Porous PVA/Zn–Fe–Mn oxide nanocomposites: methylene blue dye adsorption studies

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Keywords: metal oxides, polymer, porous, methylene blue dye, analytical techniques

Abstract

Adsorption is one of the noble techniques for remediation of organic and inorganic pollutants. The poly (vinyl alcohol) supported sol-gel and self-propagation routes have been used for the synthesis of porous ternary metal oxides nanocomposites. The optical, chemical bonding, crystallinity, morphological, textural, and electrochemical properties of the synthesized materials were characterized by DRS-UV–vis, FT-IR, XRD, SEM/EDX and TEM/HRTM/SAED, BET, and CV/EIS techniques, respectively. The characterization of the nanocomposites confirmed their porous nature, high surface area, and better electrochemical properties. The synthesized nanomaterials were tested for the adsorption property of methylene blue dye. Important parameters such as the amount of PVA supported ternary metal oxide nanocomposite, pH of the solution, contact time, and concentration of methylene blue dye were optimized. For further understanding of the adsorption process, the adsorption isotherms and adsorption kinetics models were used. The adsorption tests revealed the presence of the chemisorption type of the adsorption process.

1. Introduction

Nowadays, industries are using different dyes to dye manufactured products. The dumping of those pollutants can cause cancer and also genotoxic [1]. For a year, among several removal techniques, depending on the surface area and stability, metal oxide nanomaterials are getting attention. Of numerous metal oxides, zinc oxide has low-cost and less toxic properties. Iron oxide is abundant, low cost, environment-friendly, thermodynamically-stable, has a high surface area, and magnetic property. Furthermore, manganese oxide is also environment-friendly, has a promising surface area and magnetic property, abundant, and less costly assets. In advance, among several polymorphs of iron and manganese oxides, the hematite (α-Fe₂O₃) and Mn₂O₃ forms exhibit a unique property, respectively [2–4].

However, due to high surface energy and large surface area properties; metal oxides can aggregate/agglomerate easily. Aggregation occurred due to flow motion and net interparticle attractive forces. The aggregation process is dependent on the concentration of the NPs, reaction temperature, and agitation speed. High concentration, high temperature, and slow agitation speed facilitate the speed of aggregation. Agglomeration is formed due to the accumulation of extra molecules on the aggregated NPs surface. The classical nucleation, growth, collision, and attachment are the steps to yield aggregation. Whereas the cluster aggregation, nucleation, and growth are the steps to yield agglomeration [5].

To avoid aggregation/agglomeration, capping of the NPs with a polymer matrix is an effective method. The polymer matrix can act as a structure-directing agent by forming a non-covalent or/and a covalent bond [6]. Using polymers, synthesis of novel mesoporous materials with well-defined morphology has been strongly encouraged for the application of adsorption [7]. Among several polymers, poly (vinyl alcohol) (PVA) has
several advantageous properties [8, 9]. Besides, its hydroxyl groups on the carbon chain backbone act as a source for the formation of hydrogen bonding and enhances the formation of the nanocomposite [10]. As confirmed by various researchers [11–16], around 250, 300, 390, 400, and 400 °C–500 °C; the intramolecular decomposition, amorphous portion degradation, intermolecular breakdown, decaying of the crystalline portion of PVA, and formation of pure metal oxides had occurred, respectively.

From methods used for the synthesis of inorganic nanomaterials/nanocomposites, the top-down and bottom-up approaches are common. Compared to the former, the latter is more popular and is considered as a promising route to control the growth, morphology, and properties of the nanomaterials. From the bottom-up chemical approaches; the hydrothermal, microemulsion, wet impregnation, sonochemical, ultrasonic-microwave, electrochemical/electroless deposition, and spray-pyrolysis techniques are successfully applied. However, it is reported that these techniques follow special operating-conditions, long reaction time, low-through-put, and expensive procedure [17]. Therefore, it is essential to use effective and economically feasible methods such as sol-gel, precipitation, and impregnation. Furthermore, during the synthesis process, avoiding solvents that cause cancer and has mutagenic properties should also be taken into consideration [18].

Considering all the mentioned aspects, this work was aimed to synthesize PVA supported ternary metal oxide nanocomposite (PVA-TMONC), using a simple and green sol-gel-self propagation technique. The methylene blue dye (MBD) adsorption efficiency of the synthesized PVA-TMONC was also tested. The physical properties of synthesized materials were characterized by critical analytical techniques. Using the Langmuir, Freundlich, Dubinin-Radushkevich (D-RK), Temkin, Flory-Huggins (FH), and Fowler-Guggenheim (FG) isotherm models, the adsorption process was studied. The pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, Bangham, and intraparticle diffusion (IPD) kinetics models were used to study the adsorption-reaction and adsorption-diffusion process.

2. Material and methods

2.1. Chemicals and synthesis of single and ternary metal oxides

The analytical grade reagents were used for the synthesis of the nanomaterials (supplementary materials (S)). The simple and environmental-friendly sol-gel-self propagation technique was applied for the synthesis of the nanocomposites. First, the aqueous solution of PVA (1.5 g) was prepared by stirring and heating the solution to 115 °C for about 15 min. To form a 0.01 mol l⁻¹ aqueous solution; the zinc (90%), iron (5%), and manganese (5%) salt precursors were dissolved in the previously cooled PVA aqueous solution. Through aging the formed sol for two days, the gel was dried at ~110 °C for about 13 h and calcined at ~500 °C for 3 h to form metal oxides. The detailed synthetic procedure is depicted in [19] and figure 1. The synthesized TMONCs were coded as TMOM1 and TMOM2 for TMONCs synthesized using sol-gel and co-precipitation methods without PVA, respectively. During the co-precipitation technique, except the drop-wise addition of a base during the mixing of the salt precursors, a similar procedure was followed as the sol-gel. The code PVA-TMOP1 and PVA-TMOP2 were assigned for materials synthesized using Zn(NO₃)₂·6H₂O and Zn(CH₃COO)₂·2H₂O as a precursor with PVA, respectively.

