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Kinetics investigation of oxytetracycline sorption onto 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO triple-composites.

Research submitted as partial fulfillment requirements for the completion of the BSc Degree in Chemistry

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November - 2023

Acknowledgement & Dedication

We sincerely thank our supervisor, Dr. Faisal Algethami, for his excellent leadership and effective management. Additionally, we would like to express our gratitude to the esteemed academic members of the Department of Chemistry within the College of Science at Imam Muhammad bin Saud University for their unwavering dedication and invaluable guidance. This research is dedicated to our families as a gesture of gratitude for their unwavering support and motivation.

Figures

Abstract

Water contamination by pharmaceutical substances through industrial wastewater discharge is a worldwide environmental problem. As a result, many researchers have introduced various methods for treating pharmaceutically contaminated wastewater. In this study, a one-put fast method was used to prepare ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO composites. The synthesized composites were studied for removing oxytetracycline (OTC) from water via adsorption. The removal reached the equilibrium within 60 minutes, and about 90% of OTC removal was accomplished within the first 20 min. The ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO showed adsorption capacities of 28.8, 29.4, 50.2, and 44.3 mg g^{-1}, respectively. The kinetic rate order and rate-control mechanism were studied for adsorbing OTC by the four sorbents. The kinetic obtaining showed that OTC adsorption by ZnO-MgO, 2.5%CoO@ZnO-MgO fitted the pseudo-first-order model, while OTC sorption onto 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO followed the pseudo-second-order model. Additionally, the rate control mechanism outcomes revealed that liquid film and intraparticle diffusion models co-participated in controlling the OTC adsorption onto the four sorbents. These results nominated the 5%CoO@ZnO-MgO composite as the best sorbent among the prepared materials.

الملخص باللغة العربية

يعد تلوث المياه بالمواد الصيدلانية من خلال تصريف مياه الصرف الصناعي مشكلة بيئية عالمية. ونتيجة لذلك، قدم العديد من الباحثين طرقًا مختلفة لمعالجة مياه الصرف الصحي الملوثة صيدلانيًا. في هذه الدراسة، تم استخدام طريقة سريعة أحادية الوضع لتحضير مركبات ZnO-MgO و2.5%CoO@ZnO-MgO و5%CoO@ZnO-MgO و10%. تمت دراسة المركبات المحضرة لإزالة الأوكسيتتراسيكلين (OTC) من الماء عن طريق الامتزاز. وصلت عملية الإزالة إلى الاتزان خلال 60 دقيقة، وتم إنجاز حوالي 90% من عملية الإزالة خلال أول 20 دقيقة. أظهرت ZnO-MgO و2.5%CoO@ZnO-MgO و5%CoO@ZnO-MgO و10%CoO@ZnO-MgO قدرات امتزاز تبلغ 28.8 و29.4 و50.2 و44.3 ملجم جرام على التوالي. تمت دراسة ترتيب حركية الامتزاز وآلية التحكم في المعدل امتزاز OTC بواسطة المواد المازة الأربعة. أظهرت النتائج أن امتزاز OTC بواسطة ZnO-MgO، 2.5%CoO@ZnO-MgO يلائم نموذج الدرجة الأولى الزائف، في حين أن امتزاز OTC على 5%CoO@ZnO-MgO، و10%CoO@ZnO-MgO يتبع نموذج الدرجة الثانية الزائفة. بالإضافة إلى ذلك، كشفت نتائج آلية التحكم في المعدل أن نماذج الانتشار في السائل والنتشار داخل الجسيمات شاركت في التحكم في امتزاز OTC على المواد الماصة الأربعة. رشحت هذه النتائج المركب 5%CoO@ZnO-MgO كأفضل مادة مازة بين المواد المحضرة.

Chapter I

Introduction

1. Introduction

Nanoscale materials refer to a collection of substances with a minimum dimension that is either less than or equal to 100 nanometers. The intriguing characteristics of nanomaterials at the nanoscale, including optical, magnetic, electrical, and other capabilities, render them highly captivating. These new qualities can benefit various industries, such as electronics and health [1].

1.1. Common methods for fabricating nanomaterials

Numerous procedures have been employed in synthesizing nanomaterials, broadly categorized as bottom-up approaches involving assembling atoms or molecules to form bigger structures within the nanoscale regime. The second perspective can be characterized as a top-down approach, wherein the size of bulk materials is diminished to the nanoscale [2-4]. From these two main routes, numerous methodologies have been created. Still, the main ones are Solvothermal, sol-gel, and Green methodologies. Solvothermal is one of the most environmentally friendly and promising synthesis methods. The solvothermal approach uses solvents to optimize particle size distribution and shape control. This technique homogenizes metal salts and adjusts the medium pH to alkaline with a basic solution. The target nanomaterial controls the homogenized solution's thermal treatment temperature and time [5]. The sol-gel process is the most used method for creating nanomaterials. A reaction between precursors happens in a suitable solvent where a surfactant or nonaqueous solvent controls the particle size [6]. In green nanomaterial manufacturing, capping substrates might be plant extracts or microorganisms. Biosynthesis of nanomaterials from seeds, leaves, stems, roots, and latex. Green technology was the safest approach to making nanoparticles. Scientists use bacteria, algae, fungi, and plants to make cheap, energy-efficient, and environmentally friendly metal nanoparticles. Green synthetic methods are replacing physicochemical ones in the industry [7, 8].

Zinc oxide (ZnO) nanoparticles have wide applications in various fields. According to recent research, Alumina nanoparticles are one of the most popular nanosized materials in the United States. It is now in first or second place among nanoscale materials sales in the United States [9]. Many different technologies have found use for nanoscale ZnO, including adsorption, photocatalysis, lithium batteries, coating, rocket fuel, gelled fuel, ceramics, and solar cells [10]. Additionally, ZnO was believed to improve the anti-cancer effects of immunotherapy that uses a tumor cell vaccination [11]. Due to its low specific gravity, strength, and stiffness, MgO has many potential uses. These include but are not limited to, biosensors, computers, electronics, vehicles, aircraft, adsorbents, catalysts, superconducting products, and batteries [12]. Leilei et al., prepared NiO-MgO-Al_2O_3 nanocomposite using absolute ethanol as a solvent. The mixed ion solution was acidified by nitric acid, and the final mixture was covered and stirred at room temperature for 5.0 h. Lastly, the mixture was transferred to a petri dish, protected, and put into a 60 ◦C drying oven for 48 h. The resulting gel was calcined at 600 ◦C for 5.0 h [13]. Yi et al., prepared NiO-

$MgO-Al_2O_3$ by the wet impregnation method starting with commercial spherical Al_2O_3. $Mg(NO_3)_2$ was dissolved in water; after adding Al2O3, the mixture was kept at room temperature for 8.0 hours. The product was filtered from the mixture, dried at 110 °C for 24.0 h, and calcined at 500°C for 5.0 h. The collected material after calcination was added to Ni solution and kept at room temperature for 8.0 h. The solid was filtered, dried at 110°C overnight, and then calcined at 500°C for 5.0 h [14]. Hayder et al. prepared MgO composite using a hot plate stirrer set to 60°C to continuously mix 100 ml of deionized water with aluminum nitrate and calcium nitrate until the salts dissolve. Ammonium hydroxide (NH4OH) was gradually added with constant stirring until a gel formed, dried, and calcined for 2 hours at 550℃ [15]. Electronics, magnetism, biology, medicines, cosmetics, the environment, catalysis, and materials are just some of the many applications for nanoscale materials. The promising future of nanotechnology has led to a rise in funding for its study and development around the world. Research into, and investment in, nanotechnology has increased dramatically since 1999 [16]. The use of nanomaterials in water purification is one of their significant implications. To put it simply, water contamination is any change, whether physical or chemical, in water quality that has an adverse effect on living organisms or renders water unfit for critical uses. It has far-reaching consequences on people, families, and communities. Water pollution poses a serious threat to life on Earth because water is essential for all life forms [17]. There are many different ways to define water contamination due to the wide range of causes and consequences it might have. Basically, it lowers the standard of water, which causes problems for aquatic life and makes it less effective as a resource. Rivers, oceans, lakes, rains, wells, and groundwater are all at risk, as are fish and other aquatic life, and the economic value of the water can decrease as a result. The result of water pollution is that it makes water unsafe for human, animal, plant, and aquatic life consumption [18]. Collecting groundwater through prospecting, drilling, or springs is crucial to the river's flow [19]. Over the past few years, a scarcity of clean water for human and agricultural usage has resulted from the alarming rise in water pollution. Waterborne disease epidemics have been commonplace since the spread of polluted water systems [20]. Land-based human activities, such as manufacturing and garbage disposal, primarily contribute to ocean pollution [21].

1.2 Water treatment methods

To guarantee that residents can access potable water, public and wastewater systems use various water treatment methods:

1.2.1. Heating

Parasites and bacteria, both of which are invisible to the naked eye but can be lethal, may be present in water from a variety of sources and distribution systems. Once the water has boiled, cover it and let it cool before drinking [22].

