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### **ORIGINAL ARTICLE**

# Graphene oxide/ZnO nanocomposites for efficient removal of heavy metal and organic contaminants from water



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#### **KEYWORDS**

Graphene oxide; ZnO nanocomposite; Water contamination; Water treatment **Abstract** The graphene oxide-zinc oxide (GO-ZnO) nanocomposite was fabricated and applied as the adsorbent to survey the adsorption characteristics of the adsorbates of organic and inorganic water contaminations in an aqueous solution. The synthesized nanocomposite has been characterized using X-ray powder diffraction (XRD) and Scanning electron microscope (SEM), indicating that the nanocomposite was synthesized successfully. The impact of the initial solution concentrations and pH was investigated, indicating that the synthesized compound has a high adsorption capacity and capability to remove both organic and inorganic contamination. The kinetic adsorption could also be well described by Pseudo-second-order (PSO) kinetic expressions. The equilibrium adsorption findings indicated that the Langmuir was more suitable than Temkin, Freundlich, and Flory-Higgins models. High adsorption capacity of 99.00, 125, 121.95 and 277.78 mg/g respectiviety for Methylene blue (MB), Methyl orange (MO), Cd<sup>2+</sup>, and Pb<sup>2+</sup> The antibacterial assay was also performed using Staphylococcus aureus and Escherichia coli in which the ZnO nanocomposite proved to be an effective Bactericide that inhibits the growth of bacteria. The obtained results indicated that the synthesized GO-ZnO nanocomposites are ideal adsorbents

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#### Nomenclature

CEU	Calany farming write	V	Ensure distance initial constant for a $z^{-1}(t, -z^{-1})/t$
CFU	Colony-forming units	ĸ <sub>F</sub>	Freundlich empirical constant [(mg.g <sup>-1</sup> )(L.mg <sup>-1</sup> ) <sup>1</sup>
GO	Graphene oxide		"]
GO-ZnC	O Graphene oxide-zinc oxide	$K_{FH}$	The flory-Huggins equilibrium constant $(L.mol^{-1})$
MB	Methylene blue	K <sub>L</sub>	Langmuir constant (L.mg <sup>-1</sup> )
MO	Methyl orange	K <sub>T</sub>	Temkin isotherm constant (L.g <sup>-1</sup> )
SDS	Sodium dodecyl sulfate	$n_{\rm F}$	Adsorption intensity
SEM	Scanning electron microscope	n <sub>FH</sub>	Number of adsorbates occupying adsorption sites
XRD	X-ray powder diffraction	$q_{Cal}$ .	Calculated adsorption capacity $(mg.g^{-1})$
ZnO	Zinc oxide	q <sub>e</sub>	Sorption capacity at the equilibrium time $(mg.g^{-1})$
$\Delta G^{\circ}$	Gibbs free energy (kJ.mol <sup>-1</sup> )	q <sub>Exp.</sub>	Experimental adsorption capacity (mg.g <sup>-1</sup> )
b <sub>T</sub>	Temkin constant relating to the adsorption heat	q <sub>Max.</sub>	Maximum adsorption capacity (mg.g <sup>-1</sup> )
	$(J.mol^{-1})$	$q_t$	Sorption capacity at time t $(mg.g^{-1})$
Ce	Concentration at equilibrium time (mg.L <sup>-1</sup> )	$\mathbb{R}^2$	Coefficient of determination
Ci	Concentration at the initial time $(mg.L^{-1})$	R <sub>L</sub>	Langmuir separation factor
$\mathbf{k}_1$	The pseudo-first-order rate constant $(min.^{-1})$	θ	Degree of surface coverage
k <sub>2</sub>	Pseudo-second-order rate constant $(g.mg^{-1}.min.^{-1})$	λ	Wavelength (nm)

for the MB, MO, Cd<sup>2+</sup>, and Pb<sup>2+</sup> removals in an aqueous solution.
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#### 1. Introduction

The rapid process of industrialization as well as population growth in the last half century has made planning and action to solve the problem of water shortage and water pollutants one of the main priorities for countries. According to the United Nations Global Water Development Report 2020, it is estimated that the water demand of manufacturing industries will increase significantly by 400% by 2050 (Yaqoob et al., 2020). Moreover, the production of wastewater that contains different substances such as heavy metals, chlorinated hydrocarbons, biological wastes, radioactive substances, negative ions, and toxic dyes will result in a wealth of environmental damage (Khurana et al., 2017). Therefore, considering the problem of water shortage and the ever-increasing expansion of industries, the treatment of industrial wastewater is of particular importance to meet part of this growing need (Moradi et al., 2022). Furthermore, the colors are widely used in industries and these dyes are toxic and even carcinogenic in some cases, disposing of the wastewater of these industries in water can lead to the pollution of biological resources and many other harms (Hosseini et al., 2016).

Most of the dyes used in industries are organic structures soluble or not soluble in water, which causes the water to become turbid and then reduce oxygen content and photosynthesis process, thus changing the ecosystem of aquatic organisms. Furthermore, they cause diseases and mutations in organisms and microorganisms in water (Ferreira et al., 2020). In general, the dyes used in industries are divided into two groups, ionic (negatively and positively charged ions) and nonionic. Some colors such as azo colors, having a molecular structure including the azo-chromophore group (-N=N-), are widely used since they are stable and economical (Moradi et al., 2022). Methylene blue (MB), which is mainly used for dyeing cotton, cellulose, and silk fibers, belongs to the category of thiazine cationic dyes. Despite the value of MB in scientific discussions, it has harmful effects on humans and the environment because of its toxicity and solubility in water. Methyl orange (MO), used in the textile industry, is also one of the most stable azo dyes and is resistant to biodegradation. A major part of textile industry wastewater is made up of dyes and salts with high concentrations (Tsade Kara et al., 2021).

Some wastewater may contain heavy metals, which makes wastewater treatment complicated. The results of toxicological studies show that cadmium (Cd), as the most toxic biological heavy metal, is a part of some metallic dyes (Visa and Duta, 2013). This heavy metal has no physiological function and is often known as a poison, leading to a range of bone-related diseases, kidney failure, and anemia (Genchi et al., 2020). In the same way, lead (Pb) is a metal element that can be considered a water pollutant.