2.2. Batch adsorption studies

The adsorption studies were carried out in 100 ml Erlenmeyer flasks. The PVA-TMOP1 adsorbent to the MBD pollutant solution ratio is 2:2.5 (20 mg of PVA-TMOP1 to 25 ml of 20 mg l⁻¹ MBD solution). The dilute HCl and NaOH solutions were used to adjust the pH of the solution. The equilibration of adsorption experiments was conducted on a rotary shaker (incubating orbital shaker SO1 made in the UK) at a speed of 140 rpm. The removal efficiency and amount of MBD adsorbed on the PVA-TMOP1 were evaluated using equations (1) and (2), respectively [20].

The final concentrations of the MBD were measured using the UV–vis spectrophotometer (SM-1600). The influence of pH of the solution (using pH value of 2, 4, 6, 8, 10, and 12) and amount of PVA-TMOP1 (using dosage value of 0.005, 0.01, 0.02, 0.04, 0.08, and 0.16 g) were optimized. The adsorption kinetics study was performed using the adsorbate–adsorbent contact time of 10, 30, 50, 70, 90, 110, 130, and 150 min. Furthermore, the adsorption isotherm test was conducted using MBD concentration of 1, 5, 10, 15, 20, 25, 30, and 35 mg l⁻¹. For a proper understanding of the adsorption process, the adsorption isotherm models (equations (3)–(8)) and adsorption kinetics models (equations (9)–(13)) were used [21, 22].

\[ q_e = \frac{V}{m} x(C_0 - C_e) \]  
\[ % = \frac{C_0 - C_e}{C_0} x 100 \]
Langmuir: \[ \frac{C_e}{q_e} = \frac{C_o}{q_m K_L} \quad R_L = \frac{1}{1 + \frac{K_L C_o}{q_m}} \] (3)

Freundlich: \[ \log q_e = \frac{1}{n} \log c_e + \log K_F \] (4)

Dubinin-Radushkevich: \[ \ln q_e = -\beta e^2 + \ln q_m \quad \varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right), \quad E = \frac{1}{\sqrt{2\beta}} \] (5)

Temkin: \[ q_e = \frac{RT}{b} \ln \varepsilon_e + \frac{RT}{b} \ln K_F \] (6)

Flory-Huggins: \[ \frac{\theta}{C_o} = n \ln (1 - \theta) + \ln K_{FH}, \quad \Delta G^\circ = -RT \ln (k_{FH}) \] (7)

Fowler-Guggenheim: \[ \ln \frac{C_e (1 - \theta)}{\theta} = \frac{2w}{RT} \theta - \ln k_{FG} \] (8)

Pseudo-first-order: \[ \log (q_e - q_t) = -\frac{K_1}{2.303} t + \log q_e \] (9)

Pseudo-second-order: \[ t = q_t \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} \] (10)

Elovich: \[ q_t = \frac{1}{\beta} \ln t + \frac{1}{\beta} \ln (\alpha/\beta) \] (11)

Intra-particle adsorption diffusion: \[ q_t = K_{id} \sqrt{t} + C \] (12)

Bangham model: \[ \ln q_t = \frac{1}{m} \ln t + \ln k_b \] (13)

Where, \( C_o \) & \( C_e \) are the initial and equilibrium concentrations of MBD (mg l\(^{-1}\)), respectively; \( q_e \) & \( q_m \) are the amounts of MBD accumulated per gram of PVA-TMOP1 and its maximum uptake (mg g\(^{-1}\)), respectively; \( V \) is the volume of MBD taken (L); \( m \) is the mass of PVA-TMOP1 (g); \( K_L \) in Langmuir model is the ratio of adsorption and desorption rate constant (L mg\(^{-1}\)); \( K_F \) in Freundlich model is the distribution coefficient; \( 1/n \) is empirical constant related to the heterogeneity of the surface; \( \varepsilon \) is D-RK constant; \( q_m \) is saturation capacity; and \( \beta \) is the constant related to free energy; \( k_T \) is the Temkin equilibrium constant related to maximum binding-energy; \( \frac{RT}{b} \) is constant related to the heat of adsorption, \( n \) is the number of ions on adsorption sites, \( T \) is the temperature (K), and \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)); \( \theta (1-(C_e/C_o)) \) is fractional surface coverage; \( k_{FG} \) is FG constant; \( k_{FH} \) is constant for FH model; \( w \) is the energy of interaction; \( k_1 \) is PFO rate constant; \( k_2 \) is PSO rate

**Figure 1.** The scheme showing the co-precipitation and sol-gel-self-propagation synthesis procedure.
constant; \(k_i\) is the IPD constant; \(C\) is intercept that gives an idea about boundary layer thickness; \(m\) and \(k_b\) are Bangham constants.

2.3. Characterization

The metal-oxygen and deposited OH\(^-\)/H\(_2\)O bond were characterized by FT-IR (Spectrum 65 FT-IR (PerkinElmer)) technique using KBr pellets; the optical properties were confirmed by DRS-UV–vis technique; the SEM-EDX (EVO 18, ALTO 1000), TEM/HRTEM (JEOL TEM 2100 HRTEM), and SAED techniques were used for morphological, crystal structure, and compositional study; the BET N\(_2\) adsorption-desorption technique was used for textual property analysis; the crystallinity was explored by XRD (PXRD-7000); for electrochemical properties investigation, the CV (CHI604E potentiostat) studies were conducted using a tri-electrode system, ZnO and optimized PVA-TMOP1 were used as a working electrode, whereas, the platinum wire as a counter electrode, and Ag/AgCl as a reference electrode with 6.0 M KOH electrolyte. The EIS studies were carried out in the frequency range of 1 Hz and 1 MHz, with an AC amplitude of 5 mV.

