

Preparation and characterization of manganese oxide nanoparticles via combustion synthesis for removal pollutants from water

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Abstract

Manganese oxide nanoparticles (Mn_2O_3) were synthesized through an optimized urea-assisted combustion method and characterized for water treatment applications. The synthesized nanoparticles were characterized using X-Ray diffractometry (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) for the obtained nanoparticles demonstrated 98.2% removal efficiency for Sunset Yellow dye (SY) at pH 2 within 60 minutes with an adsorbent dose 0.05 g/L and initial dye concentration 250 ppm. In addition, the higher agreement between $q_m(cal)$ and $q_m(exp)$ confirmed that Langmuir isotherm model was the best fit isotherm model described the adsorption process of Sunset Yellow dye (SY) over manganese oxide nanoparticles surface. The high coefficients of determination (R^2) value (0.9964) indicated that Pseudo second order was the best fitting model of the adsorption process.

Keywords: Manganese oxide nanoparticles, Combustion method, Sunset Yellow dye, Adsorption studies.

1. Introduction

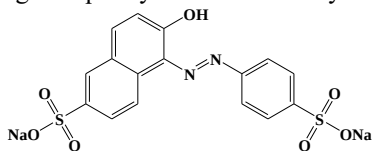
The presence of dye in water streams has significant negative effects on living organisms [1]. Dyes are consumed globally by both small and large-scale industries, with the textile sector being a major contributor to dye emissions into the ecosystem. Dyeing industries discharge substantial amounts of dye annually. The complex chemical structures of dyes allow them to absorb light and produce color. Many dyes, particularly azo dyes, are highly carcinogenic. Furthermore, their non-biodegradable nature means they persist in the environment, posing long-term hazards. Therefore, removing dye molecules from wastewater before discharge is crucial to mitigate the short and long-term severe implications reported for aquatic life [2, 3]. Manganese oxides ($MnOx$), abundant in the Earth's crust, are crucial in biogeochemical cycles and are gaining significant attention in environmental science due to their large surface area and high reactivity. Specifically, nano-sized $MnOx$ exhibit enhanced properties like high redox potential and significant surface area with a negative charge, making them highly effective for both catalytic degradation of organic pollutants via advanced oxidation processes (AOPs) and adsorption of cationic contaminants in wastewater treatment [4]. In the realm of nanotechnology, achieving nanoscale particle dimensions is paramount for material formation, offering researchers significant advantages due to the unique optical, structural, and magnetic characteristics inherent at this scale. The properties of nanoparticles are fundamentally governed by factors such as their shape, size, composition, and internal arrangement [5]. Specifically, the dimensions and overall form indicate the particle size, leading to materials exhibiting consistent and stable properties. Consequently, the synthesis of nanoparticles hinges on establishing a well-defined core structure with precise control over their size [6, 7]. Manganese oxides

nanoparticles have been synthesized using methods like hydrothermal [8-10], sol-gel [11], Co-precipitation [12], Microwave discharge in liquid [13] and green synthesis [14]. These techniques are often present complexities, require significant time, involve multiple steps, and yield less product. In contrast, solution combustion synthesis stands out as a key technique for producing nanocrystalline powder due to its high yield, reduced time and energy consumption, and straightforward equipment requirements [15-18] using urea as a fuel [17, 19]. There are many mechanisms for removing dye from waste water such as photo-catalytic degradation, Fenton degradation, electrochemical degradation, liquid-liquid extraction, ultrafiltration, ion exchange often struggles to effectively treat colored wastewaters due to the complex aromatic structures of dyes. Therefore, developing an efficient decolorization method for these wastewaters is highly sought after. Adsorption is recognized as a cost-effective and straightforward technique capable of completely removing dyes from effluents, even at high concentrations [20]. Mn_2O_3 nanoparticles were widely acknowledged as a low toxicity, environmental compatibility, highly efficient adsorbent for the removal of dyes from aqueous solutions for all morphologies nanofiber microsphere, nanotube, nano cone and nanorod that have prepared and used in adsorption of Congo red dye with removal rate up to about 90.78% [21]. In this work manganese oxides nanoparticles are prepared by auto-combustion method and applied for the removal of sunset Yellow (SY) dye with removal percentage reached to 98% at pH 2 after 60 minute.