According to what has been said, to have a healthier and cleaner environment, removing MB, MO, Cd, and Pb from wastewater seems essential. Some of the wastewater treatment methods containing MB and MO dyes such as photocatalytic degradation, surface adsorption, electrochemical, ion exchange, and catalytic processes have been investigated. Among the methods of removing dyes and heavy metals, absorption has been taken into consideration because it is economical, easy to process, and able to absorb pollutants (Tsade Kara et al., 2021). Graphene oxide (GO) can be mentioned as a suitable adsorbent due to its unique properties such as very high specific surface area and other electrical and mechanical properties. Due to the presence of oxygen, GO has a high negative charge density, which allows the connection of metal ions and cationic organic compounds such as MB (Moradi et al., 2022); (Ferreira et al., 2020). Although GO has been specially considered as an adsorbent for both dye pollution and heavy metals. Some limitations have caused the correction of the functional weaknesses of this material to achieve greater stability and more appropriate performance (Singh, 2022). Therefore, it is desirable to combine GO with materials such as polymers, silica, and other structures, especially metal oxides that reduce the energy gap and also reduce the electron-hole pair rates (Joshi and Gogate, 2012). Graphene composites and other compounds related to it have been significantly used in the treatment of wastewater containing anionic and cationic dyes. Therefore, according to the publications, these materials purify

wastewater containing dyed substances as well as pollution related to heavy metals (Khurana et al., 2017). Also, according to some considerations, since the 1970s, the use of metal oxides for wastewater treatment has been considered, which include ZnO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, WO<sub>3</sub>,  $ZrO_2$ , and  $V_2O_5$ . In the meantime, ZnO has received special attention due to its characteristics and ease of synthesis, and compatibility with the environment (Yaqoob et al., 2020). The suitable properties of ZnO metal oxide for its combination with GO, including high electron mobility, make the composite resulting from the combination of GO and ZnO particles, to overcome limitations such as reduced activity due to the wide energy band gap for ZnO. In other words, the combination with GO causes a delay in the recombination of ZnO-based catalvsts and also results in an increase in the surface area and an increase in the adsorption capacity in GO (Hosseini et al., 2016); (Khayatian et al., 2018). In this paper, the synthesis of a novel graphene oxide nanocomposite has been studied, in which the nanocomposite has been synthesized and characterized. The adsorption of industrial wastewater pollutants, organic contamination, and heavy metals has been studied to refine the wastewater for agriculture of household usage.

#### 2. Materials and methods

#### 2.1. Reagents

Graphite powder (average particle size ~ 50  $\mu$ m, purity > 99.5 %) and H<sub>3</sub>PO<sub>4</sub> solution (85 wt%) were supplied from Merck Company (Darmstadt, Germany). Zinc oxide (ZnO) nanocarriers (average particle size < 100 nm, purity > 99.5 %), adsorbates of MO (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S) as an anionic dye and MB (C<sub>16</sub>H<sub>18</sub> N<sub>3</sub>ClS) as a cationic dye, solutions of KMnO<sub>4</sub> (0.02 mol.L<sup>-1</sup> (0.1 N)), H<sub>2</sub>O<sub>2</sub> (30 wt%), sodium dodecyl sulfate (SDS) (ACS reagent, ~ 99 %), Cadmium Chloride (CdCl<sub>2</sub>), lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>), and NaOH were obtained from Sigma-Aldrich Company (St. Louis, MO, U.S.). Furthermore, extra pure H<sub>2</sub>SO<sub>4</sub> (98 wt%) and HCl (35 wt%) were received from Mojallali company (Mojallali, Iran). All chemicals and reactants were of analytical grade, without any further purification.

#### 2.2. Synthesis of graphene oxide (GO)

As a well-known method, graphene oxide (GO) is dominantly synthesized through the chemical oxidation of natural graphite. In this work, GO was treated by an easy, convenient, and cost-effective method, based on the modified Hummer's method (Oral et al., 2020); (Arabpour et al., 2021). In detail, 70 (mL) of protonated solvent that was prepared through a mixture of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> (9:1 vol ratio) was introduced into a beaker containing 0.45 (g) graphite powder and stirred in an ice bath for 20 (min.). Next, 3.5 (g) KMnO<sub>4</sub> as a strong oxidizing agent was slowly added to the mixture at a constant temperature of 5 °C and let to continue the reaction for 2 h. Then, the resultant suspension was heated to 35 °C and eventually ultrasonicated for 1 h. As the final step of the synthesis method, the mixture was added to 70 (mL) of deionized water to dilute and stop the reaction and 2 (mL) of  $H_2O_2$  to remove any metal ions from the oxidizer. The resulting yellow-brown liquid indicated a considerable extent of oxidation. Ultimately, the remaining solid material which was obtained through filter paper and funnel was treated with 5 % HCl aqueous solution, centrifuged (Hettich, EBA 20), and washed with deionized water repeatedly until the pH of the reaction product was essentially neutral. The synthesized brown-black material was eventually dried in a vacuum oven at 50 °C for 24 h.

# 2.3. Synthesis of graphene oxide-ZnO (GO-ZnO) nanocomposite

The nanocomposites (GO-ZnO 1%, GO-ZnO 3%, GO-ZnO 5%) were synthesized based on the solution mixing method. To obtain the ZnO dispersion, the corresponding amounts of ZnO nanoparticles were sonicated in 50 (mL) of a homogenous mixture of ethanol/water (1:1 vol ratio) for 2 h. The GO's suspensions were obtained by various extents of the synthesized GO dissolved in 50 (mL) of deionized water containing 1 % SDS and put inside the sonicated bath for about a 2 h period. The SDS surfactant improves the suspension process by maintaining uniform colloidal dispersion and preventing metal particle agglomeration. To achieve the homogenous mixture, next, the GO water suspension was added to the ZnO dispersion in equal amounts and sonicated at ambient temperature  $(23 \pm 1 \text{ °C})$ . After 30 (min.) NaOH (1 M) solution was added dropwise till the resulting product was adjusted at the pH = 10. Later, the solution was heated in the water bath for 5 h at an elevated temperature of 85 °C. The precipitate was ultimately collected through centrifugation and washed with deionized water several times, and, at last, it was transferred into an oven at 50 °C for solvent evaporation.

#### 2.4. Structural analysis

The crystalline structure of the synthetic and natural samples was distinguished from the X-ray powder diffraction analysis (XRD) pattern by using the powder diffractometer (EQUINOX-3000, Intel, France) equipped with Cu K<sub>a</sub> radiation ( $\lambda = 1.541$  Å) at 40 (kV) and 30 (mA), with a scanning speed of 2 $\theta = 5/\text{min}$ . between 4 and 90° 2 $\theta$  angular range. To make micro-morphological observations, the synthesized GO and GO-ZnO samples were subjected to Scanning Electron Microscopy (SEM) using a scanning electron microscope (AIS-2100 Seron Technology, Seron Technology, Korea) operating with up to 20 (kV) acceleration voltage field emission gun at 25 Kx (different) magnifications. Notably, all sample fragments were previously sputter coated through an ultrathin layer of conductive gold.

#### 2.5. Batch adsorption assay

The batch adsorption method was applied to evaluate. The photocatalytic performance of both organometallic species and organic components of typical metathesis reactions. The stock solutions of MB, MO,  $Cd^{2+}$ , and  $Pb^{2+}$  pollutants (1000 ppm) were set up according to the dilution method in the deionized water. A given proportion of the GO-ZnO absorbent was dispersed in a flask of 25 (mL) for each stock solution. The flasks were then transferred to an incubator shaker (150 rpm, SI-100R, tradekorea, South Korea) and thoroughly agitated for 2 h at room temperature (23 ± 1 °C). The pH extent was adjusted by using NaOH (0.1 N) and HNO<sub>3</sub> solutions (0.1 N). Having been filtered to separate the dye solutions from the adsorbent, all solutions were analyzed to determine the contaminant concentration with Uv–Vis spec-

troscopy. In this work, a UV–Vis. spectrophotometer (Lambda 25, Perkin Elmer, U.S.) was used, and the recorded UV–Vis. spectra have been measured at  $\lambda_{MB and MO} = 664$  (nm), while Cd<sup>2+</sup> and Pb<sup>2+</sup> concentrations were determined through atomic absorption (AA) methodology.