3. Results and Discussion

3.1. Characterization of the nanocomposites

3.1.1. XRD analysis

The XRD diffraction pattern that reveals the crystallinity and composition of ZnO and optimized PVA-TMOP1 materials are shown in figure 2. As seen in figure 2(a), the diffraction angles appeared at \(\sim 32^\circ\) (100), 34\(^\circ\) (002), 36\(^\circ\) (101), 47\(^\circ\) (102), 57\(^\circ\) (110), 63\(^\circ\) (103), and 68\(^\circ\) (112), corresponds to ZnO (ICSD: 00-036-1451). As seen in figure 2(a) inset, ZnO has a Wurtzite type of hexagonal phase structure that belongs to the P6\(_3\)mc (\#186-1) space group. Figure 2(b) is for PVA-TMOP1, the inset XRD pattern in figure 2(a) compares the width and sharpness of ZnO and PVA-TMOP1. Except for peak intensity reduction and width widening, no diffraction peaks and shifts were found. Most probably, this is due to the small percentage of iron and manganese oxides. The non-shifting of band position may also indicate the absence of any structural distortion on ZnO attributed to Fe\(^{3+}\) or Mn\(^{3+}\) ion inclusion [23]. Compared to the ternary PVA-TMOP1, the sharpness of the peaks for ZnO synthesized without PVA show its high crystallinity. Furthermore, the width of the peaks (full width at half maximum (FWHM)) indicates the size of the particles, the wider the FWHM the smaller the size of the particles. The obtained optimum particle size (using Debye–Scherrer formula (equation (14))) for PVA-TMOP1 is \(\sim 10\) nm, whereas the size for ZnO is \(\sim 59\) nm.

\[
D = \frac{K\lambda}{\beta \cos(\theta)},
\]

(14)

Where \(\lambda\) is the wavelength of the x-ray radiation (for Cu 0.15418 nm), \(K\) is constant, \(\beta\) is the FWHM and \(\theta\) is the diffracting angle.

The calculated average particle size for single and TMONCs is given in table S1 is available online at stacks.iop.org/MRX/7/065002/mmedia. The XRD pattern that shows the sharpness and broadness of the peaks for all single and TMONCs are given in figure S1. Compared to the co-precipitation method, a sol-gel technique has yielded a high surface area to volume ratio. The material synthesized using nitrate as a precursor is creating
greater self-propagation process, so small particle size founding. The conducted amount of PVA loading and precursor’s percentage optimization study was also reported earlier [19].

3.1.2. FT-IR analysis
The FTIR technique that gives the chemical bonding information of the as-synthesized materials is shown in figure 3. The common broad absorptions band around ∼3600 and ∼1650 cm⁻¹ are due to the stretching vibration of chemisorbed hydroxyl groups and physisorbed water molecules. Due to interatomic vibration, semiconductor metal oxides exhibit a strong absorption band below 1000 cm⁻¹. Due to two transverse optical stretching modes, the FTIR spectrum of ZnO shows a characteristic absorption band in the range of 400–550 cm⁻¹. These absorption peaks correlated with the TO-phonon and the LO-phonon frequency [24]. The shape, number, and wavenumber position of the bands are dependent on the chemical composition, morphology, and crystal structure of the materials. If the morphology of the materials changed from spherical (zero) dimension to one, two, or three-dimensional morphology, the broadness and splitting also found to increase [25, 26]. As confirmed on SEM images, that’s why different numbers and wavenumber position shifts were observed for ZnO and PVA-TMOP1. For the crystalline ZnO within the range of 400–550 cm⁻¹, the two absorption peaks were observed, whereas for PVA-TMOP1 only one peak was observed. As reported [27, 28], the source for the other peaks is expected to be from intermediate impurities created during synthesis. The absorption peaks appeared at ∼1640 and ∼1400 cm⁻¹ is most probably, either due to C= C and C–C stretching, respectively, or from the symmetric and asymmetric stretching vibration of the C=O/C–O group. The absorption peaks appeared at ∼3000 cm⁻¹ is due to the symmetric and asymmetric stretching vibration of CH₂ [29, 30]. The absorption bands appeared at ∼1300 and ∼940 cm⁻¹ was ascribed to symmetric C–H and bending vibration of –CH₃ group, respectively. The peak at ∼1100 cm⁻¹ is identified as CO (H) and CO (C) vibrations. Comparing the broad absorption band of ZnO with PVA-TMOP1, shifting of PVA-TMOP1 peaks towards lower wavenumber was observed. This shift is expected to be due to the surface passivation influences of PVA. Indirectly this is indicating that the presence of hydrogen bond between PVA (O–H group) and metal oxides surface [8].

3.1.3. DRS-UV–vis studies
The optical properties along with Kubelka–Munk (K–M) plots of ZnO and PVA-TMOP1 were studied using DRS-UV–vis techniques, as shown in figure 4. The spectra of the samples are showing characteristics absorption edge near to 380 nm. Pure ZnO show high reflectance in the visible region. In fact, due to its wide bandgap energies (3.17 eV), it only responds to the UV region. The PVA-TMOP1 has low reflectance (∼45%) in the visible region. In the parabolic band structure, the bandgap energy, E_g and the absorption coefficient of a direct bandgap semiconductor α are related through equation (15):
(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (15)

Where, \( h \) is Planck’s constant, \( \nu \) is the photon’s frequency, and \( A \) is the slope of the Tauc plot in the linear region. Taking the K–M scattering coefficient \( S \) as a constant concerning the wavelength, and using the remission function in equation (15), the following expression was derived (equation (16)):

\[ (F(R)h\nu)^2 = A(h\nu - E_g) \]

Where, \( F(R) \) is equal to \( K/S \), the molar absorption coefficient \( K \) is equal to \((1-R)^2\), the scattering factor \( S \) is equal to \( 2R \), and \( R \) is the reflectance of the materials and is defined as \( \%R/100 \).

As shown in figure 4(b), the bandgap energies of the materials were measured by the extrapolation of the linear portion of the direct K–M function plots. However, no obvious band energy changes between them were observed. As confirmed on the XRD pattern, this is due to the non-incorporation of either \( Fe^\text{0}/Mn^\text{0} \) or \( Fe^\text{2+}/Mn^\text{3+} \) ions in the ZnO crystalline lattice [31]. Furthermore, compared to single ZnO the observed slight bandgap tuning (blue shift) for the composite could be attributed to confinement effects [32].