2. Materials and Methods

2.1. Materials and chemicals

Manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99.9%, Qualikems) was utilized as the metal source, while urea ($\text{CO}(\text{NH}_2)_2$, 99.5%, Adwic) served as the fuel in the synthesis process. Additionally, Sunset Yellow dye (SY) ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$, Adwic) was employed in this study. All materials and chemicals with the highest quality and used directly.



Scheme (1): Chemical structure of Sunset Yellow (SY) dye.

2.2. Auto-combustion synthesis of manganese oxide nanoparticles

Specific amounts of manganese acetate tetrahydrate (0.02 moles) as the oxidant source were dissolved in 50 ml deionized water and drops of concentrated nitric acid and allowed to stirring on hotplate-stirrer for complete dissolution. 2g of urea as the reducing agent were added to the previous solution with continuous stirring using hotplate-stirrer. The resulting solution was heated under continuous stirring to evaporate the excess water, leading to the formation of a viscous gel. Following water evaporation, the temperature was further increased under the same conditions to approximately 300 °C to initiate the self-propagating combustion reaction. This process resulted in the evolution of various gases and the formation of a precursor powder. The obtained powder was subsequently calcined at 600 °C for 1 hour in a muffle furnace to remove any residual organic matter and to obtain the crystalline manganese oxides nanoparticles.

2.3. Characterization

Synthesized manganese oxide nanoparticles sample was characterized using Fourier Transform Infrared (FTIR) spectroscopy and X-ray Diffraction (XRD) analysis. FTIR spectra measurements were carried out using a Bruker FT-IR spectrometer (Invenio S, Germany in a wavenumber range of 400–4000 cm^{-1} . For structural analysis, X-ray Diffraction patterns were recorded using a Bruker D8 Advance diffractometer with monochromatic $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.54178 \text{ \AA}$). The measurements were conducted in the angular range of 10–80° (2 θ) with a step size of 0.02° and a scan step time of 0.4 seconds. Dye removal efficiency was recorded with respect to the changes in the absorption peak intensity at $\lambda_{\text{max}} = 480 \text{ nm}$ for Sunset Yellow (SY) dye using double beam (UV-Vis) spectrophotometer model (Jasco V-670, USA).

2.4. Adsorption studies

The Batch technique was carried out to achieve the optimum operating conditions for elimination and

separation of Sunset Yellow dye on manganese oxide nanoparticles. Different parameters such as solution pH (2–11), manganese oxides nanoparticles dose (0.01–0.125 g/L), initial Sunset Yellow dye concentration (50–300 mg/L), and contact time (2–100 min). To carry out the adsorption experiments, the solution pH was adjusted at first using 25 mL of (SY) dye solution using 0.1 M HCl and 0.1 M NaOH solutions. An optimized adsorbent dose of 0.05 g of manganese oxides nanoparticles were added to pH series of (SY) dye and allowed to stirring. The final concentration of (SY) dye in the clear solution was estimated at $\lambda_{\text{max}} = 480 \text{ nm}$ by double beam UV-Vis spectrophotometer. The percentage removal (%R) of Sunset Yellow dye and adsorption capacity (q_t) were calculated using the following Eq. (1,2):

$$\% R = (W_o - W_e) / W_o \times 100 \quad (1)$$

$$q_t = (W_o - W_t) / (V/m) \quad (2)$$

Where q_t is the adsorption capacity of (SY) dye adsorbed on manganese oxide nanoparticles at the time of equilibrium (mg/g), W_o and W_e are the initial and final concentration of (SY) (mg/L), V is the volume of sample, and m is the mass of adsorbent. Finally, besides percentage removal (%R) of (SY) dye and adsorption capacity (q_t), isotherm and adsorption kinetics were performed under the variable experimental parameters.