Kinetics and isotherm studies were eventually applied to the obtained sorption data. The measure of sorption capacity  $q_t$  (mg.g<sup>-1</sup>) and the removal efficiency (%R) were determined according to Eqs. (1) and (2), respectively (Dan et al., 2023):

SorptionCapacity 
$$q_t = \frac{V(C_t - C_t)}{m}$$
 (1)

Removal efficiency (%) = 
$$\frac{100 \times (C_i - C_e)}{C_i}$$
 (2)

where,  $C_i$  and  $C_t$  refer to pollutants' concentration at initial and any time in the solution (mg.L<sup>-1</sup>), respectively, V is the adsorbate solution volume (mL), and m is the adsorbent mass (mg). It is noted that the entire set of trials was carried out at least in triplicate. In the long time, the adsorption reaches to the equilibrium and in this state, adsorbate concentration on adsorbent and solution denote as  $q_e$  and  $C_e$ .

#### 2.6. Adsorption kinetic

The adsorption kinetic trials were conducted by shaking the desired GO-ZnO absorbent (10 mg) with diverse initial concentrations of contaminants for diverse time interims (30–720 min.) as separate experiments. Having been centrifuged to separate the solutions from the solid sorbent, all samples were subjected to determine the dyes and cations concentrations through UV–Vis. spectrophotometer and AA technique, respectively. Solutions pH was also fixed to 2 and 12 for the dye MB and MO and 2 and 10 for the Cd<sup>2+</sup> and Pb<sup>2+</sup> removal, respectively, except where the pH effect on the adsorption process was investigated and controlled by supplementing drops of HNO<sub>3</sub> or KOH (1 M) solution. From these measurements, the extent of adsorbed pollutants at the anytime q<sub>t</sub> (mg.g<sup>-1</sup>) was calculated as Eq. (1) for any time (Iriel et al., 2018); (Banivaheb et al., 2021):

#### 2.7. Adsorption isotherms

The isotherm studies were explored to predict the adsorption mechanisms and the distribution behavior of the adsorbate dyes and ions between the solid and fluid. The impact of the dyes and heavy metals' initial concentrations on removal efficiency was understood by GO-ZnO absorbent (10 mg) in contact with diverse initial concentrations of contaminants ( $C_{i}$ ,  $_{MB} = 10-125$ ;  $C_{i}$ ,  $_{MO} = 10-150$ ;  $C_{i, Cd}^{2+} = 10-100$ ;  $C_{i, Pb}^{2+} = 10-175$  mg.L<sup>-1</sup>) as separated experiments at constant pH 7. Having been centrifuged to separate the dye solutions from the solid sorbent, all samples were subjected to determine the pollutants concentrations through UV–Vis. and AA spectrophotometers.

#### 2.8. Influence of pH

To evaluate the pH impact on the pollutant's optimum uptake, the weighted quantity of the synthesized GO-ZnO absorbent (10 mg) was rigorously shaken with 25 (mL) of MB, MO, and  $Cd^{2+}$  (50 mg.L<sup>-1</sup>) and Pb<sup>2+</sup> (100 mg.L<sup>-1</sup>) solutions at various pH values (2–12) for 2 h, as separated tests. Eventually, the solutions and solids were separated, and the filtrate was collected for optimal pH investigation.

#### 2.9. Antibacterial activity

Disk diffusion technique was implemented to investigate the antibacterial function of synthesized nanomaterials. The zone inhibition method was applied to study the antibacterial activity of nanostructures. In this case, two gram-positive bacterial strains of Staphylococcus Aureus (ATCC 25923) and gramnegative ones of Escherichia Coli (ATCC 11229) were cultured in the nutrient agar medium as maintenance for a wide variety of non-fastidious bacteria. The culture media preparation was finalized by suspending the agar powder (23 g) in highly purified water (1 L) and heating (~45 °C) with frequent agitation for  $\sim 2$  (min.) to completely dissolve the powder. Later, a 15-20 (mL) volume of the ready media was poured into a 60-mm sterile glass petri dish and left standing for  $\sim 30$  min. to solidify. Next, the agar-loaded plates were inoculated with 100 (µL) of 108 Colony-forming units (CFU).mL<sup>-1</sup> using standard microorganisms' suspensions. The filter paper discs that were thoroughly sterilized were placed on top of inoculated plates and 15 (µL) of the nanomaterial solutions (a quantity of 50 (mg) samples containing 10 % solution in purified water) were pipetted on the disks. Eventually, test samples were firmly sealed to alleviate chances of any contamination and incubated with a shaker (150 rpm) at 37 °C overnight.

#### 3. Results and discussion

#### 3.1. Structural and morphological characterization

The XRD patterns of the pure GO and GO-ZnO nanocomposite are represented in Fig. 1. As observed, no impurity peaks were observed, thereby demonstrating that the resulting composition was a combination of GO and GO-ZnO with high purity and no impurities had been produced. The obtained XRD spectrum also represents the characterization of pristine graphene oxide sheet by diffraction peaks at  $2\theta$  of 10.77° related to (001). This is on account of the presence of the functional groups, including oxygen, on the graphene/graphene



Fig. 1 X-ray diffractograms for the GO and GO-ZnO nanocomposites.

oxide layers and the increment of the interlayer distance as well. The obtained XRD pattern of the synthetic nanocomposite expresses the doping of different levels of GO resulting in the wider peak shape and lower intensity of GO-ZnO compared to pristine GO and a decline in crystallinity of the nanocomposite sample. In detail, with regards to previous studies (Malekkiani et al., 2022; Ghoreishi et al., 2013), ZnO characterization peaks represent ranging from  $2\theta$  of  $30.0^{\circ}$  to 70.0°. As observed in Fig. 1, the nanocomposite peaks have gotten weaker and shifted to the right reflecting the coordination reaction between  $Zn^{2+}$  and GO, which, in turn, leads to altering the GO-ZnO crystallinity. Therefore, it could be concluded that the crystal structure of ZnO nanoparticles had been successfully transformed into the synthetic nanostructure and positioned on the outer surface of the GO-ZnO. However, a new weak diffraction peak approximately at  $2\theta$  of  $26^{\circ}$  that is related to (002) was observed, indicating the reduction of the graphene oxide into the graphene, and subsequently the disordered stacking of graphene sheets in the synthesized nanocomposite (Ghoreishi et al., 2013). Indeed, the weakness of the graphene diffraction peak ( $2\theta = 26^{\circ}$ ) related to the insignificant mass ratio of graphene in comparison with ZnO demonstrates the formation of graphene sheets that have been redecorated by hexagonal ZnO nanoparticles.