3.1.4. BET analysis

For efficient adsorption applications, the physical features of the materials should have a great number of surface–active sites and optimized pore volume [33]. The BET method is the most widely used procedure for measuring the surface area and pore size distribution of the materials. Based on the density functional theory and molecular simulation at 77 K, \( N_2 \) gas is used as adsorbate for the characterization of the textural properties of amorphous, semi-crystalline, or crystalline porous materials. The ink-bottled, cylindrical, and slit-shaped are the three basic pore shape models. As seen in figures S2 and S3, all the nanocomposites have a resemblance to the cylindrical shape model. To have information about the textural properties of the synthesized materials, the BET data is treated according to BET adsorption isotherm linear equation (17):

\[ \frac{P/P_\text{e}}{n(1 - P/P_\text{e})} = C - \frac{1}{(n_m C)} \left( \frac{P/P_\text{e}}{n_m C} \right) + \frac{1}{n_m C} \]

(17)

Where, \( P_\text{e} \) and \( P \) are saturated and partial vapor pressure of \( N_2 \) gas at equilibrium in pa, respectively; \( n \) is the volume of \( N_2 \) gas adsorbed at STP in mL; \( n_m \) is BET monolayer capacity; \( C \) is dimensionless constant related to the enthalpy of \( N_2 \) gas adsorption on the adsorbent. According to the BET theory, the value of \( C \) (slope/intercept + 1) has a close relationship with the shape of the isotherms. If its value is \( \geq 80 \), the isotherm becomes sharp, \(< 50 \) indicate the presence of overlap between monolayer and multilayer adsorption, for \( < 2 \) the isotherm becomes either Type III or Type V. For well defining of the BET monolayer capacity of the nanocomposites, the value should be \( \geq 80 \) [34]. As seen from table S2, except for ZnO and Mn\text{2O}3, the C values for the other is \( \geq 80 \). For PVA-TMOM1 and PVA-TMOP1 since their slope is 0, not possible to define the value of C.

The linear plots of equation (17), [(\( P/P_\text{e} \))/\((n(1 - P/P_\text{e}))\)] versus \( P/P_\text{e} \), should yield a straight line in the approximate relative pressure range of 0.05 to 0.3. To be acceptable, it is advisable the linear regression value \((R^2)\) to be greater than 0.995. There is some problem with the \( R^2 \) value of ZnO (0.9943) and \( Mn\text{2O}3 \) (0.9887), however, for all the other, the value is well-agreed (table S2). From the linear plots, the slope \((C - 1)/n_m C\) and the intercept \((1/n_m C)\) were obtained. \( n_m \) is defined as \( 1/(\text{slope + intercept}) \). The specific surface area in \( m^2\cdot g^{-1} \) is calculated as equation (18):
Where, \( a_s \) is the BET specific surface area of the single and TMONCs of mass \( m \) in grams, \( L \) is Avogadro constant \((6.022 \times 10^{23} \text{ mol}^{-1})\), \( \sigma_m \) is molecular adsorptive cross-sectional area occupied by \( \text{N}_2 \) gas molecule in the complete monolayer (equal to 0.162 \( \text{nm}^2 \) for \( \text{N}_2 \) gas), the 22400 is the volume occupied by 1 mole of \( \text{N}_2 \) gas at STP, in \( \text{mL} \). The symbols used were those given in the 2007 edition of the IUPAC manual \([35]\).

According to the IUPAC classification of mesoporous materials, among six types of adsorption isotherms (Type I-VI) \([36]\), it should look like a Type II and/or VI (see figure S2(a)). The adsorption hysteresis loop shape that arises due to none-overlying of the adsorption-desorption arc also has a great correlation with the size distribution, shape, and connectivity of the pores. The appearances of the synthesized materials look like a typical IV isotherm with an H3 hysteresis loop. High adsorption capacities and sharp inflection at a high relative pressure \((P/P_0 > 0.8)\) on PVA-TMOM2 and PVA-TMOP1 composites signifying the coexistence of mesopores and macropores size distribution \([37]\). The sharp capillary condensation step between 0.40–0.85 for PVA-TMOP2 reflecting the presence of a narrow pore size distribution.

The pore size distributions of the synthesized materials were expressed in terms of the Barrett–Joyner–Halenda (BJH) curve. According to IUPAC classification, materials that have a pore size diameter of < 2.0 nm categorized as microporous, in the range between 2.0 to 50.0 nm as mesoporous, and > 50.0 nm as macroporous \([7, 34, 38]\). For the synthesized materials (table S2), the average pore size in the range of 9–43 nm indicating the mesoporous pore size distribution properties. Except for figure S2(c) and d inset, the sizes of mesopores in the architecture of all materials look uniform; the difference is only in intensity. Most of the pores fall into a size ranging from 5 to 50 nm, indicating the mesopores size distribution. The appearance of the peaks > 60 nm indicates the presence of some macroporous distribution \([37]\). The relatively large surface area and narrow mesoporous channels provide enough space and facilitate the rapid adsorption of molecules. The narrowly distributed pore size between 1 and 5 nm (figure 5 insets (PVA-TMOP1)) is corresponding to micropores, (see also figure S3(c) \((P/P_0, 0.0–0.05)\)). The pore size distribution curves show the relatively wide distribution for PVA-TMOP1, which is consistent with the SEM result. Therefore, the PVA-TMOP1 porous material has the micro-meso-macropore size distribution properties, yet the mesoporous type is dominant. As seen in figure 5, compared to the other composites, PVA-TMOP1 is showing enhanced surface area and optimized pore volume.

\[ a_s = \frac{n_m L \sigma_m}{m \times 22400} \]  

(18)

3.1.5. SEM-EDX analysis

For morphological and microstructure properties of synthesized materials, the SEM analysis was studied. The SEM images of TMOM1, TMOM2, and PVA-TMOP2 nanocomposites are given in figures S4(a–c) and the SEM image of PVA-TMOP1 were given in figure 6(a). As confirmed on the XRD spectra, the morphology of TMOM1 and TMOM2 synthesized without PVA (figures S4(a) and (b)) shows greater crystallinity compared to
PVA-TMOP1 and PVA-TMOP2 synthesized using PVA (figure 6(a) and figure S4(c), respectively). Furthermore, as confirmed on the N2 adsorption study, the porosity of PVA-TMOP1, which provide sufficient active sites for the adsorption of pollutant is more visible than the others. The appearance of Zn, Mn, Fe, and O that are not detected on the SEM images and XRD pattern of the composite were confirmed on EDX compositional analysis (figure 6(b)). The cause for S is most probably from the standard used during analysis [21].