3. Results and discussion

3.1. Characterization of manganese oxide nanoparticles

Fourier Transform Infrared (FTIR) spectrum of the sample exhibited characteristic absorption bands at specific wavenumbers, providing information about its functional groups and bonding. Notably, prominent peaks were observed at 657.63 cm^{-1} and 515.60 cm^{-1} . These bands are attributed to the stretching vibrations of Mn-O bonds within the manganese oxide structure. Additionally, less intense peaks were present at 557.63 cm^{-1} and 435.05 cm^{-1} , potentially indicating other vibrational modes or structural features within the material as presented in Fig 1. The presence and positions of these peaks are consistent with the reported spectral features of Mn_2O_3 , suggesting its formation as a major component in the analyzed sample. Further detailed analysis and comparison with literature are recommended for a comprehensive assignment of all observed vibrational modes [10].

X-ray diffraction (XRD) analysis was performed. The resulting diffraction pattern, as presented in Fig. 2 identified morphology of sample structure nanoscale, confirms the presence of Bixbyite (Mn_2O_3) as the primary crystalline phase and (Mn_3O_4) as secondary phase according to cards No. 1514230 and 1514236 respectively. The observed diffraction peaks were indexed to a cubic crystal system with space

group *I a -3* (No. 206) refinement of the lattice parameters yielded values of $a = b = c = 9.41000 \text{ \AA}$ consistent with the reported structure of Bixbyite. Prominent peaks are observed at 2θ values of 18.85, 23.13, 32.95, 38.23, 45.16, 55.17, and 65.78 degrees, corresponding to the (200), (211), (222), (400), (332), (440), and (622) planes, respectively [10, 22]. The crystalline manganese oxide nanoparticles (Mn_2O_3) can be extracted by using the Scherrer eq. (3):

$$C = Z\lambda/\beta\cos\theta_B \quad (3)$$

Where λ is the wavelength of X-ray radiation, Z is constant, β is the full width at half the maximum of the diffraction peak and θ_B is the Bragg diffraction angle. The calculated average particle size of the annealed manganese oxide nanoparticles (Mn_2O_3) is found to be 38 nm.

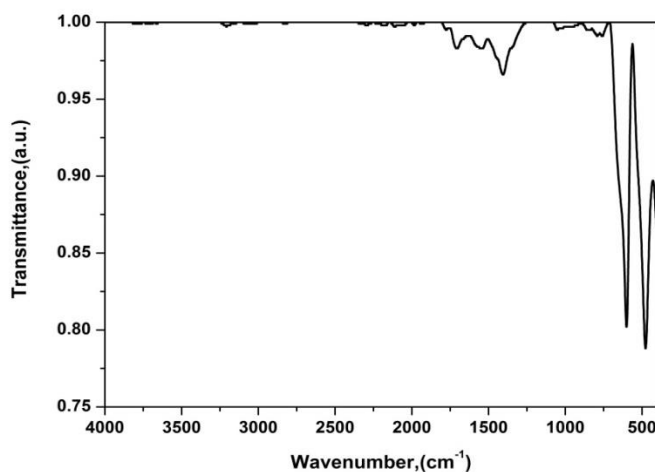


Fig (1) (FTIR) of manganese oxide nanoparticles prepared by auto-combustion method.

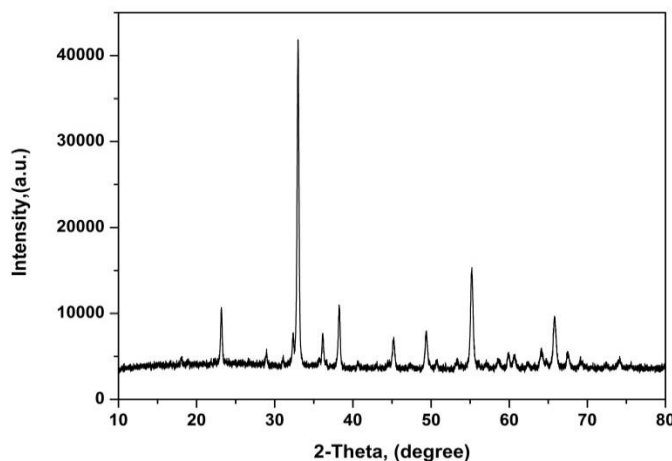


Fig (2) (XRD) of manganese oxide nanoparticles prepared by auto-combustion method.