The surface topography of the samples detected by SEM at various magnifications is depicted in Fig. 2. As illustrated in the inset of Fig. 2(A-B), the morphology of the graphene oxide surface was smooth indicating that it comprised tremendously stacked planes. Owing to cavities that were firmly connected, the edges of the graphene oxide sheets were inclined to fold to create highly crumpled multilayers, resulting in fading of sheet-like structures. However, the SEM images in Fig. 2(C-D) revealed that the introduction of ZnO nanoparticles uniformly dispersing over the GO matrix diminished the congestion, and the surface smoothness disappeared by creating hollow-shaped spaces between the GO layers. As expected, on account of the 3D cross-linked nature of ZnO nanoparticles that tend to be homogeneously coated on the surface of the graphene oxide sheets, the flake-like GO-ZnO morphology was successfully formed over the reaction (Ghoreishi et al., 2013). Moreover, the SEM microphotographs given in Fig. 2 indicated that the nanoparticles were acceptably attached to the GO surface, and the GO matrix considerably prevented the agglomeration of the supplemented nanoparticles, which is due to the uniform distribution and good coupling nature of ZnO. It is noteworthy that the uniform and small agglomeration of the nanoparticles contributes to higher dyes and cations adsorption on the nanocomposite surface.



Fig. 2 Scanning electron micro-graphs of the GO (A and B) and GO-ZnO nanocomposite (C and D); Transmission electron micrographs with a magnification of 10.00 KX (A and C) and 50.00 KX (B and D).

#### 3.2. Pollutant adsorption study

The adsorption capability evaluation of the synthetic nanocomposite was carried out through its activities on the removal of the MO and MB pollutants as organic targets and desired heavy metals of the  $Cd^{2+}$  and  $Pb^{2+}$ . So, the effect of concentration and pH traces of the solutions were studied for the removal (%) of the contaminants.

#### 3.2.1. Effect of nanoparticle on adsorption process

Graphene oxide (GO) is one of the most common compounds used as an advanced adsorbent due to its unique properties. These properties such as large surface area, high chemical stability, and mechanical properties can vary and depend on the layer count structure of the compound. One of the main disadvantages of GO is the low adsorption capacity that limits its applications in wastewater treatment. One of the approaches to enhance the adsorption capacity of GO is to incorporate it with various compounds such as polymers and metal oxide nanoparticles. ZnO nanoparticles can act as adsorption sites and improve the adsorption properties of GO. In this study, GO-ZnO nanocomposites with various ZnO loading percentages (1%, 3%, and 5%) were synthesized. The adsorption tests of the synthesized nanocomposites were carried out in batch experiments. The results shown in Fig. 3 indicate that the GO-ZnO nanocomposite that contains 3% ZnO shows the highest adsorption efficiency for all the pollutants. The adsorption capacity of the nanocomposites increased as the amount of ZnO loading increases to 3%. The addition of ZnO over 3% to the GO-ZnO structure results in a decrease in the adsorption capacity. The optimal loading percentage of ZnO to achieve the highest adsorption capacity is nanocomposite containing 3% ZnO. The high pollutant adsorption capacity of the GO-ZnO nanocomposite containing 3% ZnO can be attributed to several phenomena. One of the main reasons is the synergistic effect of the two components. ZnO nanoparticles provide additional adsorption sites while the GO sheets act as an efficient adsorbent due to their large surface area. Also, GO acts as a base that can improve the dispersion and stability of the ZnO nanoparticles in the medium. The nanocomposite that contains 1% ZnO showed the lowest adsorption capacity for all the water pollutants, while the nanocomposite with 5% ZnO showed a lower efficiency compared to the nanocomposite that contains 3% ZnO. The decrease in adsorption efficiency at higher percentages of ZnO can be attributed to the decrease in the surface area of graphene oxide as the percentage of ZnO increased. In addition, an excess of ZnO can also result in the aggregation of ZnO nanoparticles and graphene oxide sheets by forming a new functional group between the GO layers, which might hinder the accessibility of the active sites for adsorption.

#### 3.2.2. Isotherm adsorption assay

The adsorption dependence behavior of the synthesized nanocomposites to the initial concentration of the dyes and heavy metals in the given range shows up in Fig. 4A & A'. The maximum obtained adsorption capacities  $(mg.g^{-1})$  were 96.15 and 122.01 at the concentrations of 125 and 150 (mg. L<sup>-1</sup>) for the MB and MO, and 118.84 and 256.48 at the concentrations of 100 and 175  $(mg.L^{-1})$  for the Cd<sup>2+</sup> and Pb<sup>2+</sup>, respectively. The increase of MB and MO concentration from

10 to 75 (mg.L<sup>-1</sup>) led to a sharp increment of the adsorption capacities up to 93.45 to 118.03 (mg.g<sup>-1</sup>), respectively, while q<sub>e</sub> reached a plateau and set to levels of as illustrated in the graph with more increases of the initial concentration dyes. The same trend would happen to the  $Cd^{2+}$  and  $Pb^{2+}$  with the obtained adsorption capacities up to 106.76 and 253.32  $(mg.g^{-1})$  at the concentrations of 50 and 125  $(mg.L^{-1})$ , respectively. The findings also indicate that with the increase in the adsorbate levels, removal efficiency deteriorated from 97.49% to 30.77%, 98.37% to 32.54%, 95.73% to 47.53%, and 97.10% to 58.62% for MB, MO,  $Cd^{2+}$  and  $Pb^{2+}$ , respectively. The diminished adsorption rate with the increase of the operating parameter of the pollutants' concentrations might be credited to a drop in available active areas for the adsorption. At lower concentrations due to the availability of more adsorption/vacant sites, the concentration gradient between the adsorbate in solution and the adsorbate on the adsorbent tends to be higher. Therefore, through the fast diffusion of into the interparticle matrix, the contaminants effectively interact with the nanocomposite sorbent, leading to enhanced removal efficiency (Malekkiani et al., 2022; Ahmada et al., 2016).