3.1.6. TEM analysis
The TEM morphology of the optimized PVA-TMOP1 nanocomposite is shown in figure 7, it contains agglomerates with a size ranging from 7–30 nm. This is in agreement with the result obtained from the XRD pattern. The TEM analysis also confirms the porous nature of the composite, which is in good agreement with BET and SEM results. As seen in figure 7(a), between the agglomerates, the oriented attachment that occurs between metal oxides exists. During oriented attachment, due to the presence of fission as a driving force, the particles were found to share a common crystallographic orientation [39–41]. Figure 7(c) shows the magnified HRTEM image of PVA-TMOP1. From characteristics lattice fringes appeared on HRTEM image, using Gatan
Digital Micrograph Software the d-spacing value for (002) plane of ZnO was found to be 0.28 nm. The d-spacing value of 0.34 nm is matching to (221) plane of α-Mn$_2$O$_3$ [42, 43]. However, the lattice fringe of α-Fe$_2$O$_3$ was not found on the TEM image which is possibly due to highly dispersed states of α-Fe$_2$O$_3$.

The output from the lattice fringe analysis was given in figures 7(d) and (e). The occurrence of stacking faults on the surface of the NPs suggests the semi-crystalline nature of the nanocomposites (see the IFFT (4) images of figures 7(d) and (e)). As seen in figure 7(b), the obtained approximate interplanar spacing of diffraction rings from the electron diffraction diffuse ring pattern (SAED), 0.29, 0.25, 0.20, 0.17, 0.15, 0.13, and 0.11 also matches with XRD pattern of PVA-TMOP1 (figure 7(b) inset); 32°(100), 34°(002), 36°(101), 47°(102), 57°(110), 63° (103), and 68°(112). The SEAD pattern also indicates the presence of a partly amorphous region on the sample.

3.1.7. CV and EIS studies
The electrochemical property of ZnO and PVA-TMOP1 was characterized by EIS and CV analytical techniques. The CV plots of ZnO and PVA-TMOP1 at different scan rate is given in figures S5(a) and (b), respectively. For the PVA-TMOP1 CV plot, with increasing the scan rate, the oxidation peak shift towards more positive potential and slight increment in redox peak current was observed. For contrast, the CV plot of ZnO and PVA-TMOP1 at a scan rate of 30 mV s$^{-1}$ was depicted in figure 8(a). At the upper potential, the PVA-TMOP1 CV curve shows a greater current rise over the ZnO curve. This indicates the presence of an obvious electrochemical oxidation process. The linear relationship plotted between the oxide peak current (Ip) versus the scan rate (υ) was drawn as seen in figure 8(a) inset. The result suggests that the electrocatalytic process is adsorption controlled.

To further understand the improvement in the electrochemical properties of PVA-TMOP1, the EIS test was conducted. The Nyquist plot was used to understand the resistance properties of the material. The semicircular portion at a higher frequency is equal to the electron transfer resistance ($R_{ct}$) at the contact interface of the electrode and electrolyte solution [44]. As seen in figure 8(b), the semicircular diameter of PVA-TMOP1 is much smaller than ZnO. This indicates that PVA-TMOP1 has taken much lower resistance/higher electron transfer ability than ZnO. The value of $R_{ct}$ is equal to the radius of the semicircle [45]. The $R_{ct}$ value of PVA-TMOP1 is ~7 Ω, which is much smaller than the $R_{ct}$ value of ZnO (~65 Ω). As confirmed on the TEM image, the increased conductivity of PVA-TMOP1 may be due to the formation of heterojunction between the metal oxides and the porous nature of the material. The linear portion at lower frequencies is known as the Warburg resistance, which is related to ion transport/diffusion from the electrolyte to the surfaces of the electrode.

3.2. Adsorption studies
3.2.1. Optimization
As seen in figure S6(b) of PVA-TMOP1 adsorbent dosage optimization; the adsorption of MBD increases rapidly as the dosage of the PVA-TMOP1 increases from 0.005 to 0.02 g. This is due to the presence of unoccupied active sites of the adsorbent. However, after the saturation site of 0.02 g, further increasing the dosage does not result in enhancing the removal efficiency [46]. Therefore, 0.02 g was taken as the optimum PVA-TMOP1 adsorbent amount for MBD adsorption.

The degree of ionization of the MBD and the surface charges of the PVA-TMOP1 adsorbent is dependent on the pH of the solution. In the acidic pH range, due to $H^+$, the surface site of the PVA-TMOP1 functional group
protonated, while in alkaline pH due to the OH\(^-\) ion, the surface occupies a negative charge. At acidic pH, the electrostatic repulsion between positively charged PVA-TMOP1 with cationic MBD occurred, and the MBD adsorption efficiency is less (see figure S6(c)). At alkaline pH, the electrostatic attraction between the deprotonated negatively charged PVA-TMOP1 with cationic MBD occurred, so as enhancement of the adsorption process. As seen in the proposed mechanism of the adsorption of MBD on PVA-TMOP1 in figure 11, at basic pH the positively charged nitrogen atom from MBD can form a hydrogen bond with the hydroxide groups from the PVA-TMOP1 adsorbent.

