also be found that in certain cases, increasing adsorbent dosage also lead to decrease in adsorption which is assumed to be due to particles aggregation causing decrease in active sites (table 3) (figures 6(a), 6(b)).

| S. No. | Adsorbents                        | Optimum time for adsorption (min) |
|--------|----------------------------------|-----------------------------------|
| 1      | Mg(OH)₂/GO                       | 60                                |
| 2      | ZIF-8                            | 80                                |
| 3      | ZIF-8/NH₂                         | 60                                |
| 4      | ZIF-8/NH₂/GO                     | 60                                |
| 5      | ZIF-8/Mg(OH)₂/GO                 | 60                                |
| 6      | ZIF-8/NH₂/Mg(OH)₂/GO             | 40                                |

Figure 4. (a) Removal efficiency (b) adsorption capacity of Mg(OH)₂/GO, ZIF-8, ZIF-8/NH₂, ZIF-8/NH₂/GO, ZIF-8/Mg(OH)₂/GO and ZIF-8/NH₂/Mg(OH)₂/GO with respect to time.
3.2.4. Effect of initial Cr(VI) concentration on adsorption

Chromium uptake by ZIF-8 and its composites was found to be enhanced with increase in the initial chromium concentration while adsorption process ceases when all the adsorption sites are occupied and no further increase in removal efficiency could be observed (figures 7(a), (b)) (table 4).

Similarly, to study the availability of molecules at equilibrium between solid and liquid phases, various isotherms were employed namely Langmuir model and Freundlich model. Results of both applied models demonstrate strong agreement with Langmuir isotherm having suitable correlation coefficients. According to the obtained data, binding sites have equal distribution of energies over nanocomposite surface and (adsorbed) molecular interaction was minimized. In a similar manner, adsorption kinetics data were also calculated.

Reaction kinetics explains impact of contact time on the elements. Several models are available for analyzing adsorption kinetics or reaction mechanisms such as zero, first, second, third order, pseudo first, first order reversible, second order and the Elovich.

Table 3. Optimum adsorbent dosage for chromium adsorption

| S. No. | Adsorbents            | Dosage (mg) |
|--------|-----------------------|-------------|
| 1      | Mg(OH)$_2$/GO         | 200         |
| 2      | ZIF-8                 | 500         |
| 3      | ZIF-8/NH$_2$          | 150         |
| 4      | ZIF-8/NH$_2$/GO       | 150         |
| 5      | ZIF-8/Mg(OH)$_2$/GO   | 100         |
| 6      | ZIF-8/NH$_2$/Mg(OH)$_2$/GO | 100      |

Figure 5. (a) Removal efficiency (b) adsorption capacity of Mg(OH)$_2$/GO, ZIF-8, ZIF-8/NH$_2$, ZIF-8/NH$_2$/GO, ZIF-8/Mg(OH)$_2$/GO and ZIF-8/NH$_2$/Mg(OH)$_2$/GO with respect to pH.

Figure 6. (a) Removal efficiency (b) adsorption capacity of Mg(OH)$_2$/GO, ZIF-8, ZIF-8/NH$_2$, ZIF-8/NH$_2$/GO, ZIF-8/Mg(OH)$_2$/GO and ZIF-8/NH$_2$/Mg(OH)$_2$/GO with respect to adsorbent dosage.

3.2.4. Effect of initial Cr(VI) concentration on adsorption

Chromium uptake by ZIF-8 and its composites was found to be enhanced with increase in the initial chromium concentration while adsorption process ceases when all the adsorption sites are occupied and no further increase in removal efficiency could be observed (figures 7(a), (b)) (table 4).

Similarly, to study the availability of molecules at equilibrium between solid and liquid phases, various isotherms were employed namely Langmuir model and Freundlich model. Results of both applied models demonstrate strong agreement with Langmuir isotherm having suitable correlation coefficients. According to the obtained data, binding sites have equal distribution of energies over nanocomposite surface and (adsorbed) molecular interaction was minimized. In a similar manner, adsorption kinetics data were also calculated.

Reaction kinetics explains impact of contact time on the elements. Several models are available for analyzing adsorption kinetics or reaction mechanisms such as zero, first, second, third order, pseudo first, first order reversible, second order and the Elovich.
We have demonstrated that in our case, adsorption follows the Pseudo second order model since $R^2$ values for pseudo second order are comparatively lower. The results show slower adsorption kinetics for all the adsorbents. As the adsorption is following pseudo second order model, it could be concluded that rate limiting step has involved chemisorption i.e. valence forces are involved due to exchange and sharing of electrons.