1.2.2. Filtration

Regarding chemical and physical processes, filtration is one of the most reliable options for purifying water. Large-scale chemicals and microscopic contaminants are removed from the air thanks to filtration. Because filtering does not entirely remove mineral salts, filtered water is preferable to unfiltered water for health reasons [23].

1.2.3. Ozonation

Water purification by ozonation includes adding the powerful oxidant ozone to the water supply. Ozone, or triatomic oxygen, is a highly reactive gas that may destroy many chemicals and bacteria. Water purification and destroying organic and pollutant compounds are two of the many benefits of ozone treatment, an enhanced oxidation process [24].

1.2.4. Ion Exchange

Chemical and environmental engineers have used the ion exchange (IX) technique for years. Initially, its primary usage was in water softening, which removes calcium and magnesium ions from water at the treatment plant or as a point-of-use treatment procedure [25].

1.2.5. Chemical Precipitation

The chemical precipitation of heavy metals from wastewater is a standard treatment method. Removal of impurities from water using precipitating agents (coagulants) such as ferrous or aluminum sulfates by altering the pH, electro-oxidizing potential, or coprecipitation [26].

Taking in Water (1.3.7)

Adsorption is the phenomenon whereby chemicals move from one phase to another, whether between liquid and solid, gas and liquid, or gas and solid. Intermolecular forces are effective at removing contaminants from wastewater. Adsorption can have either a physical or chemical form. Reversible physisorption occurs in the presence of weak physical forces like van der Waals. This adsorption type occurs at or near the adsorbate's critical temperature. Chemisorption, on the other hand, involves the adsorbate and solid surface forming a chemical connection. However, it always exists as a single layer, and the adsorbates are easily removed by washing. Both processes are possible simultaneously or as needed. Surface area, adsorbate type and beginning concentration, solution pH, temperature, competing chemicals, and adsorbent nature and dose are all important variables to consider when studying adsorption processes [27, 28].

1. 3 Aim of the study

This study aims to synthesize ZnO-MgO, 2.5%@ZnO-MgO, 5%@ZnO-MgO, and 10%@ZnO-MgO nanocomposites using one put route. The prepared nanomaterials will be studied fro removing pharmaceutical pollutants exemplified by oxy tetracycline drug (OTC). The rate order and the step controlling the OTC removal by the four sorbents will be investigated.

Chapter II

Materials and Methods

2. Materials and methods

2.1. Materials

Oxytetracycline (**OTC**) was supplied from Fluka, USA. Glucose sugar (Gl) was provided from Redl De-Haen, Germany. Zinc acetate, Magnesium acetate, and cobalt acetate were provided from Win-lab, England.

2.2. Preparation of ZnO-MgO based triple nanocomposites

A total of 13.45 grams of zinc acetate dihydrate (Zn(Ac)2-2H2O), 24.6 grams of magnesium acetate tetrahydrate (Mg(Ac)2-4H2O), and 5 grams of glucose (Gl) were carefully put into a 600 milliliter beaker. Approximately 30 milliliters of distilled water was introduced. The combination was subjected to heating at a temperature of 120°C until it underwent a phase transition into a transparent solution. Subsequently, the temperature was further increased to approximately 220°C, leading to the carbonization of Gl. The black product that was acquired was transformed into a powdered form and thereafter transferred into a porcelain dish. It was then subjected to a calcination process at a temperature of 700°C for a duration of 4.0 hours. The procedure was replicated employing the conventional quantities of Zn-Mg, supplemented with an appropriate quantity of Co(Ac)2, in order to produce the nanocomposites of 2.5%@ZnO-MgO, 5%@ZnO-MgO, and 10%@ZnO-MgO.

2.3. Adsorption of OTC

A stock solution of OTC at a concentration of 100 mg L^{-1} was prepared by dissolving 0.1 grams of OTC in 1.0 L of distilled water with the aid of an ultrasonic path. The influence of contact time was examined for adsorbing of OTC onto ZnO-MgO, 2.5%CoO@ZnO-MgO, 5% CoO@ZnO-MgO, and 10% CoO@ZnO-MgO. A mass of 50 mg was weighed from each sorbent in a 150 mL beaker, and 120 mL OTC solution was added to each peaker, followed by stirring via a magnetic stirrer. A volume of 5.0 mL was picked and filtered, and the absorbance of OTC was followed from each combination until equilibrium was reached. The adsorption process was monitored at 2, 5, 10, 20, 30, 45, 60, 90, and 120 minutes. After each time interval, a sample was collected, filtered using a filter syringe, and analyzed using a UV-Vis spectrophotometer at $\lambda = 275$ nm.

Chapter III

Results & discussion

3. Results and discussion

3.1. Contact time study

The obtained absorbance from the contact time study was employed for calculating the concentration of the unadsorbed OTC at each time interval via Eq. 1. The adsorption capacity (the milligrams of OTC adsorped on one gram of sorbent, q_t, mg g^{-1}) was computed using Eq. 2.

$$C_t = \frac{Absorbance_{sample}}{Absorbance_{standard}} \times conc._{standard} \qquad (1)$$

$$\mathrm{q_t} = \frac{(\mathrm{C_o} - \mathrm{C_t})\,\mathrm{V}}{\mathrm{m}}, \qquad (2)$$

Figures 1, 2, 3, and 4 demonstrate the performance of ZnO-MgO, 2.5%CoO@ZnO-MgO, 5% CoO@ZnO-MgO, and 10% CoO@ZnO-MgO composites in adsorbing OTC as a function of contact time. The OTC adsorption started quickly and increased progressively until it almost stopped within 60 minutes. Worth mentioning, about 90% of the OTC adsorption by ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO composites was accomplished within the first 20 min, and maximum q_t values were 28.8, 29.4, 50.2, and 44.3 mg $g^{-1,}$ respectively. These results revealed that each one of the tested sorbents could be employed for removing OTC from contaminated water with a superiority of 5%CoO@ZnO-MgO composite (Fig. 5).

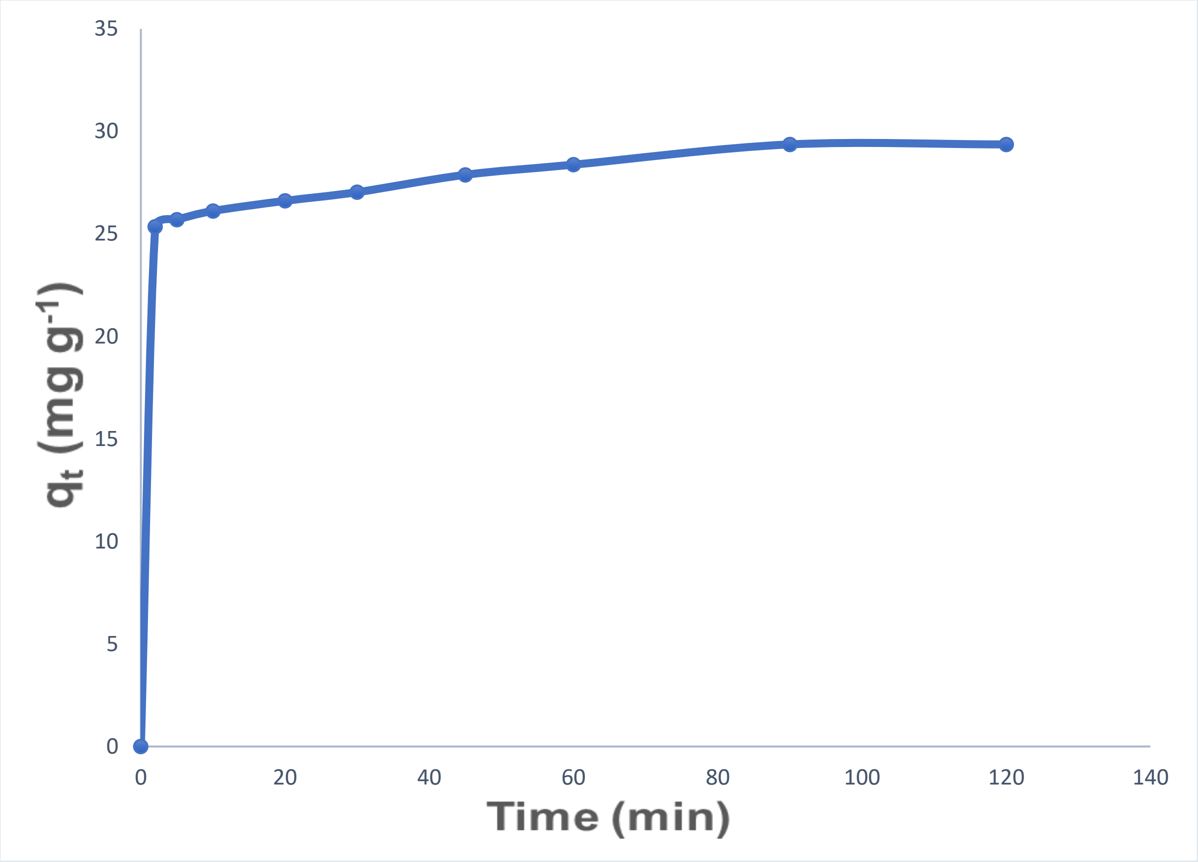

Fig. 1 The contact time study of the OTC adsorption on ZnO-MgO, **nanocomposite.**