3.2.2. Adsorption kinetics studies
Among the three adsorption process of adsorption kinetics, (i) external surface adsorption, (ii) IPD, and (iii) equilibrium adsorption [47], the first fast external adsorption process was occurred up to 70 min, the second IPD were occurred up to 90 min, and the third equilibrium adsorption process starts at 110 min (see figure 9(a)) [46]. Moreover, as seen in figures 9(b)–(f), the linear equations of the PFO, PSO, Elovich, IPD, and Bangham models were used for further time-dependent experimental data interpretation. The respective absorption coefficient and constant values are also given in table 1.

Comparing the \(R^2\) values of those kinetics models, the PSO (figure 9(c)) adsorption-reaction model and the Bangham model relatively fit well. The well-fitting of the PSO indicates, the chemisorption types of adsorption process to be the rate-determining step. To say that the PFO (figure 9(b)) and PSO models fit well, their theoretical and experimental values should be close to each other. Frequently, the obtained theoretical value becomes less than yet close to the experimental value. The theoretical (9.43 mg g\(^{-1}\)) and experimental (3.64 mg g\(^{-1}\)) values of PFO have not had close relation; while the theoretical (9.43 mg g\(^{-1}\)) and experimental (9.91 mg g\(^{-1}\)) values of PSO have a close relation. As seen in figure 9(e), the IPD adsorption-diffusion model is not showing good fitting and its linear line also does not pass through the origin. Hence, the adsorption process is not under the control of the adsorption-diffusion type. Therefore, the MBD adsorption on the PVA-TMOP1 is dependent on the adsorption-reaction type. This may have confirmation from the CV Ip versus \(\nu\) linear plot which suggests that the electrocatalytic process is adsorption controlled (see figure 8(a) inset).

3.2.3. Adsorption isotherms
The concentration optimization data conducted using different initial MBD concentrations (figure S6(d)) were fitted with isotherm models, as seen in figure 10. The adsorption isotherm models can give a clue about the adsorption process, characteristics, and adsorption efficiency of PVA-TMOP1 adsorbent. The respective absorption coefficient and constant values are also given in table 2. Depending on the \(R^2\) values of the adsorption isotherm models, the Langmuir and FH are showing relatively better fitting. From the Langmuir plot (figure 10(a)), the \(R_L\) value lying between 0 and 1 (0.05), indicates the favorability of the adsorption process. The
Table 1. Kinetics coefficient and constant values of MBD adsorption on PVA-TMOMP1.

|        | PFO |          |          | PSO          |          |          |          | IPD          |          |          | Bangham       |          |
|--------|-----|----------|----------|--------------|----------|----------|----------|--------------|----------|----------|--------------|----------|
|        | $q_e$ (mg g$^{-1}$) | $K_1$ | $R^2$    | $q_e$ (mg g$^{-1}$) | $K_1$ | $R^2$ | $\beta$ | $R^2$ | $C$ | $K_{ad}$ | $R^2$ | $m$ | $k_b$ | $R^2$ |
| PFO    | 9.43 | 0.037 | 3.64 | 0.82524 | 1.85 | 9.91 | 0.94857 | 0.95 | 0.9368 | 0.049 | 2.83 | 0.9921 | 2.22 | −0.42 | 0.9846 |
|        |      |        |        |          |        |        |          |      |        |          |        |      |        |      |

* is the theoretical equilibrium absorption capacity.
The Langmuir model also shows the presence of monolayer MBD coverage on the surface of PVA-TMOP1 adsorbent, which is consistent with the PSO model interpretation. The maximum adsorption capacity of the adsorbent determined from the Langmuir isotherm model is 7.75 mg g⁻¹.

Comparing the Freundlich (figure 10(b)), D-RK (figure 10(c)), Temkin (figure 10(d)), and FG (figure 10(f)) isotherm models, which are responsible for the heterogeneity of the adsorbent sites, adsorption mean free energy, adsorbate/adsorbate interactions, and surface characteristics of the adsorbate, respectively; the Freundlich and Temkin models are relatively well-fitting. The obtained n values from the Freundlich model lying between 1 and 10 (1.59) indicates the favorability of the reaction. As confirmed on the Langmuir isotherm model, being the value of 1/n closer to one also shows the homogeneous nature of the PVA-TMOP1 adsorbent surface. The Temkin equilibrium binding constant, kT (1.002 l mg⁻¹) is related to the maximum bonding energy. The indication of the characteristic surface coverage and spontaneity of the reaction (−3.8 kJ mol⁻¹) were deduced from the FH model equation (figure 10(e)). The obtained negative heat of adsorption (w) value of −17.838 kJ mol⁻¹ from the FG model confirmed the presence of repulsive interaction between adsorbed molecules. This can confirm the Langmuir monolayer coverage interpretation.

4. Conclusion

The PVA-TMONCs were effectively synthesized using the sol-gel-self-propagation technique. Compared to the co-precipitation, the sol-gel technique gave a better surface area to volume ratio. The zinc nitrate precursor is giving good self-propagation progression than zinc acetate salt precursor, so surface area enhancement. The porous nature of the material was confirmed by SEM and BET analysis. Using the XRD pattern, the approximate particle size of the optimized composite was determined to be 10 nm. This is in agreement with the size determined using TEM analysis of 7–30 nm. The EDX and HRTEM analysis assists the fitting of the composition of the materials. The nobilities of the electrochemical properties and adsorption process of the PVA-TMOP1 were verified through CV and EIS techniques. The Langmuir and FH adsorption isotherm models were found relatively well-fitting. From the Langmuir model, the MBD removal efficiency of the optimized nanocomposites was determined to be 7.75 mg g⁻¹. The PSO adsorption-reaction kinetics model fits well. These adsorption process tests are showing the domination of monolayer/chemisorption type of adsorption. From a future perspective, the efficiency of this adsorbent that has good porosity, surface area, and efficient charge separation properties; will also be tested on the photocatalytic degradation of MBD.
Table 2. Adsorption isotherm coefficient and constants for adsorption of MBD on to PVA-TMOP1.

|                | Langmuir | Freundlich | D-RK | Temkin | FH  | FG  |
|----------------|----------|------------|------|--------|-----|-----|
| $q_m$ (mg g$^{-1}$) | $K_F$ (l mg$^{-1}$) | $R_L$ | $k_f$ | $1/n$ | $E$ (kJ mol$^{-1}$) | $\beta$ | $b$ (kJ mol$^{-1}$) | $k_F$ | $\Delta G$ (kJ mol$^{-1}$) | $k_{FH}$ | $k_{FG}$ | $W$ (kJ mol$^{-1}$) |
| 7.75           | 0.94     | 0.05       | 0.21 | 0.629  | 8.5 | 0.033 | 2.16 | 1.002 | -4.96   | -3.80 | 0.216 | 7.58e-5 | -17.838 |
Acknowledgments

The authors are grateful to the management of Adama Science and Technology University for financial support and Mr Guta Amanu for his assistance during laboratory work.