3.2. Batch adsorption experiments

pH solution is a very valuable parameter in the dye adsorption process, as it controls the type of electrostatic charges that are gained by the charged dye species. For this, the pH effect of the adsorption process of (SY) dye on manganese oxide nanoparticles was studied by observing the percentage removal of (SY) dye using 25 mL of 100 ppm dye solution with

0.05 g manganese oxide nanoparticles in the pH range of 2–11.

The maximum removal efficiency (%R= 98.03%) was observed at pH 2 for the removal of (SY) dye on manganese oxide nanoparticles as showed in Figure 3(a). The removal and dye adsorption were observed to vary significantly with pH, likely due to changes in surface charge and dye speciation [23, 24].

Contact time is one of the significant factors in the adsorption process which clarifies the interaction between the adsorbent surface of the manganese oxide nanoparticles and the Sunset Yellow dye. The contact time effect of Sunset Yellow dye adsorption efficiency using manganese oxide nanoparticles as an adsorbent was investigated using 100 ppm dye solution in 25 mL at pH 2 in the time range of 2–100 min. adsorption capacity of Sunset Yellow dye increased with increasing time using manganese oxide nanoparticles; for example, increased from 24 mg/g at 5 minutes to 49 mg/g at 60 minutes, as showed in Figure 3(b). until equilibrium occurred [23].

The results showed that the dye removal efficiency (%R) increased as the dose of manganese oxide nanoparticles were raised, reaching up to 98.32% for higher doses (0.05 g/L and above). This indicates that manganese oxide nanoparticles were highly effective in removing Sunset Yellow dye. The concentration of dye remaining in the solution (C_e) decreased as the dose increased, showing the adsorbent's strong ability to capture the dye. Additionally, the amount of dye adsorbed per gram of manganese oxide nanoparticles

(qe) also increased with higher doses, confirming the effectiveness of manganese oxide nanoparticles in dye removal as showed in Figure 3(c). These findings highlight the potential of manganese oxide nanoparticles as an efficient material for treating wastewater contaminated with synthetic dyes.

The results indicated that the highest adsorption efficiency of 98.33% and an adsorption capacity of 49.17 mg/g were observed at an initial dye concentration of 100 ppm. With the increase in the initial dye concentration, the adsorption capacity continued to rise, reaching 71.45 mg/g and 93.54 mg/g at concentrations of 150 and 200 ppm, respectively, while maintaining high removal efficiencies of 95.26% and 93.54% for these concentrations. Importantly, the study demonstrated a remarkable effectiveness of manganese oxide nanoparticles in removing the dye even at a high concentration of 250 ppm, where a removal efficiency of 92.53% and a high adsorption capacity of 115.65 mg/g were achieved, further proving the efficiency of manganese oxide nanoparticles in the removal of anionic dyes at elevated concentrations as showed in Figure 3(d).