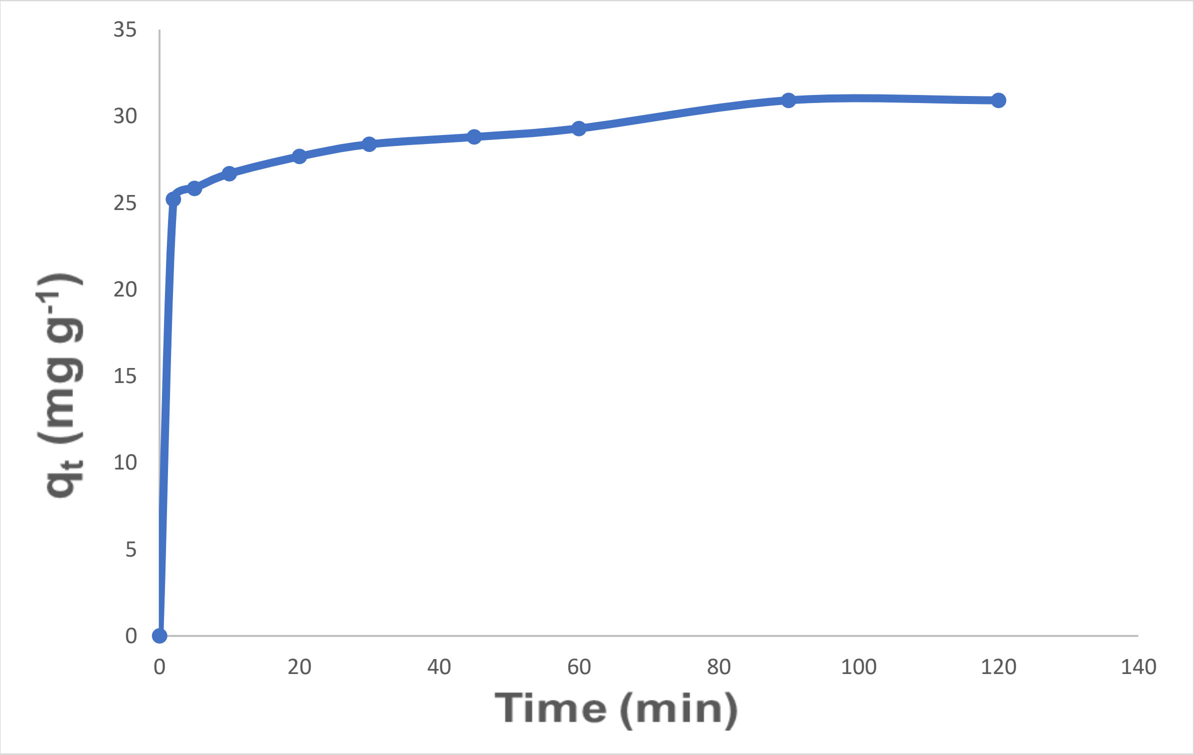

Fig. 2 The contact time study of the OTC adsorption on 2.5%CoO@ZnO-MgO, **nanocomposite.**

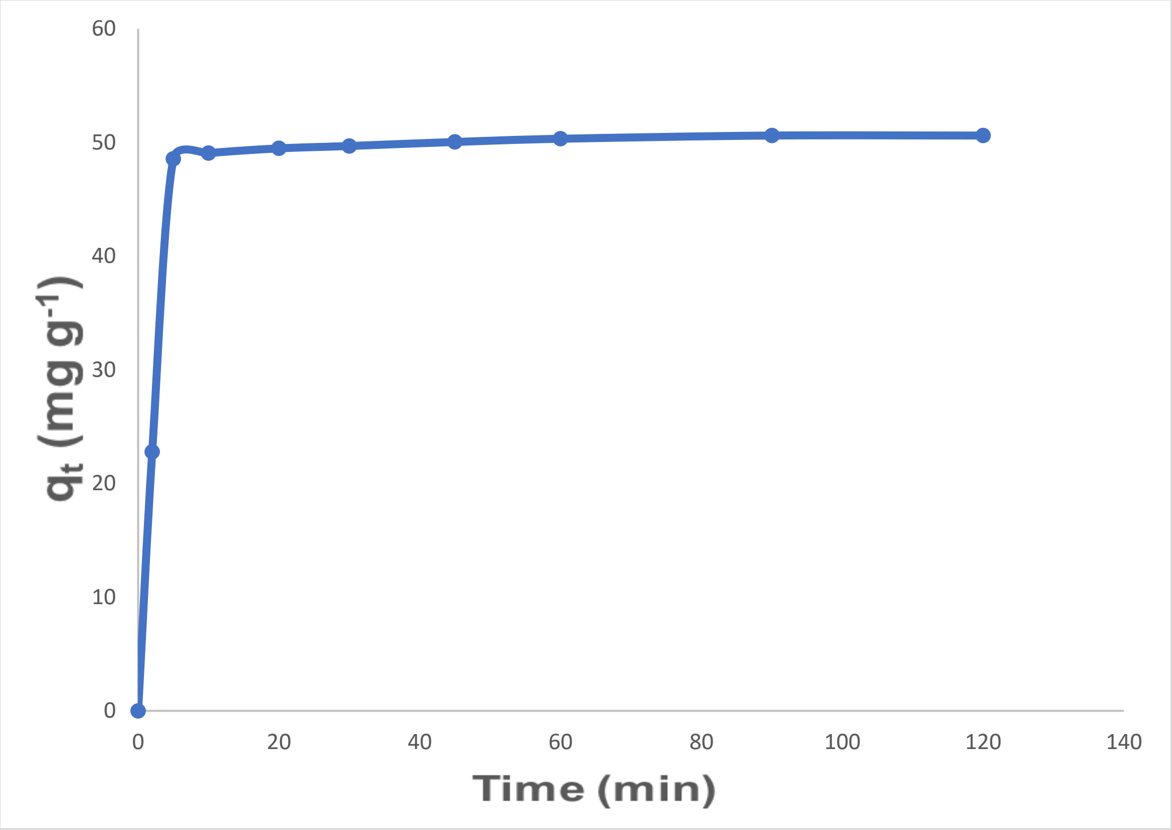

Fig. 3 The contact time study of the OTC adsorption on 5%CoO@ZnO-MgO **nanocomposite.**

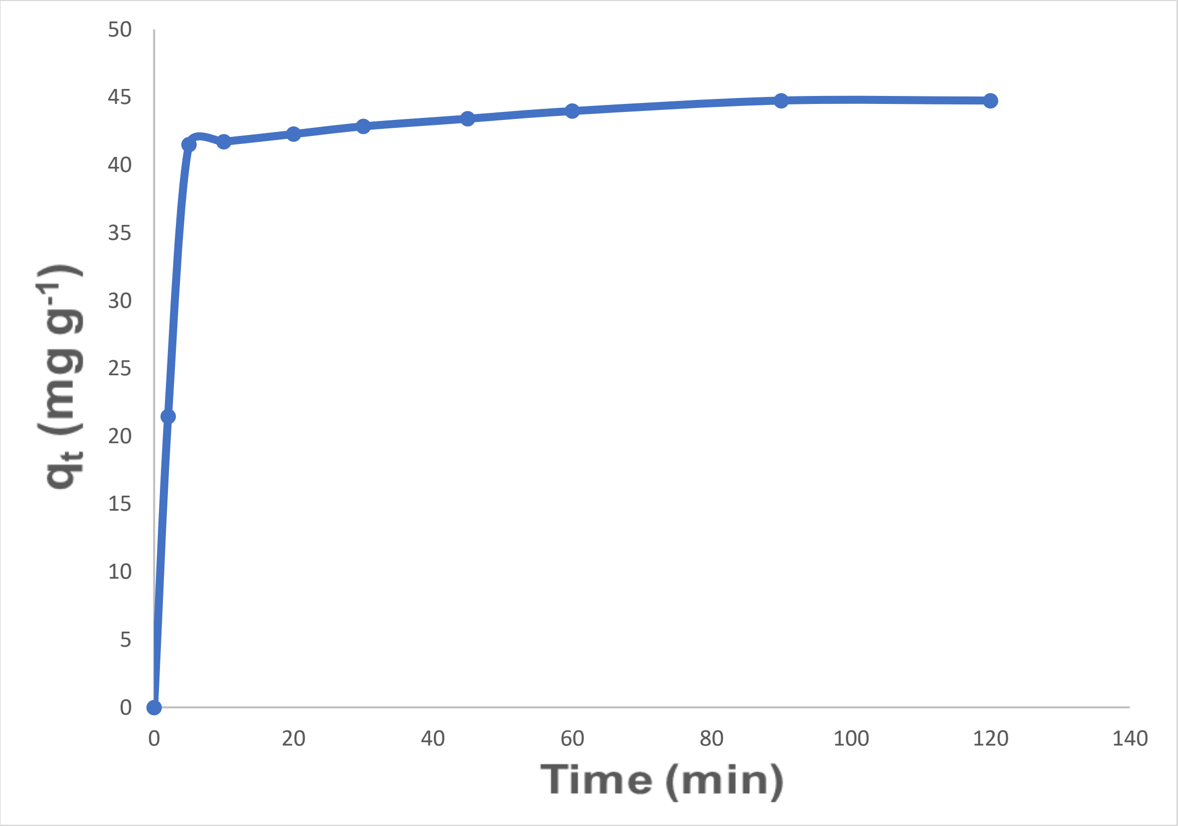

Fig. 4 The contact time study of the OTC adsorption on 10%CoO@ZnO-MgO **nanocomposite.**