3.3. Adsorption mechanism
The selective adsorption ability of ZIF-8 is associated with its distinct structure having surface functionality via NH$_2$, GO and Mg(OH)$_2$ groups and unique pore structure. CrO$_4^{2-}$ exists at pH $\geq$ 7. We have conducted all our batch experiments at pH of 7.0 due to relative instability of ZIF-8 in highly acidic and basic conditions. So CrO$_4^{2-}$ is our main specie which gets adsorbed and faces competition with hydroxyl ions. Since ZIF-8 has positive surface charge at neutral pH, an adsorption coupled reduction mechanism can be proposed in the present case. Surface of ZIF-8 is positively charged because $-$N$\equiv$, $-$NH$-$ and $-$NH$_2$ groups of imidazolate ligands are protonated in aqueous system which provides electrostatic interaction for Cr(VI) for adsorption resulting in the production of Cr(III). Bonding of hydroxyl groups to zinc and presence of GO and Mg(OH)$_2$ may further enhance interaction with Cr(III), reducing it partly to Cr(III). Furthermore, positively charged Mg$^{2+}$ may also coordinate with oxyanion, causing chemisorption and providing a platform for adsorption of species. Therefore, it can well be proposed that all functional groups supposedly have synergistic effect in promoting adsorption process of Cr(VI) species [36, 61, 62].

4. Adsorption capacity and removal efficiency
ZIF-8 and its composites are good candidates for the removal of hexavalent chromium since ZIF-8 has reasonably high surface area with the pore volume suitable for the size of chromate ion. Additionally, amine modified ZIF-8 demonstrated increased adsorption capacity as well as removal efficiency where amine groups act as chelating agents for chromium ions. Furthermore, in order to provide better support for ZIF-8 and additional adsorption sites for chromium ions, composite of ZIF-8 with graphene oxide was prepared. However, incorporation of graphene oxide caused a decrease in the surface area. Therefore, in order to address this issue, GO was decorated with magnesium hydroxide nano flakes which has not only increased surface area but also increased cationic character. Such modification has demonstrated synergistic effects of magnesium hydroxide decorated GO and ZIF-8/NH$_2$ resulting in increase in the removal efficiency and adsorption capacity (table 5).

![Figure 7. (a) Removal efficiency (b) adsorption capacity of Mg(OH)$_2$/GO, ZIF-8, ZIF-8/NH$_2$, ZIF-8/NH$_2$/GO, ZIF-8/Mg(OH)$_2$/GO and ZIF-8/NH$_2$/Mg(OH)$_2$/GO with respect to initial chromium concentration.](image)

| S. no. | Adsorbents          | Initial chromium concentration (ppm) |
|-------|---------------------|-------------------------------------|
| 1     | Mg(OH)$_2$/GO       | 10                                  |
| 2     | ZIF-8               | 5                                   |
| 3     | ZIF-8/NH$_2$        | 10                                  |
| 4     | ZIF-8/NH$_2$/GO     | 10                                  |
| 5     | ZIF-8/Mg(OH)$_2$/GO | 10                                  |
| 6     | ZIF-8/NH$_2$/Mg(OH)$_2$/GO | 10 |
5. Comparison of prepared adsorbent with reported materials

Table 6 shows the comparison of adsorbent activity of ZIF-8/NH$_2$/Mg(OH)$_2$/GO with other adsorbents in the removal of Cr(VI) from aqueous systems in terms of adsorbent dosage, adsorption capacity (mg g$^{-1}$), removal efficiency (R%) which were reported in recent years.

It is evident from the data that adsorption capacity of ZIF-8/NH$_2$/Mg(OH)$_2$/GO is higher in comparison to all other adsorbents. Furthermore, in terms of relatively short contact time and adsorbent dosage, neutral environment, low cost production, and chemical stability, our reported composite can be considered as an alternative and better choice for removing toxic Cr(VI) from water.

6. Conclusions

ZIF-8, ZIF-8/NH$_2$ and their composites with GO and Mg(OH)$_2$/GO were synthesized successfully by using sonochemical and hydrothermal synthesis. Prepared samples were characterized and used for chromate ions removal from the aqueous medium. These nano composites, especially ZIF-8/NH$_2$/Mg(OH)$_2$/GO composite have demonstrated to be excellent adsorbents for the Cr (VI) removal. Experimental data are well fitted with the adsorption-isotherm models and follow pseudo-second-order-kinetics. The results have demonstrated that the removal efficiency was influenced by the morphology, abundant external surface area, accessibility of functional groups as well as the temperature and pH of the system. Due to low cost, simple and room temperature synthesis and low toxicity, these nano composites are considered to be potential materials as adsorbents for chromium removal from the aqueous media.

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