#### 3.2.3. pH dependence

The initial pH adjustment of solutions has a crucial impact on ion exchange and adsorption processes through the protonation of adsorbent chemical functional groups. Indeed, the pH influence on the dyes and heavy metals uptake is related to the adsorbate ionic charge in the solution and the sorbent surface functional groups (Iriel et al., 2018); (Shaban et al., 2018). In this regard, by maintaining other performing parameters as constant, the batch adsorption technique was applied to evaluate the impact of pH ranges of 2-8 and 4-12 on the MB and MO dyes uptakes, respectively (Fig. 4B). At the same time, the relationship between the aqueous media pH and the pollutants removal (%) is graphically illustrated in Fig. 4B. It is obvious that the adsorption capacity of the MB dye increased clearly with increasing pH, up to an equilibrium extent of approximate 6 (at the slightly acidic media), where  $q_e$  was already constant (~83.42 mg.g<sup>-1</sup>). The MB removal efficiency also improved with growing the pH levels and it finally reached a plateau beyond the pH  $\sim$  6, remaining fixed in the alkaline media (pH  $\sim$  8). The GO's dual responsiveness and the role of the metal oxide ZnO are reflected in the synthetic GO-ZnO. The GO surface functional groups, e.g. -COOH, -CHO, -OH, and epoxy, provide an amphoteric behavior that results in becoming negatively or positively charged depending on the solution pH scale. Owing to the deprotonation in acid pH (<6), the GO forms stable colloids of ionized oxygen functional groups (-COOH) electrostatic repulsion, contributing to inducing the chemisorption of positively charged MB molecules. In other words, highly negatively charged sheets of graphene oxide in suspension could not only improve the electrostatic attraction between them and cationic MB molecules but also disperse homogeneously through electrostatic repulsion, clearly upgrading the adsorption feature (Peng et al., 2016; Ederer, 2022). Furthermore, the MB is a dye that holds several active functional groups interacting with ZnO, leading to a hydrogen bond between the ZnO and MB and an increase in the adsorption of the MB dye. According to Mohamed Shaban et al. (Shaban et al., 2018), increasing the mass over 0.15 g of natural serpentine adsorbent which



Fig. 3 Effect of different amounts of nanoparticle on the adsorption capacity of the nanocomposite; MB (A), MO (B),  $Cd^{2+}$  (C) and  $Pb^{2+}$  (D).

was associated with an increase in the level of the dissolved carbonate, as impurities within the serpentine minerals, would cause to decrease in the pH value, and hence the removal (%)

of MB. On the other side, the nanocomposite adsorption capacity for the MO dye molecules seems to reduce steadily (from 95.6 to  $30.77 \text{ mg.g}^{-1}$ ) with expanding the pH levels from



Fig. 3 (continued)



**Fig. 4** Influences of the initial solution concentrations (A) and pH (B) on the dyes and cations  $q_e$  and removal (%) by the synthetic nanocomposite GO-ZnO; Initial conditions: 25 (mL) of the MB, MO, and  $Cd^{2+}$  (50 mg.L<sup>-1</sup>) and Pb<sup>2+</sup> (100 mg.L<sup>-1</sup>) adsorbates, the adsorbent 10 (mg).

4 to 12. The findings were entirely consistent with the research by shi (Shi, 2022) reporting that the studied graphene oxidechitosan (GO-CS) composite tended to adsorb MO at low pH. This trend is reflected in diminishing the removal efficiency from 76.48% to 24.62%. This tendency can be explained by considering that the acidic conditions brought

about the adsorbent surface protonation, resulting in improving the uptake of the acidic MO dye and enhancing the pH caused a reduction in the removal percentage. Moreover, the decrease in the adsorption feature might be because the ZnO nanoparticles lost their oxygen atoms, in weakly alkaline solutions, through a reaction with the hydrogen ion  $(H^+)$ . In this case, the MO adsorption on the adsorbent surface might be considered to be a competition of the dye adsorbate with the generated cations  $(Zn^{2+})$ , occupying more ionic exchange sites and resulting in a drop in the MO removal (Shaban et al., 2018; Malekkiani et al., 2022; Peng et al., 2016). Conversely, as indicated by Syed Shahabuddin et al. (Shahabuddin et al., 2016), the adsorption of MO dye onto the surface of polyani-(PANI)-Co<sub>3</sub>O<sub>4</sub> nano cube-doped nanocomposites line appeared to be pH dependent in a positive relationship. This trend can be deduced from the fact that MO exists in anionic form at pH values less than the pKa value of ( $\sim$ 3.4), and hence gets protonated. As shown in Fig. 4B', the impact of pH ranging from 2 to 10 of the  $Cd^{2+}$  and  $Pb^{2+}$  solution was investigated. It was obvious that the uptakes and removal efficiencies increased moderately quickly from pH 2 to 8, and then increased very slowly from pH 8 to 10. It was found that the solution pH was likely to influence the deprotonation degree and the speciation of the surface functional groups of the GO-ZnO nanocomposite. With growing pH, the surface charge was more negative, meaning that the electrostatic interactions between the GO nanosheets and the heavy metal ions would become stronger resulting in the improvement in  $Cd^{2+}$  and  $Pb^{2+}$  ions sorption. Furthermore, it is the fact that cadmium and lead species might present the various forms of Cd<sup>2+</sup>, Cd (OH)<sub>3</sub><sup>-</sup>, Cd (OH)<sup>+</sup>, Cd (OH)<sub>2</sub><sup>0</sup>, Pb<sup>2+</sup>, Pb (OH)<sub>3</sub><sup>-</sup>, Pb (OH)<sup>+</sup>, and Pb (OH) $_2^0$  at diverse pH levels. The removal of the Cd<sup>2+</sup> and Pb<sup>2+</sup> pollutants, as predominant cadmium, and lead species at low pH levels, is chiefly achieved through an adsorption reaction. The low  $Cd^{2+}$  and  $Pb^{2+}$  uptakes which took place under very acidic conditions may be attributed to the competition between positive lead species and hydrogen ions on the sites of the surface (Wang, 2015; Zhao et al., 2011). Similarly, Yaoguang Wang et al. (Wang, 2015) showed an increase in the removal efficiency of lead species by increasing the pH from 2.7 to 5.0, and then a decrease from pH 5.0 to 6.6 using magnetic hydroxypropyl chitosan/oxidized multiwalled carbon nanotubes (MHC/OMCNTs). According to Aghdas Heidari et al. (Heidari et al., 2009), the sorption efficiency of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Ni<sup>2+</sup> metal ions by NH<sub>2</sub>-MCM-41would grow with an increase in the solution pH from 1.5 to 5.0., meaning that the solution pH influenced the adsorption of the metal ions through electrostatic binding of ions to corresponding -NH<sub>2</sub> groups. In the present research, with the increase in pH up to  $\sim 8$ , the levels of hydrogen ions relatively diminished, meaning that the proportion of adsorbed Cd<sup>2+</sup> and Pb<sup>2+</sup> which were competitive to hydrogen ions would grow. Overall, pH levels of  $\sim 6$  and  $\sim 8$  would appear to be the ideal conditions and they were chosen for the succeeding trials.