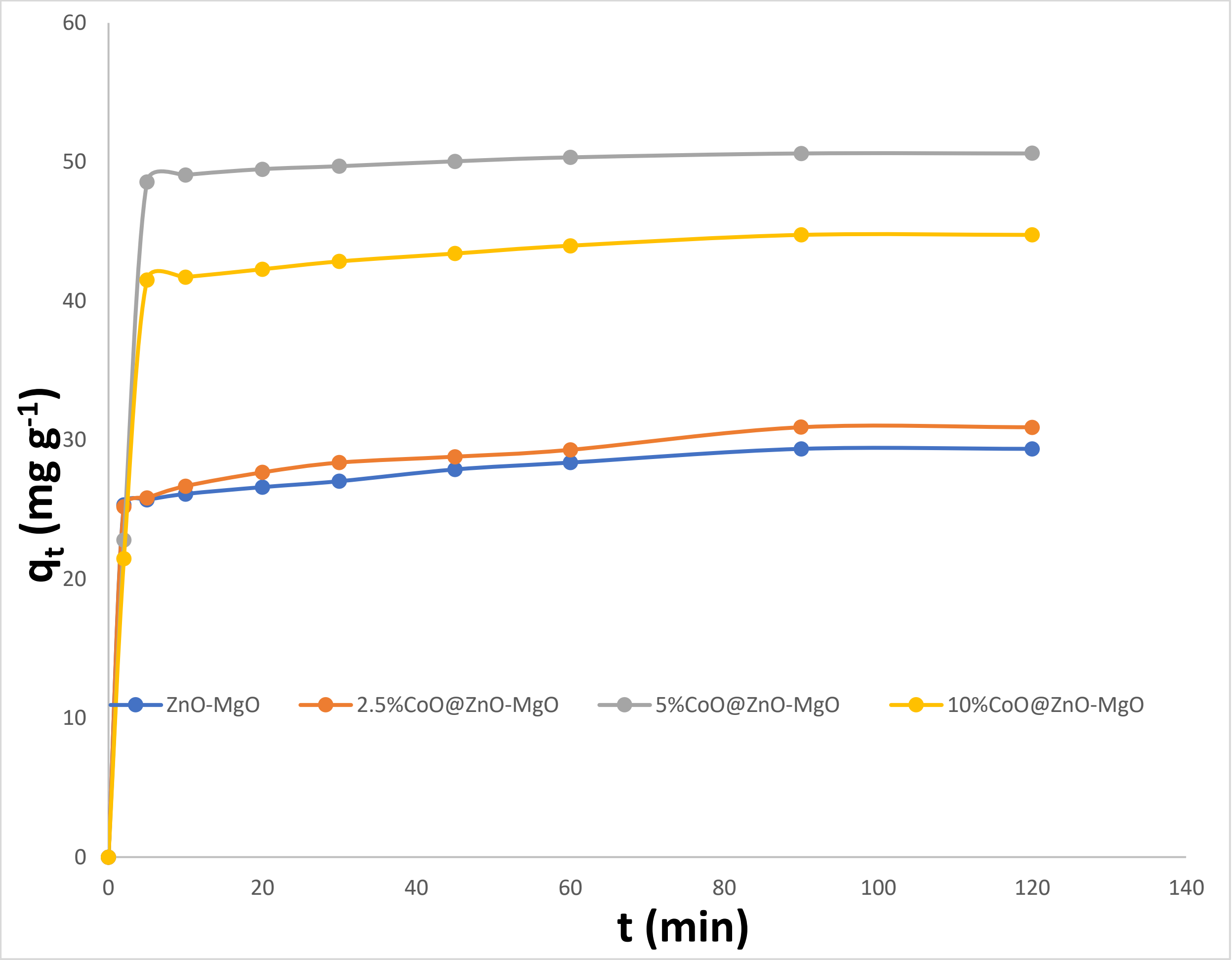

Fig. 5 Comparing the performance of ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO composites in removing OTC from water.

3.2 Adsorption rate order

The adsorption rate order for the OTC removal by ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO composites was studied. The pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models were utilized. These models are expressed in Equations 3 and 4, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1.t \qquad (3)$$

$$\frac{1}{q_t} = \frac{1}{k_2.q_e^2\,t} + \frac{1}{q_e} \qquad (4)$$

Where m, v, C_t, and C_o were the mass of the sorbent in grams, the volume of the solution in milliliters, and the concentration of the solution in milligrams per liter at time t, respectively; q_e (mg g^{-1}) represents the adsorption capacity at equilibrium. The PFO and PSO constants are expressed as k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}), respectively. The linear plots of the PFO result for the adsorption of OTC on ZnO-MgO, 2.5%CoO@ZnO-MgO, 5% CoO@ZnO-MgO, and 10% CoO@ZnO-MgO composites are depicted in Figures 6, 7, 8, and 9, respectively. Additionally, Figures 10, 11, 12, and 13 show the PSO plots for removing OTC by ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO, respectively. The obtaining gathered in Table 1 showed that OTC adsorption by ZnO-MgO, 2.5%CoO@ZnO-MgO fitted the PFO, while OTC sorption onto 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO followed the PSO.

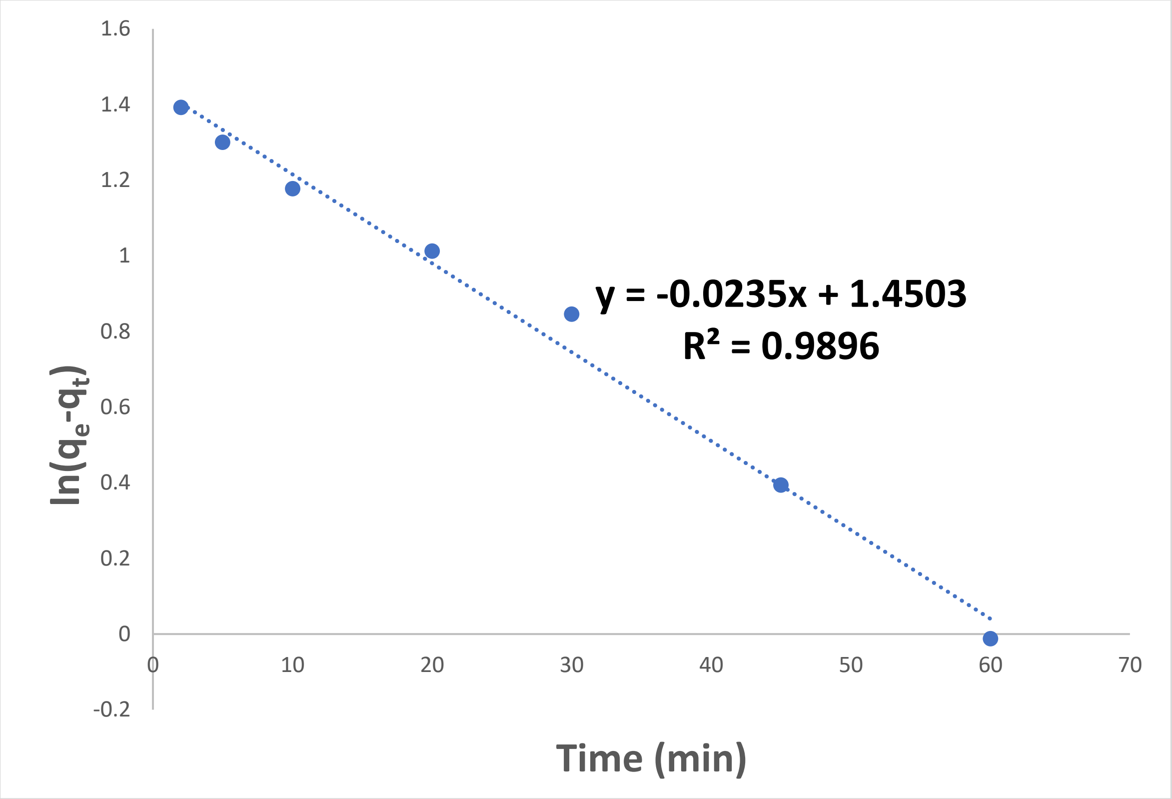

Fig. 6 The PFO investigation for OTC adsorption onto ZnO-MgO nanocomposite.