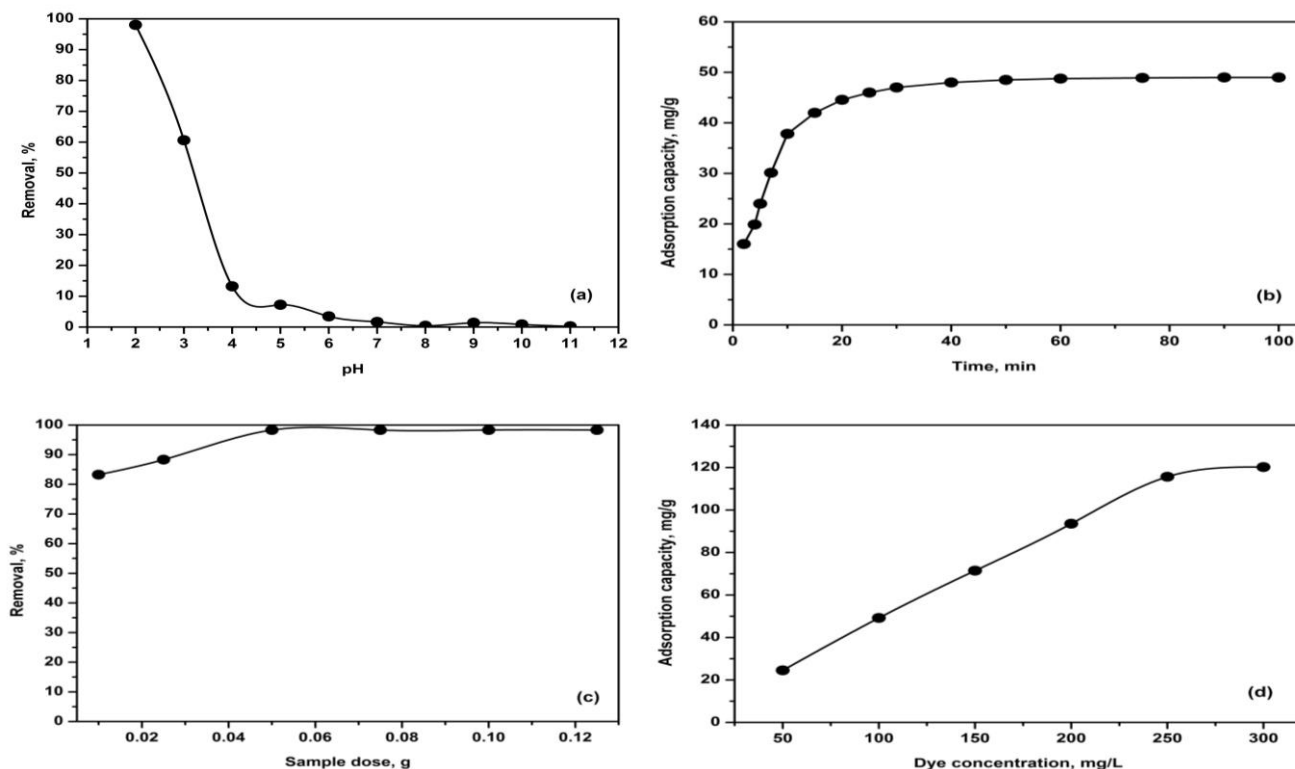


Fig (3) Effect of pH (a), contact time (b), manganese oxide nanoparticled amount (c) and initial dye concentration (d) for the adsorption of (SY) dye on manganese oxide nanoparticle.

Models of adsorption isotherm were employed to investigate the (SY) (adsorbate) molecules adsorbed at the manganese oxide nanoparticles surface (adsorbent) when the concentration of the adsorbate reached equilibrium, and to describe the adsorption capacity of the adsorbent. To examine the isotherm behavior of Sunset Yellow dye adsorption onto the manganese oxide nanoparticles, the theories of Langmuir, Freundlich, and Temkin were applied [25, 26]. The high coefficients of determination (R^2) value indicate the best fitting model. The linear forms of Langmuir, Freundlich, and Temkin isotherms are illustrated in Figures 4(a-c), and the three models are represented by Equations (4-6) as follows:

$$\frac{W_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{W_e}{Q_m} \quad (4)$$

$$\ln Q_e = \ln K_F + \frac{1}{p} \ln W_e \quad (5)$$

$$Q_e = G \ln K_T + G \ln W_e \quad (6)$$

Where C_e represents the equilibrium concentration of Sunset Yellow dye in solution, Q_e is the equilibrium adsorption capacity of Sunset Yellow dye using manganese oxide as the adsorbent, K_L is the Langmuir

3.3. Adsorption isotherm models

parameter related to the affinity of binding sites, K_F is the Freundlich constant indicative of adsorption capacity, $(1/P)$ is the Freundlich exponent related to the surface heterogeneity, Q_m is the maximum monolayer adsorption capacity. In the Temkin model, K_T is the equilibrium constant for maximum binding, while X reflects the heat of adsorption, and the constant G equals RT/X . Applying the established isotherm theories of Langmuir, Freundlich, and Temkin to the adsorption of (SY) dye using the synthesized manganese oxide nanoparticles, the experimental data, as detailed in Table (1), indicated that the Langmuir model exhibited a superior fit ($R^2 \approx 0.9963$) when compared to the Freundlich model ($R^2 \approx 0.8838$) and the Temkin model ($R^2 \approx 0.9442$). The maximum monolayer adsorption capacity $q_m(\text{cal})$ as determined from the Langmuir model and the experimental adsorption capacity $q_m(\text{exp})$ were 128.205 mg/g and 117.941 mg/g respectively. This strong correlation with the Langmuir model suggests the formation of a monolayer of Sunset Yellow dye on the homogeneous surface of the manganese oxide nanoparticles, indicating a finite number of identical adsorption sites.