#### 3.3. Adsorption kinetics

Time is a key factor for adsorption system designs. The influence of the contact time on the components' adsorption was evaluated to obtain the relevant kinetics parameters under the controlled conditions of pH = 6 and pH = 8 for the dyes and metal ions solutions, respectively, at the initial concentrations up to 50 and 125 (mg.L<sup>-1</sup>) for the MB, 75 and 150 (mg.L<sup>-1</sup>) for the MO, 50 and 100 (mg.L<sup>-1</sup>) for the Cd<sup>2+</sup>, and 75 and 150 (mg.L<sup>-1</sup>) for the Pb<sup>2+</sup> pollutants. The measured reaction kinetic of the dyes and heavy metals adsorption as a function of time were fitted to both pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic expressions. The kinetics models applied for characterizing the adsorption tendency are expressed as (Bhattacharya and Venkobachar, 1984):

$$Log(q_e - q_t) = Logq_e - \frac{k_1 t}{2.303}$$
(3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where,  $q_t$  and  $q_e$  (mg.g<sup>-1</sup>) correspond to the components' adsorption capacity on the nanocomposite GO-ZnO at time t (min.) and the equilibrium, respectively;  $k_1$  (min.<sup>-1</sup>) and  $k_2$  $(g.mg^{-1}.min.^{-1})$  as the pseudo-first-order (Eq. (3)) and pseudo-second-order (Eq. (4)) rate constants, respectively, which equal the slopes of the fitting lines. The  $t/q_t$  as well as linear plots of  $ln(q_e-q_t)$  vs. t are depicted in Fig. 5 and all the kinetics parameters calculated from the intercept and slope of the linear regression plotting are also recorded in Table 1. According to the observed findings, although the adsorption behavior of the MB and MO dve,  $Cd^{2+}$  and  $Pb^{2+}$  displayed very well fitness with the pseudo-2nd -order model, the PFO model was the poorest in fitting the graphs based on visual observations. Likewise, this kinetic model satisfactorily predicted the adsorption trend over the whole range of time explored which was reflected by the extremely high correlation coefficient ( $\mathbb{R}^2 > 0.99$ ). Moreover, the calculated levels of adsorption capacities for the MB, MO,  $Cd^{2+}$ , and  $Pb^{2+}$  (q<sub>e</sub>, <sub>Cal</sub>) conformed with the experimentally measured capacities  $(q_{e, Exp.})$ , meaning that the adsorption of dyes and the heavy metals, on the synthetic media, might be again wellcharacterized by the PSO kinetics reaction. It could be declared that the controlling step was chemical adsorption (chemisorption). Mohamed Shaban (Shaban et al., 2018) reported that the adsorption behaviors of MB dye displayed very well fitness with the PSO model, which was reflected by the high  $R^2 > 0.99$ . According to Syed Shahabuddin et al. (Shahabuddin et al., 2016), the MO adsorption onto the PANI homopolymer and PANI-Co2, 4, and 8 nanocomposites follows the PSO kinetic model. The findings were also in agreement with the literature (Ahmada et al., 2016; Wang, 2015; Rodríguez et al., 2020) that demonstrated that when the adsorption of the Cd, Pb, Al, and Cu ions, the PSO kinetic model had a high linear  $R^2$  (~ > 0.9939), which was higher than the PFO kinetic model, suggesting that the Pb, Al, and Cu ions adsorption processes would obey the PSO model and the chief rate determining step was chemisorption.

#### 3.4. Equilibrium adsorption isotherms

A deep understanding of adsorption isotherms is crucial for productive adsorption system designs as well as overall the upgrade of adsorption mechanism pathways. Indeed, the connection between adsorbates and adsorbents, in the equilibrium state, can be characterized through adsorption isotherms. To



**Fig. 5** Pseudo-first-order and Pseudo-second-order adsorption kinetics models for the MB (A & B), MO (A' & B'),  $Cd^{2+}$  (C & D), and Pb<sup>2+</sup> (C' & D') adsorptions on the synthetic nanocomposite GO-ZnO; Initial conditions: 25 (mL) of the adsorbates, the adsorbent 7.5 and 10 (mg).

	Ci	Pseudo-1st-	Pseudo-1st-order			Pseudo-2nd-order			
	(ppm)	k <sub>1</sub> (min. <sup>-1</sup> )	$q_{(e, Exp.)}^{*}$ (mg.g <sup>-1</sup> )	$q_{(e, Cal.)}^{*}$ (mg.g <sup>-1</sup> )	R <sup>2</sup>	$k_2$ (g.mg <sup>-1</sup> .min. <sup>-1</sup> )	$q_{(e, Exp.)}$ $(mg.g^{-1})$	$q_{(e, Cal.)} \ (mg.g^{-1})$	$\mathbb{R}^2$
MB	50	0.120	83.425	153.350	0.8973	0.0018	83.425	89.285	0.9947
	125	0.109	93.317	133.930	0.8565	0.0017	93.317	102.041	0.9961
MO	75	0.137	118.47	174.020	0.9155	0.0023	118.47	123.457	0.9985
	150	0.07	121.97	127.614	0.9471	0.0009	121.97	133.333	0.9966
$Cd^{2+}$	50	0.101	106.763	174.783	0.876	0.0012	106.763	114.942	0.996
	100	0.054	118.837	101.765	0.899	0.0008	118.837	129.870	0.998
$Pb^{2+}$	75	0.061	163.425	93.993	0.9078	0.0018	163.425	163.934	0.9989
	150	0.082	256.475	333.042	0.9584	0.0004	256.475	277.778	0.9968

Table 1	Kinetics parameters for	r the adsorption of the	e MB, MO, Cd <sup>2+</sup>	, and $Pb^{2+}$	pollutants on	the synthesized	nanocomposite.
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 $q_{(e, Exp.)}$  and  $q_{(e, Cal.)}$  refer to the experimental and calculated components' adsorption capacity on the nanocomposite GO-ZnO, respectively, at the equilibrium.

clarify very well-fitting adsorption models, a linear regression analysis has been frequently applied since it has the potential to verify the theoretical assumption consistency of adsorption isotherm models and quantify adsorbates distributions (Ayawei et al., 2017). To understand the maximum adsorbed quantity via the GO-ZnO for the MB and MO dyes and heavy metals of  $Cd^{2+}$  and  $Pb^{2+}$ , equilibrium trials were conducted at different initial concentrations and pH  $\sim$  6 and  $\sim$  8 with an adsorbent dose of 10 mg, alongside during the contact time of 45 min. Eventually, the experimental data obtained in the batch adsorption experiments were adjusted to Langmuir, Freundlich, Temkin, and Flory-Huggins isotherms (Temkin, and Flory-Huggins isotherms are described in detail in Appendix A). All the experimental equilibrium data of the pollutant's adsorption were fitted to the applied linearized isotherms (Fig. 6) and the corresponding parameters were reported in Table 2.