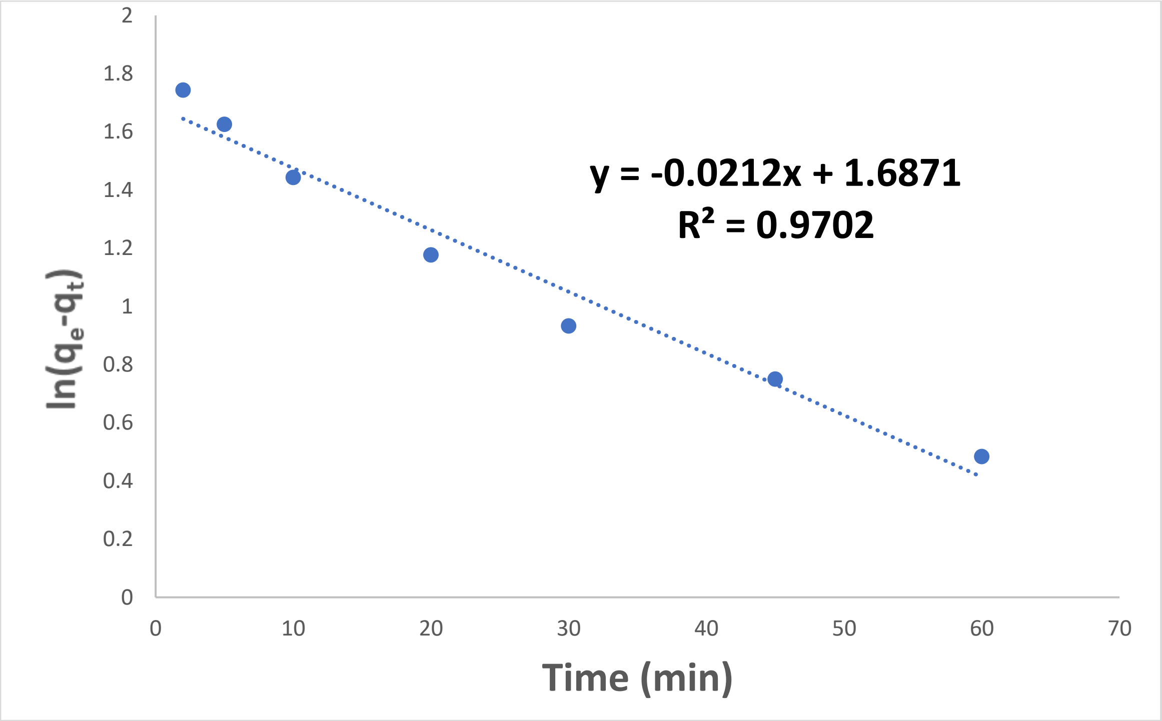

Fig. 7 The PFO investigation for OTC adsorption onto 2.5%CoO@ZnO-MgO nanocomposite.

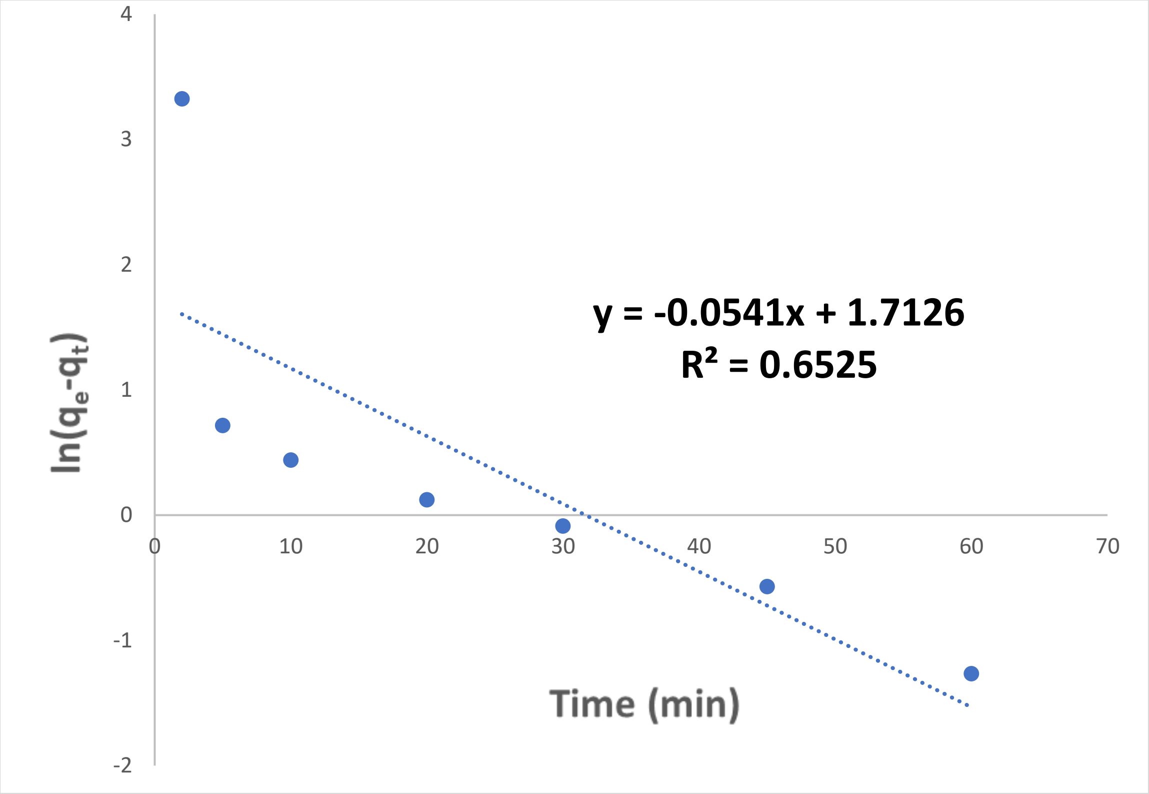

Fig. 8 The PFO investigation for OTC adsorption onto 5%CoO@ZnO-MgO nanocomposite.

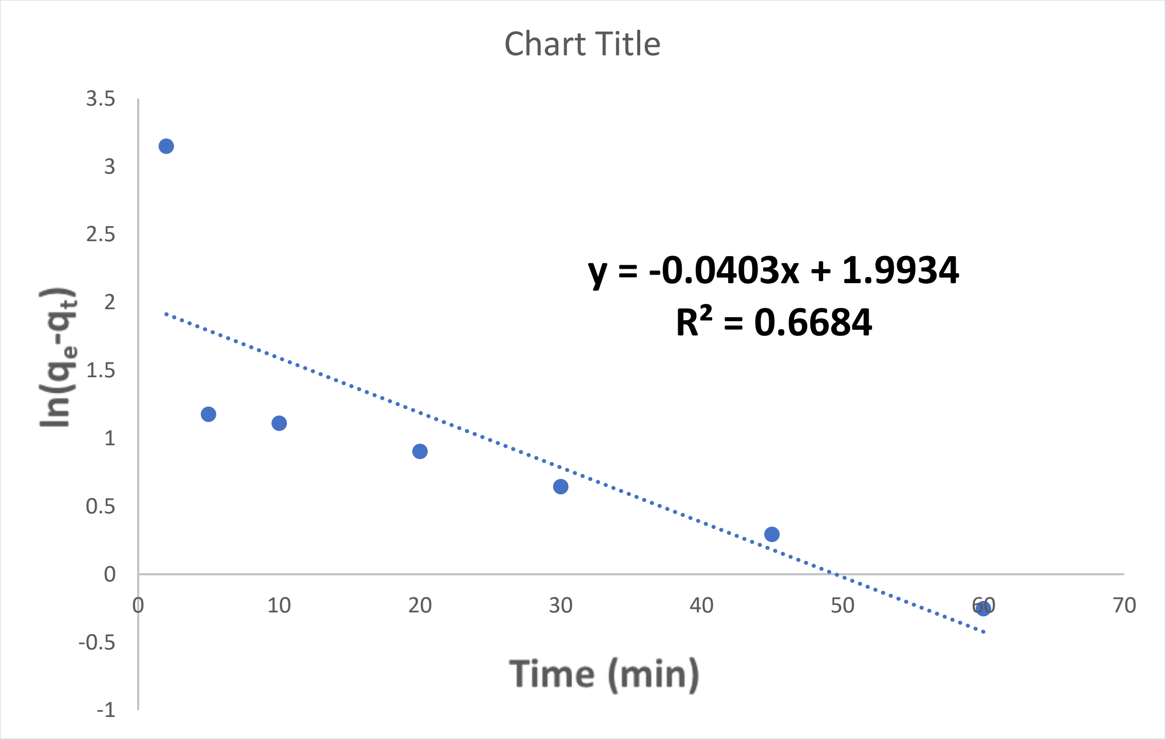

Fig. 9 The PFO investigation for OTC adsorption onto 10%CoO@ZnO-MgO nanocomposite.