Conflicts of interest

There are no conflicts to declare.

Author’s contributions

The nanomaterial’s synthesis, characterization, and first draft manuscript write up by Buzuayehu Abebe. Sample characterization, advising, and manuscript write up improvement by H C Ananda Murthy. Further, advising and manuscript write up improvement by Enyew Zerefa. UV–vis analysis during the adsorption studies by Eticha Abdisa.

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References

[1] Noorimotlagh Z, Darvishi Cheshmehsoltani R, Shams Khorraramabadi G, Godini H and Almasian M 2016 Performance of wastewater sludge modified with zinc oxide nanoparticles in the removal of methylene blue from aqueous solutions Desalin. Water Treat. 57 1684–92
[2] Lee S and Xu H 2016 Size-dependent phase map and phase transformation kinetics for nanometric iron(III) oxides (γ → ε → α pathway) J. Phys. Chem. C 120 13316–22
[3] Yang G, Yan W, Wang J and Yang H 2014 Fabrication and formation mechanism of Mn2O3 hollow nanofibers by single-spinneret electrospinning Cryst. Eng. Comm. 16 6907–13
[4] Janotti A and Van de Walle C G 2009 Fundamentals of zinc oxide as a semiconductor Reports Prog. Phys. 72 126501
[5] Tasshy D, Budars J F and Wiesner M 2012 Impact of aggregate size and structure on the photocatalytic properties of TiO2 and ZnO nanoparticles Environ. Sci. Technol. 46 6934–41
[6] Wu Z and Wu W 2015 Shape control of inorganic nanoparticles from solution Nanoscale 8 1237–59
[7] ALOthman Z 2012 A Review: Fundamental Aspects of Silicate Mesoporous Materials Materials (Basel). 5 2874–902
[8] Hong R Y, Li J H, Chen L L, Liu D Q, Li H Z, Zheng Y and Ding J 2009 Synthesis, surface modification and photocatalytic property of ZnO nanoparticles Powder Technol. 189 426–32
[9] Madkour M, Bumajjad A and Al-sagheer F 2019 To what extent do polymeric stabilizers affect nanoparticles characteristics? Adv. Colloid Interface Sci. 270 38–52
[10] Mallakpour S and Sadat M A 2016 Preparation and characterization of nanocomposites based on poly (vinyl alcohol) and vitamin B 1-modified TiO2 and evaluation of the optical, mechanical, and thermal properties Colloid Polym. Sci. 294 2099–187

Figure 11. The adsorption mechanism of methylene blue dye on PVA-TMOP1 nanocomposite.
[11] Kumar S, Krishnakumar B, Sobral A J F N and Koh J 2019 Bio-based (chitosan/PVA/ZnO) nanocomposites film: thermally stable and photoluminescence material for removal of organic dye Carbohydr. Polym. 205 559–64

[12] Abd-Elrahman M I 2013 Synthesis of polyvinyl alcohol–zinc oxide composite by mechanical milling: thermal and infrared studies Nanoscale Microscale Thermophys. Eng. 17 194–203

[13] Rahmanian R, Mozaffari S A and Abedi M 2015 Disposable urea biosensor based on nanoporous ZnO film fabricated from emissible polymeric substrate Mater. Sci. Eng. C 57 387–96

[14] Radhamani A V, Shareef K M and Rao M S R 2016 ZnO/MnO2 core–shell nanofiber cathodes for high performance asymmetric supercapacitors ACS Appl. Mater. Interfaces 8 30531–42

[15] Ghafari E, Feng Y, Liu Y, Ferguson I and Lu N 2017 Investigating process–structure relations of ZnO nanofiber via electrospinning method Compos. Part B Eng. 116 40–5

[16] Mallakpour S, Abdolmaleki A and Moosavi S E 2015 Green route for the synthesis of alanine-based (polyamide-imide) nanocomposites reinforced with the modified ZnO by poly(vinyl alcohol) as a biocompatible coupling agent Polym. Plast. Technol. Eng. 54 1448–56

[17] Sebastian S, Kalluri S and Anish Madhavan A 2019 Green synthesized α–Fe2O3 mesoporous network for heterogenous Fenton oxidation of thiazine dye Mater. Lett. 100 3057

[18] Lider C, S. Hayler I D, Hendlerksen R K, Redman A M, Shukla L, Shuster I E and Sneddon H F 2016 Updating and further expanding GSK’s solvent sustainability guide Green Chem. 18 3879–90

[19] Abebe B, Murthy H C A, Zereda E and Adimaru Y 2020 PVA assisted ZnO based mesoporous ternary metal oxides nanomaterials: synthesis, optimization, and evolution of antibacterial activity Mater. Res. Express 7 045011

[20] Abebe B, Taddesses A M, Kebede T, Teju E and Diaz I 2017 Fe–Al–Mn ternary oxide nanosorbent: synthesis, characterization and phosphate sorption property J. Environ. Chem. 5 1330–40

[21] Abebe B and Amada Murthy H C 2018 Synthesis and characterization of Ti–Fe oxide nanomaterials for lead removal J. Nanomater. 2018 1–10

[22] Abebe B, Amada Murthy H C and Dessie Y 2020 Synthesis and characterization of Ti–Fe oxide nanomaterials: adsorption–degradation of methyl orange dye Arab. J. Sci. Eng. (https://doi.org/10.1007/s13369-019-04328-1)