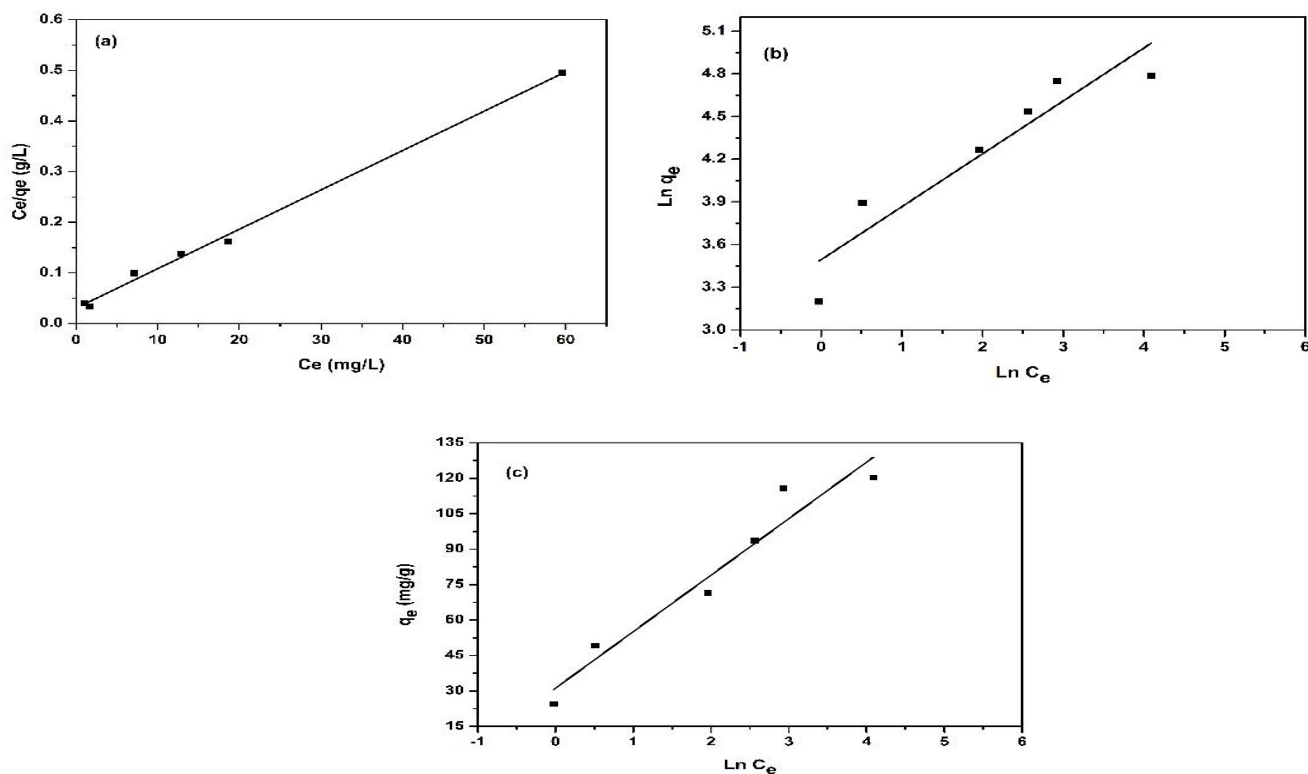


Fig (4) Langmuir (a), Freundlich (b) and Temkin (c) models for the adsorption of (SY) dye on manganese oxide nanoparticle.

Table (1) Langmuir, Freundlich, and Temkin isothermal constants for the adsorption of (SY) dye on manganese oxide nanoparticle.