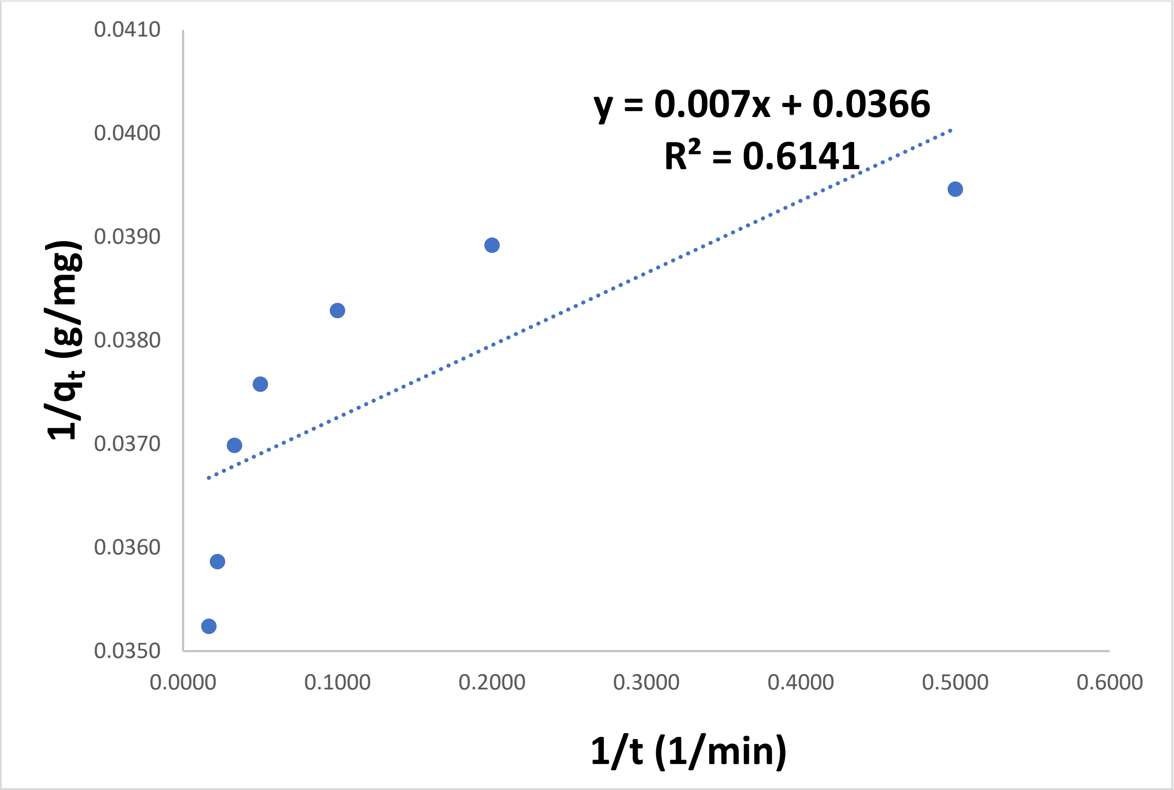

Fig. 10 The PSO investigation for OTC adsorption onto ZnO-MgO nanocomposite.

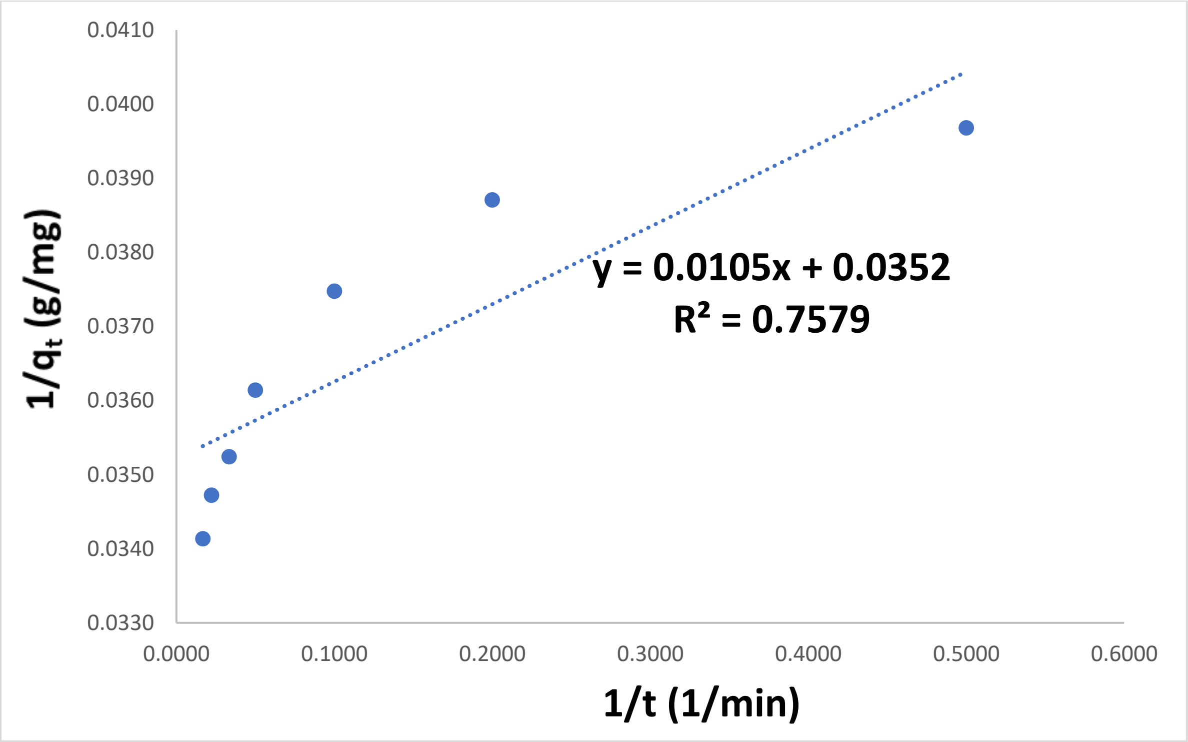

Fig. 11 The PSO investigation for OTC adsorption onto 2.5%CoO@ZnO-MgO nanocomposite.

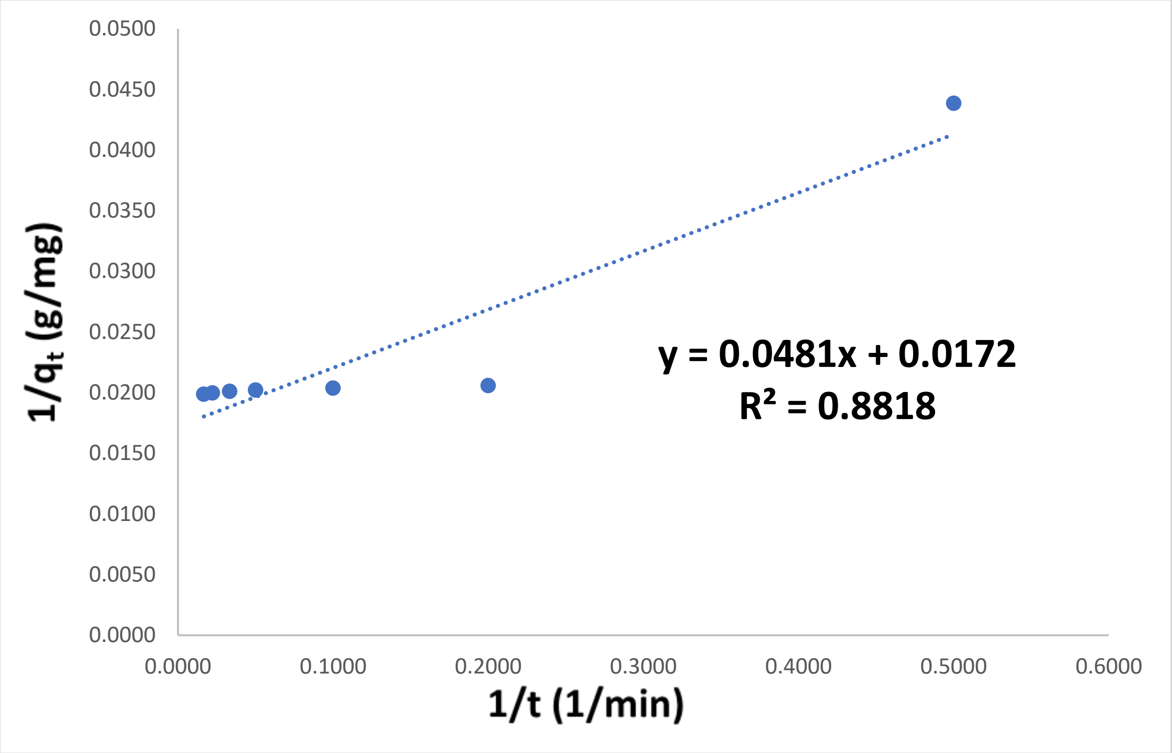

Fig. 12 The PSO investigation for OTC adsorption onto 5%CoO@ZnO-MgO nanocomposite.