[23] Lachheb H, Ajala F, Hamrouni A, Houa A, Parnirro F and Palmisano L 2017 Electron transfer in ZnO–Fe2O3–O2 aqueous slurry systems and its effects on visible light photocatalytic activity Catal. Sci. Technol. 7 4041–7

[24] Yang Z, Zong X, Ye Z, Zhao B, Wang Q and Wang P 2010 The application of complex multiple forklke ZnO nanostructures to rapid and ultrahigh sensitive hydrogen peroxide biosensors Biomaterials 31 7534–41

[25] Fatehah M O, Aziz H A and Stoll S 2014 Stability of ZnO nanoparticles in solution. influence of pH, dissolution, aggregation and disaggregation effects J. Colloid Sci. Biotechnol. 3 75–84

[26] Sigol F A, Davolos M R and Jafelici M 1997 Morphological evolution of zinc oxide originating from zinc hydroxide carbonate J. Alloys Compd. 262–263 292–5

[27] Znaidi L, Soler Illia G J A A, Benyahia S, Sanchez C and Kanaev A V 2003 Oriented ZnO thin films synthesis by sol–gel process for laser application Thin Solid Films 428 257–62

[28] Anzilovar A, Kojeg K, Crniak Orel Z and Zigon M 2011 Polyol mediated nano size zinc oxide and nanocomposites with poly(methyl methacrylate) Express Polym. Lett. 5 504–19

[29] Huang C–Y, Hu K–H and Wei Z–H 2016 Comparison of cell behavior on pva–pva-gelatin electrospun nanofibers with random and aligned configuration Science 3. 6 73960

[30] Lin S–Y, Cheng W–T, Wei Y–S and Lin H–L 2011 DSC–FTIR microspectroscopy used to investigate the heat–induced intramolecular cyclic anhydride formation between Eudragit E and PVA copolymer Polym. J. 43 577–80

[31] Maya-Treviño M L, Villanueva-Rodríguez M, Guzmán–Mar J L, Hinojosa–Reyes L and Hernández–Ramírez A 2015 Comparison of the solar photocatalytic activity of ZnO–Fe2O3 and ZnO–Fe on 2,4–D degradation in a CPC reactor Photochem. Photobiol. Sci. 14 543–9

[32] Shah A H, Manikandan E, Basheer Ahamed M, Ahmad Mir D and Ahmad Mir S 2014 Antibacterial and Blue shift investigations in sol–gel synthesized Cr2O3–InO2 Nanostructures J. Lumin. 145 944–50

[33] Rosman N, Wan Salleh W N, Aziz F, Ismail A F, Harun Z, Bahri S S and Nagai K 2019 Electrosynthesized nanofibres embedding ZnO/Ag2CO3/AgO heterojunction photocatalyst with enhanced photocatalytic activity Catalysis 9 565

[34] Thommes M, Kaneo K, Neimark A V, Olivier J P, Rodriguez–Reinoso F, Rosuqueol J and Sing K S W 2015 Physiosorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report) Pure Appl. Chem. 87 1051–69

[35] Cohen E R, Mills I, Strauss H L, Frey J G, Mills I, Homann K and Kuchitsu K 2007 Quantities, units and symbols in physical chemistry Int. Union Pure Appl. Chem. 233 31–3

[36] Kumar P, Kim K–H, Kwon E E and Szulejko J E 2016 Metal–organic frameworks for the control and management of air quality: advances and future direction J. Mater. Chem. A 4 435–61

[37] Liu J, He J, Wang L, Li R, Chen P, Rao X, Deng L, Rong L and Lei J 2016 NiO–PTA supported on ZIF–8 as a highly effective catalyst for hydrocracking of Jatropha oil Sci. Rep. 6 23667

[38] Zhao X S, Lu G Q (M) and Millar G J 1996 Advances in mesoporous molecular sieve MCM–41 Ind. Eng. Chem. Res. 35 2075–90

[39] Penn R L 1998 Imperfect oriented detachment: dislocation generation in defect–free nanocrystals. Science (80-) 281 969–71

[40] Zhang J, Huang F and Lin Z 2010 Progress of nanocrystalline growth kinetics based on the evaluation of nanocrystallite shape Acs Nano 4 18–34

[41] Muñoz-Rojas D, Oró–Solé J and Gómez–Romero P 2008 From nanosnakes to nanosheets: a matrix–mediated shape evolution J. Phys. Chem. C 112 20312–8

[42] Liu X, Ye L, Liu S, Li Y and Ji X 2016 Photocatalytic reduction of CO2 by ZnO micro–nanomaterials with different morphologies and ratios of [001] facets Sci. Rep. 6 38471

[43] Zhao J, Zhao Z, Li N, Nan J, Yu R and Du J 2018 Visible–light–driven photocatalytic degradation of ciprofloxacin by a ternary MnO2/MnO/MnO3 valence state heterostructure Chem. Eng. J. 353 805–13

[44] Li Z, Mi Y, Liu X, Liu S, Yang S and Wang J 2011 Flexible graphene/MnO2 composite papers for supercapacitor electrodes J. Mater. Chem. 21 4706

[45] Li Z, Zhou Z, Yun G, Shi K, Lv X and Yang B 2013 High–performance solid–state supercapacitors based on graphene–ZnO hybrid nanocomposites Nanoscale Res. Lett. 8 473

[46] Lan Huang P T, Tu N, Lan H, Thang L H, Van Quy N, Tuan P A, Dinh N X, Phan V N and Le A–T 2018 Functional manganese ferrite/graphene oxide nanocomposites: effects of graphene oxide on the adsorption mechanisms of organic MB dye and inorganic As(V) ions from aqueous solution RSC Adv. 8 12376–89

[47] Cui L, Wang Y, Hu L, Gao L, Du B and Wei Q 2015 Mechanism of Pb(II) and methylene blue adsorption onto magnetic carbonato hydroxyapatite/graphene oxide RSC Adv. 5 9759–70