Langmuir adsorption is one of the equilibrium isotherms applied to quantify as well as contrast the adsorptive capacity of varied adsorbents. This isotherm explaining affinity between adsorbents and adsorbates assumes that an adsorption process occurs on homogeneous sites of the solid media and that just monolayer formation takes place without any interactions between the adsorbed molecules (Shaban et al., 2018). Accordingly, Langmuir isotherm clarifies the surface coverage by balancing the respective adsorption and desorption rates (dynamic equilibrium) (Iriel et al., 2018). The  $q_e (mg.g^{-1})$  for Langmuir isotherm was obtained in the linearized form (Eq. (5)) (Dan et al., 2023).

$$\frac{C_e}{q_e} = \frac{C_e}{q_{Max}} + \frac{1}{q_{Max}K_L} \tag{5}$$

where,  $C_e$  (mg.L<sup>-1</sup>) represents the equilibrium concentration of the studied pollutants in the solution,  $q_{Max}$ . (mg.g<sup>-1</sup>) relating to the monolayer adsorption capacity represents the maximum coverage of the color pollutants and heavy metals adsorbed per unit weight of the nanocomposite, and the Langmuir constant  $K_L$  (L.mg<sup>-1</sup>) expresses the adsorption enthalpy quantifying the affinity between the involved segments of adsorption reaction. The basic feature of the Langmuir isotherm can be characterized by a dimensionless parameter called the separation factor  $R_L$  (Eq. (6) and Table 2) illustrating the adsorption reaction to be likely unfavorable for  $R_L > 1$ , linear for



**Fig. 6** Linearized fits of the Langmuir, Freundlich, Temkin, and Flory-Huggins (F-H) isotherms (A, B, C, and D, respectively) for the adsorption of the dye pollutants of the MB and MO (at  $pH \sim 6$ ) and the heavy metals of the  $Cd^{2+}$  and  $Pb^{2+}$  (at  $pH \sim 8$ ) onto the synthetic GO-ZnO; Initial conditions: 10 mg of the adsorbent, the initial concentration range: 10–175 (mg.L<sup>-1</sup>) at 298 K.

Isotherm model	Parameters	Linearized isotherm <sup>a</sup>				
		MB	МО	$Cd^{2+}$	Pb <sup>2+</sup>	
Langmuir	$q_{Max.}$ (mg.g <sup>-1</sup> )	99.00	125	121.951	277.778	
	$K_L (L.mg^{-1})$	0.429	0.382	0.590	0.176	
	R <sub>L</sub>	0.011-0.59	0.009-0.64	0.01-0.49	0.01-0.68	
	$R^2$	0.999	0.999	0.999	0.995	
Freundlich	$1/n_{\rm F}$	0.238	0.251	0.310	0.4422	
	$K_{\rm F} [(mg.g^{-1})(L.mg^{-1})^{1/n}]$	38.582	44.871	43.164	50.451	
	$R^2$	0.949	0.961	0.842	0.967	
Temkin	$\beta_{T}$	13.241	16.736	20.609	48.825	
	$K_{T}$ (L.g <sup>-1</sup> )	23.700	20.409	10.460	3.086	
	$b_T (J.mol^{-1})$	182.973	144.762	117.557	49.621	
	$\mathbb{R}^2$	0.982	0.969	0.905	0.949	
Flory-Huggins	$K_{FH}$ (L.mol <sup>-1</sup> )	0.0029	0.0027	0.0025	0.0010	
	n <sub>FH</sub>	-1.067	-0.975	-1.091	-1.251	
	$R^2$	0.911	0.912	0.974	0.988	

 Table 2
 The constants and coefficients extents of the linear forms of the studied two-parameter isotherms for the dyes and heavy metals adsorption onto the synthetic GO-ZnO.

<sup>a</sup> The nanocomposite dosage is 10 mg; pH  $\sim$  6 (for dyes) and 8 (for heavy metals) and contact time 1 h.

 $R_L = 1$ , favorable for  $0 < R_L < 1$ , alongside irreversible for  $R_L = 0$  (Ayawei et al., 2017; Arabpour et al., 2021).

$$R_L = \frac{1}{1 + K_L C_e} \tag{6}$$

The obtained  $q_{Max.}$ , based on the Langmuir isotherm (Fig. 6A and Table 2), was determined as 99, 125, 121.951 and 277.778 (mg.g<sup>-1</sup>) for the MB, MO, Cd<sup>2+</sup>, and  $Pb^{2+}$ , respectively, that is, the adsorption process using the synthesized adsorbent was very good for the MO dye as it had the highest maximum monolayer adsorption capacity. The K<sub>L</sub> extent for the four adsorption systems showed a relatively small level (0.429, 0.382, 0.590, and 0.176  $(L.mg^{-1})$  for MB, MO, Cd<sup>2+</sup>, and Pb<sup>2+</sup>, respectively), meaning that there was weak interaction between the adsorbates molecules and the absorbent since the active sites adsorbed only one molecule. Meanwhile, the adsorption of the GO-ZnO adsorbent matched the Langmuir isotherm with a coefficient correlation  $(R^2 > 0.99)$  too far closer to 1. This signified that the studied adsorption using the GO-ZnO adsorbent permitted monolayer formation. All the calculated R<sub>L</sub> levels were also in the range of 0–1, reflecting the favorable adsorption of the contaminants through the examined nanostructure.

The obtained equilibrium data was also fitted by using the applicable Freundlich isotherm (Eq. (7)) considering a heterogeneous adsorption surface and an exponential distribution of activated sites and their energies. To rephrase it, Freundlich isotherm is contingent on a non-uniform, multilayer, alongside heterogeneous adsorption (Chikate and Kadu, 2014).

$$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \tag{7}$$

where  $1/n_F$  and  $K_F [(mg.g^{-1})(L.mg^{-1})^{1/n}]$  represent adsorption intensity ( $n_F > 1$  represents favorable adsorption conditions), and the Freundlich empirical constant is connected to the adsorption capacity of adsorbate, respectively. The greater the term  $n_F$  is, the more remarkable  $1/n_F$  and adsorption capability as well, which expresses the heterogeneity index, whose lower levels reflect a greater amount of heterogeneity (Naseem, Oct. 2022). It's a known fact that a favorable adsorption process is proclaimed when  $0 < 1/n_F < 1$  (Ragadhita and Nandiyanto, 2021). As demonstrated in Fig. 6B and Table 2, four  $1/n_F$  levels were less than unity indicative of an adsorption process with a physical interaction. Furthermore, it was comparatively uncomplicated for the sorbent to adsorb these pollutants and this nanocomposite was good at adsorbing the pollutants.

 $R^2$  extents ranging from 0.999 to 1.000 indicate that the empirical adsorption data of the adsorbate on the adsorbent were very well good mathematically fitted in the corresponding model. The Langmuir isotherm described the adsorption behavior of the desired dyes and heavy metals on the synthesized GO-ZnO better than the other studied two-parameter models as the related coefficients of the Langmuir equation were higher for all pollutants ( $\mathbb{R}^2 > 0.99$ ). Therefore, based on  $\mathbb{R}^2$  according to (Table 2), the Freundlich, Temkin, and Flory-Higgins isotherms were not suitable for the studied dyes and heavy metals adsorption onto the given nanocomposite. The adsorption system with the synthetic GO-ZnO adsorbent for all studied pollutants followed suit with the order of the Langmuir > Temkin > Freundlich > Flory-Higgins. In addition, equilibrium data could not be applied to firmly establish the nature of the present adsorption process. To put it in another way, this model might be characterized by presuming a mono-layer adsorption reaction, that is, the adsorbed layer comprised only one molecule in thickness, accordingly adsorption was able to only occur at a finite sites number. Cautiously, based on the linear curve of the Temkin adsorption (Fig. S1A), the adsorption system with the examined adsorbent was compatible with the Temkin isotherm model. Indeed, the uptake behavior of the selected pollutants was described satisfactorily using the Temkin isotherm model with a reasonable correlation coefficient. At last, it can be concluded that these present dyes and metals adsorption represented, to some extent, by the Langmuir isotherm model followed by Temkin isotherm, meaning that the adsorption by the synthetic GO-ZnO

occurred in a multilayer form. According to Ederer et al. (Ederer, 2022), the Temkin isotherm can be applied to describe MB pollutants on GO. The presence of diverse indirect MB interactions with the GO surface that is confirmed by the data of the nonlinear fitting probably comes from the interactions of the MB with GO carbon honeycomb structure and functional groups. Several researches have been also conducted with graphene oxide for the removal of diverse metallic ions, such as Cd, Al, Cu, Ni, Zn, Pb, and Co (Ahmada et al., 2016; Rodríguez et al., 2020; Kong, 2020; Wang, 2018). In all these cases, the Langmuir adsorption model had a very good fit for experimental data.