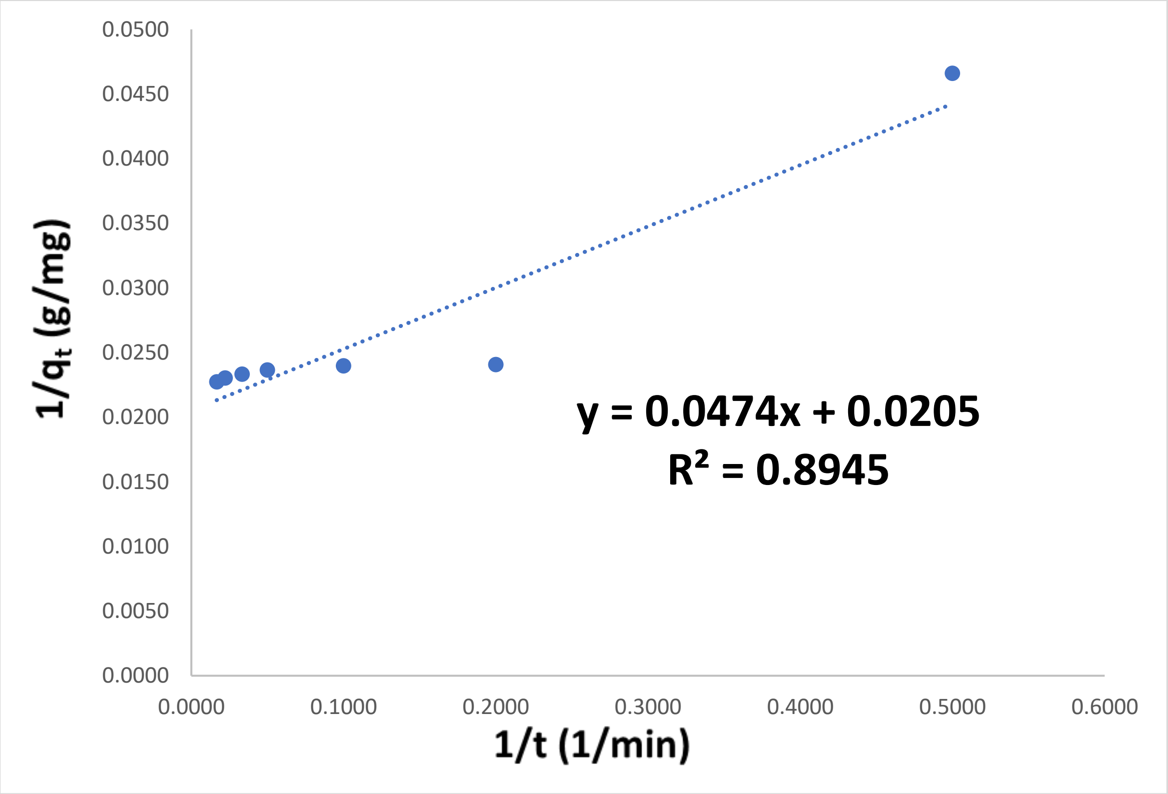

Fig. 13 The PSO investigation for OTC adsorption onto 10%CoO@ZnO-MgO nanocomposite.

Table 1 The adsorption rate order results for removing OTC by ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO.

		PFO		*PSO*	
adsorbent	qe exp. (mg g^{-1})	R^2	k_1	R^2	k_2
ZnO-MgO	29.36	0.990	0.024	0.614	0.014
2.5%CoO@ZnO-MgO	30.92	0.970	0.021	0.758	0.037
5%CoO@ZnO-MgO	50.61	0.653	0.054	0.882	0.007
10%CoO@ZnO-MgO	43.98	0.668	0.040	0.895	0.007

3.3 Adsorption control mechanism

The process of adsorption is thought to involve two stages, the first of which consists of the movement of adsorbate molecules from the liquid to the surface of the solid sorbent. In the second step, the sorbate molecules must diffuse through the solid sorbent into its internal layers. The adsorption rate is controlled by the sorption step that is the slowest, which is also known as the rate control mechanism. The intraparticle-diffusion (IPD) model (Eq. 5) and the liquid-film-diffusion (LFDM) model (Eq. 6) were used to achieve this goal of studying the rate-control mechanism for OTC adsorption on ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO [29].

$$q_t = K_{IP} * t^{\frac{1}{2}} + C_i \quad (5)$$

$$\ln(1 - F) = -K_{LF} * t \quad (6)$$

Where the IPDM constant is denoted by K_{IP} (mg g^{-1} $min^{-1/2}$), and the LFDM constant is designated by K_{LF} (min-1), respectively. C_i, the boundary layer factor, expressed as mg g^{-1}. The linear LFD plots for the OTC adsorption onto ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO nanocomposites were monitored in Fig. 14, 15, 16, and 17. The IPD plots are shown in Fig. 18, 19, 20, and 21, respectively. The results of LFD and IPD were collected in Table 2. The rate control mechanism outcomes revealed that both LFD and IPD models shared controlling the OTC adsorption onto the four sorbents.

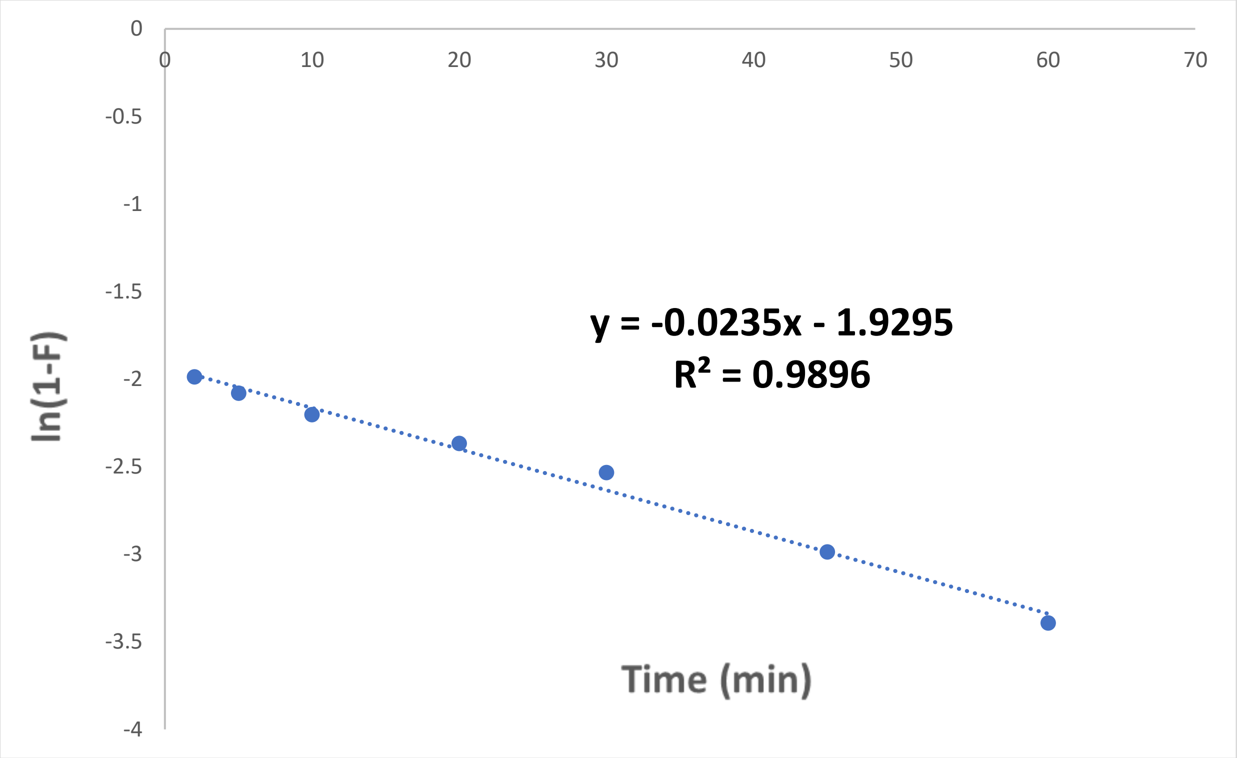

Fig. 14 The LFD study of OTC adsorption on ZnO-MgO nanocomposite.