Adsorption isotherm	Constants	Values
Langmuir	K_L (L/mg)	0.2557377
	R_L	0.0725-0.01287
	R^2	0.9963
	q_m (cal) (mg/g)	128.205
	q_m (exp) (mg/g)	117.941
Freundlich	$K_F [(L/mg) (L/mg)^{1/n}]$	32.954
	P (L/mg)	2.688
	R^2	0.8838
	q_m (cal) (mg/g)	257.002
	q_m (exp) (mg/g)	117.941
Temkin	K_T (L/mg)	3.687
	X (J/mol)	101.895
	G	12.961
	R^2	0.9442

3.4. Adsorption kinetics

To elucidate the adsorption kinetics of Sunset Yellow (SY) dye over manganese oxide nanoparticles, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were applied, as described by Equations (7-9) [25, 27, 28]. The results of which are presented in Figure 5(a-c).

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1 t}{2.303} \quad (7)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (8)$$

$$Q_t = K_{IPD} t^{0.5} + Y \quad (9)$$

where Q_e represents the amount of Sunset Yellow (SY) dye adsorbed at equilibrium, and Q_t represents

the amount of Sunset Yellow (SY) dye adsorbed at a specific time t (in minutes). k_1 is the pseudo-first-order rate constant of adsorption, while k_2 is the pseudo-second-order rate constant of adsorption. K_{IPD} stands for the intra-particle diffusion rate constant, and C is a constant associated with the intra-particle diffusion model. As shown in Table (2) and based on the magnitude of the coefficient of determination (R^2), the pseudo-second-order model ($R^2 = 0.9959$) provided the best fit for the adsorption of Sunset Yellow (SY) dye on the manganese oxide nanoparticles as an adsorbent compared to the pseudo-first-order model ($R^2 = 0.989$).

Table (2) Adsorption kinetic parameters of the removal of sunset yellow (SY) dye on manganese oxide nanoparticles.

Model	Parameters	Values
Pseudo first order	K_1 (min ⁻¹)	0.0850
	R^2	0.989
	q_m (cal) (mg/g)	32.998
	q_m (exp) (mg/g)	48.966
	K_2 (g/mg.min)	0.0047
Pseudo second order	R^2	0.9959
	q_m (cal) (mg/g)	51.662
	q_m (exp) (mg/g)	48.966
	K_i (mg/g min ^{0.5})	10.487
Intra-particle diffusion	C (mg/g)	0.841
	R^2	0.9762
	K_i (mg/g min ^{0.5})	0.5339
	C (mg/g)	44.157
	R^2	0.7557

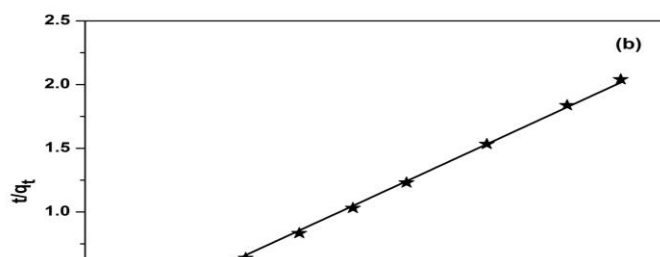
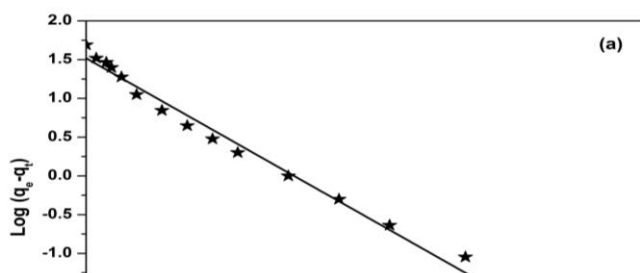


Fig (5) Pseudo-first-order (a), pseudo-second-order (b), intra-particle diffusion (c) for adsorption of (SY) dye on manganese oxide nanoparticles.

Conclusion

Manganese oxide nanoparticles were synthesized via the auto-combustion method using urea as a fuel. This synthesized material was utilized as an adsorbent for removing the anionic dye Sunset Yellow (SY) from aqueous solutions. The obtained manganese oxide nanoparticles were characterized using (FTIR) and (XRD) tools. The crystalline size determined from (XRD) was found to be 38 nm. The adsorption capacity for the removal of Sunset Yellow dye over the synthesized manganese oxide nanoparticles were

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