Table 3 represents a maximum adsorption capacity comparison among various adsorbents and components with their given experimental conditions and mathematical models applied for data fitting towards MB and MO dyes and the metallic ions of  $Cd^{2+}$  and  $Pb^{2+}$ . There are noteworthy differences in q<sub>Max</sub>, values as may be expected. However, the lower uptakes of the GO/magnetic cellulose composite, magnetic multi/wall carbon nanotube, GO/polyaniline, CPOM, and fly ash/chitosan do not mean that they are inefficient subjects. The low q<sub>Max.</sub> levels of the studied pollutants through the adsorbents reported by other authors (Table 3) should be probably connected with some factors, including synthesis procedures, GO oxidation degree, the hydroxyl groups number of adsorbents' surface, and eventually the degree of structural vacancy defects in the honeycomb structures of the adsorbents such as GO. Conversely, due to any ionized and activated interactions with the dye structure at pH  $\sim$  7, the GO/SiO<sub>2</sub> nanocomposite tends to improve considerably the MB adsorption capacity up to 555.50 (mg.g<sup>1</sup>). Overall, the comparison of the studied pollutants' adsorption on the synthetic nanocomposite and other individual components indicates that the present GO-ZnO would be likely to exhibit acceptable adsorption efficiency towards both given dyes and metal ions.

#### 3.5. Antibacterial assay

Agar testing is a widely used method for evaluating the antibacterial activity of various materials. In this method, a nutrient-rich agar medium is used to grow bacterial colonies, which are then treated with the test material. The agar plates are then incubated under specific conditions to promote bacterial growth, and the degree of bacterial growth inhibition is evaluated by analyzing the size and number of bacterial colonies on the agar plates. The GO-ZnO nanocomposite might be a promising candidate for applying as an antibacterial agent due to its unique combination of properties. The high surface area of the nanocomposite enables it to adsorb bacterial cells, while the photocatalytic activity of the ZnO nanoparticles generates reactive oxygen species (ROS) that damage and kill bacterial cells. The graphene oxide component of the nanocomposite also contributes to its antibacterial activity by disrupting the cellular processes of bacteria. In the case of the agar testing, bacterial colonies of E. coli and Staphylococcus aureus were grown on agar plates, and the GO-ZnO nanocomposite was applied to the surface of the plates. The plates were then exposed to light to activate the photocatalytic activity of the nanocomposite. The results of the agar testing demonstrated (Table 4) that the synthetic GO-ZnO nanocomposite was highly effective against both bacterial pathogens. The nanocomposite significantly reduced the size and number of bacterial colonies on the agar plates, and in some cases, completely inhibited bacterial growth. The effectiveness of the nanocomposite in agar testing is likely due to a combination of factors. The high surface area of the nanocomposite allows for the adsorption of bacterial cells, while the photocatalytic activity of the ZnO nanoparticles generates ROS that damage and kill bacterial cells. Additionally, the graphene oxide component of the nanocomposite may disrupt the cellular processes of bacteria, contributing to its antibacterial activity.

Overall, the agar testing confirms the antibacterial activity of the synthetic GO-ZnO nanocomposite against E. coli and

**Table 4**Anti-bacterial activity of the synthesized GO-ZnOnanocomposite against the diverse bacteria.

Inhibition zone (mm)	GO (mm)	GO-ZnO(mm)
Staphylococcus aureus	13	19
Escherichia coli	11	16

**Table 3** Comparison of maximum adsorption capacity of the synthetic GO-ZnO towards the MB, MO,  $Cd^{2+}$ , and  $Pb^{2+}$  pollutants with other values from the literature.

Adsorbent (Langmuir mathematical isotherm)	Pollutant	$q_{Max}$ . (mg.g <sup>-1</sup> )	Refs.
Magnetic multi/wall carbon nanotube	MB	11.86	(Gong, 2009)
GO/magnetic cellulose composite	MB	70.00	(Shi et al., 2014)
GO/SiO <sub>2</sub>	MB	555.50	(Dan et al., 2023)
GO/polyaniline	MB	6.70	(El-Sharkaway et al., 2019)
AC from sugarcane mills boiler residue	МО	161.8	(Martini et al., 2018)
Chitosan-grafted-polyaniline-OMMT (CPOM)	$Cd^{2+}$	54.64	(Ahmada et al., 2016)
Fly Ash/chitosan	$Cd^{2+}$	87.72	(Pandey and Tiwari, 2015)
NH <sub>2</sub> -MCM-41	$Pb^{2+}$	57.74	(Heidari et al., 2009)
Sulfur functionalized graphene oxide (GO-SO <sub>x</sub> R)	$Pb^{2+}$	285.00	(Pirveysian and Ghiaci, 2018)
GO-ZnO nanocomposite	MB	99.00	This work
•	MO	125	
	$Cd^{2+}$	121.95	
	$Pb^{2+}$	277.78	

Staphylococcus aureus and suggests its potential for use in various antibacterial applications. The results of the study demonstrate the need for further investigations to determine the optimal concentration and exposure time of the nanocomposite to maximize its antibacterial activity. Additionally, further studies are necessary to fully understand the mechanism of action of the GO-ZnO nanocomposite and its potential side effects before it can be used in practical applications.

#### 4. Conclusions

ZnO nanocomposite has been synthesized and characterized using different analysis techniques to study the structural properties of the nanocomposite, including XRD, to study the molecular structure of the synthesized compound and SEM to determine the distribution of nanoparticles on the graphene oxide layers, which has proven to be successful. Nanoparticles have been evenly distributed which gives the nanocomposite special properties such as high adsorption capacity and antibacterial activity against bacterial contaminations. The synthesized nanocomposite synthesized using a novel graphene oxide synthesis method has proven to be more efficient and useful in water treatment applications regarding to the high adsorption capacity and antibacterial activity, ability to adsorb high amounts of organic and inorganic pollutants 99, 125, 121.95and 277.77 (mg.g<sup>-1</sup>) for the MB, MO, Cd<sup>2+,</sup> and Pb<sup>2+</sup>, respectively, proves that the synthesized nanocomposite is suitable to be applied to surface waters and wastewater to reduce the environmental pollution disturbance.

#### **Declaration of Competing Interest**

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Hassan Hashemipour].

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2023.105176.

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