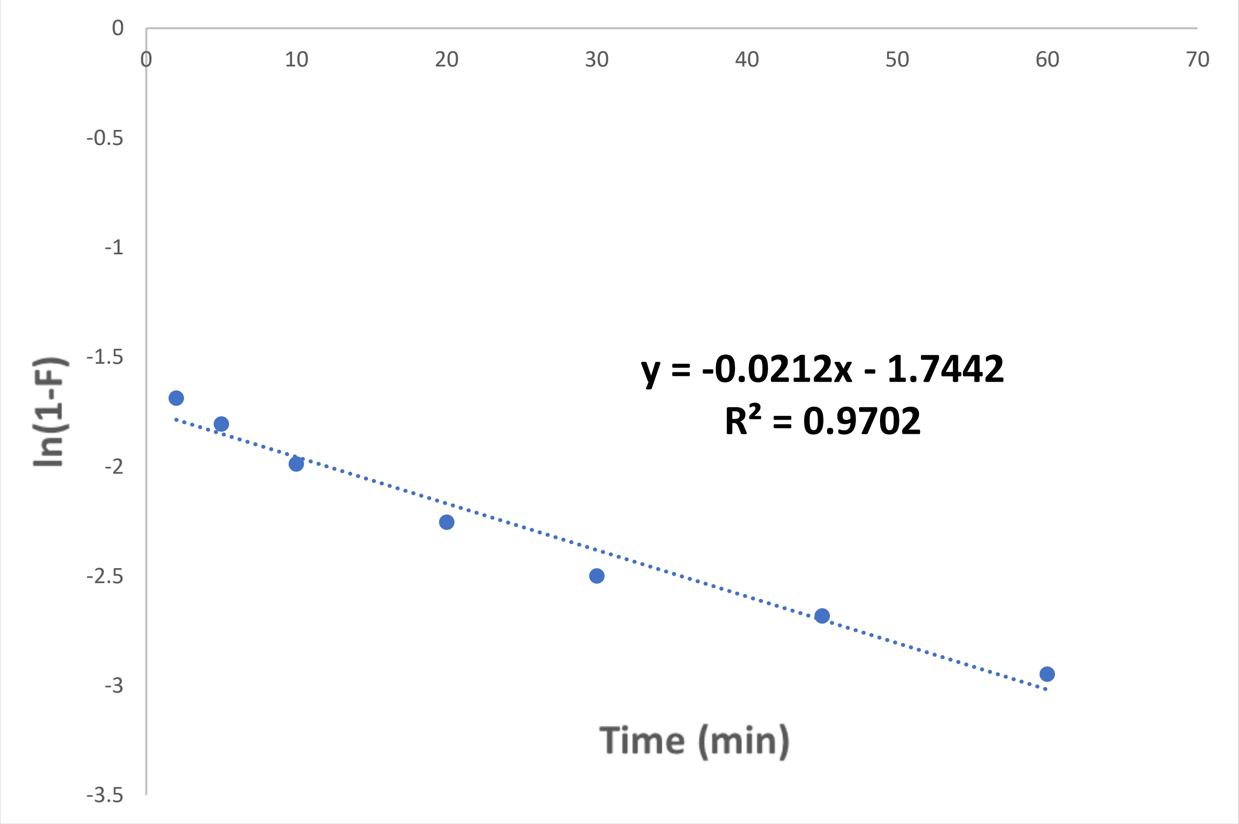

Fig. 15 The LFD study of OTC adsorption on 2.5%CoO@ZnO-MgO nanocomposite.

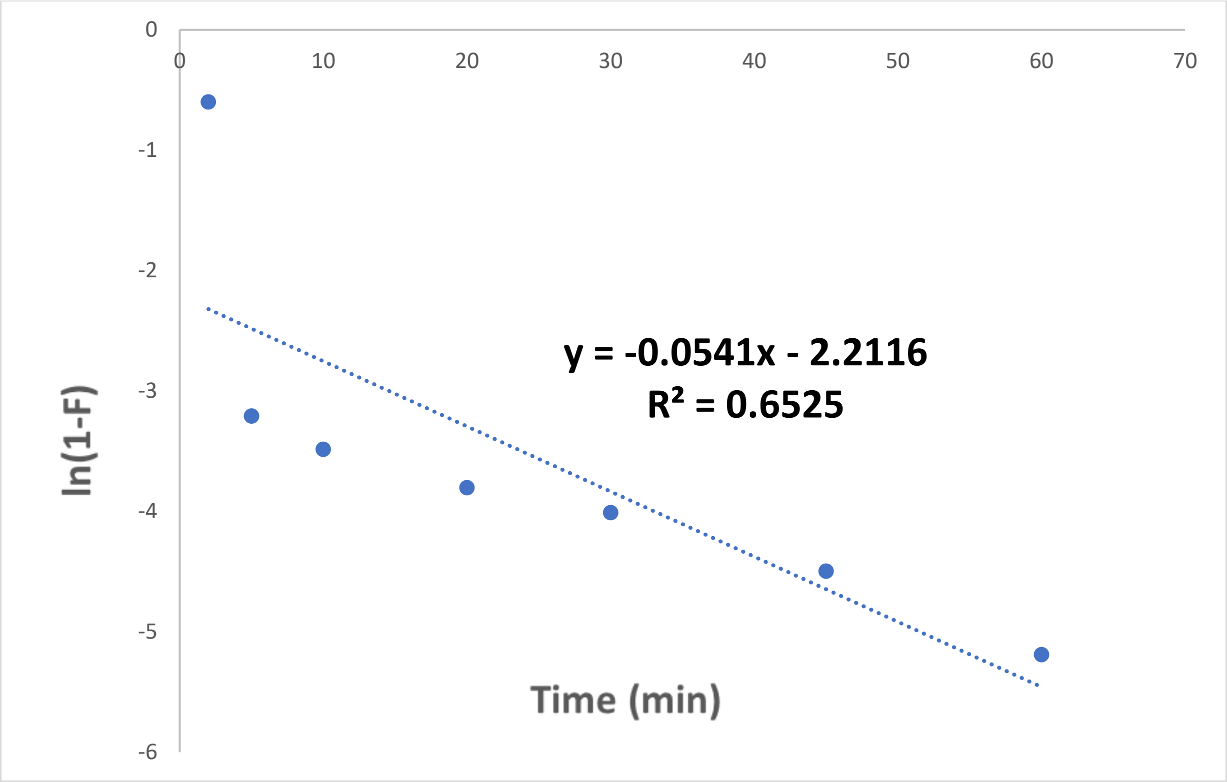

Fig. 16 The LFD study of OTC adsorption on 5%CoO@ZnO-MgO nanocomposite.

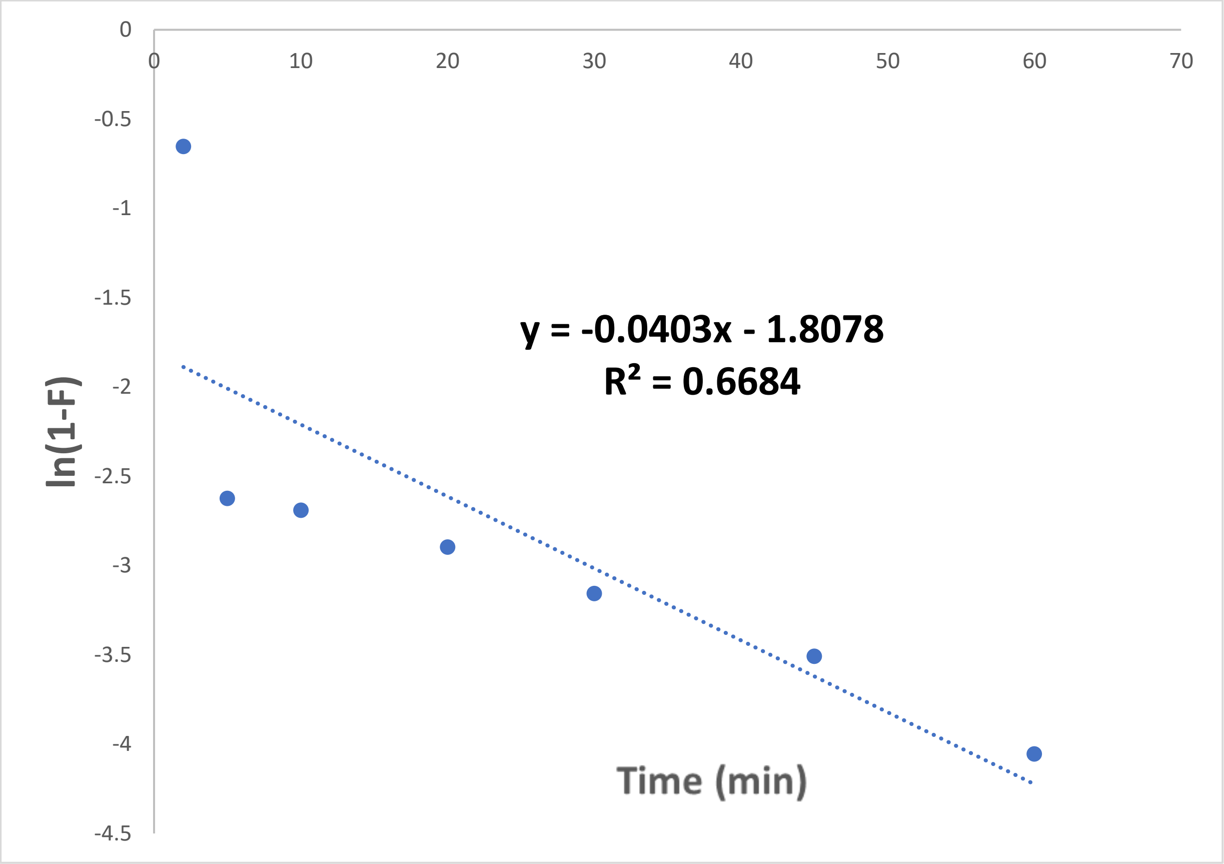

Fig. 17 The LFD study of OTC adsorption on 10%CoO@ZnO-MgO nanocomposite.

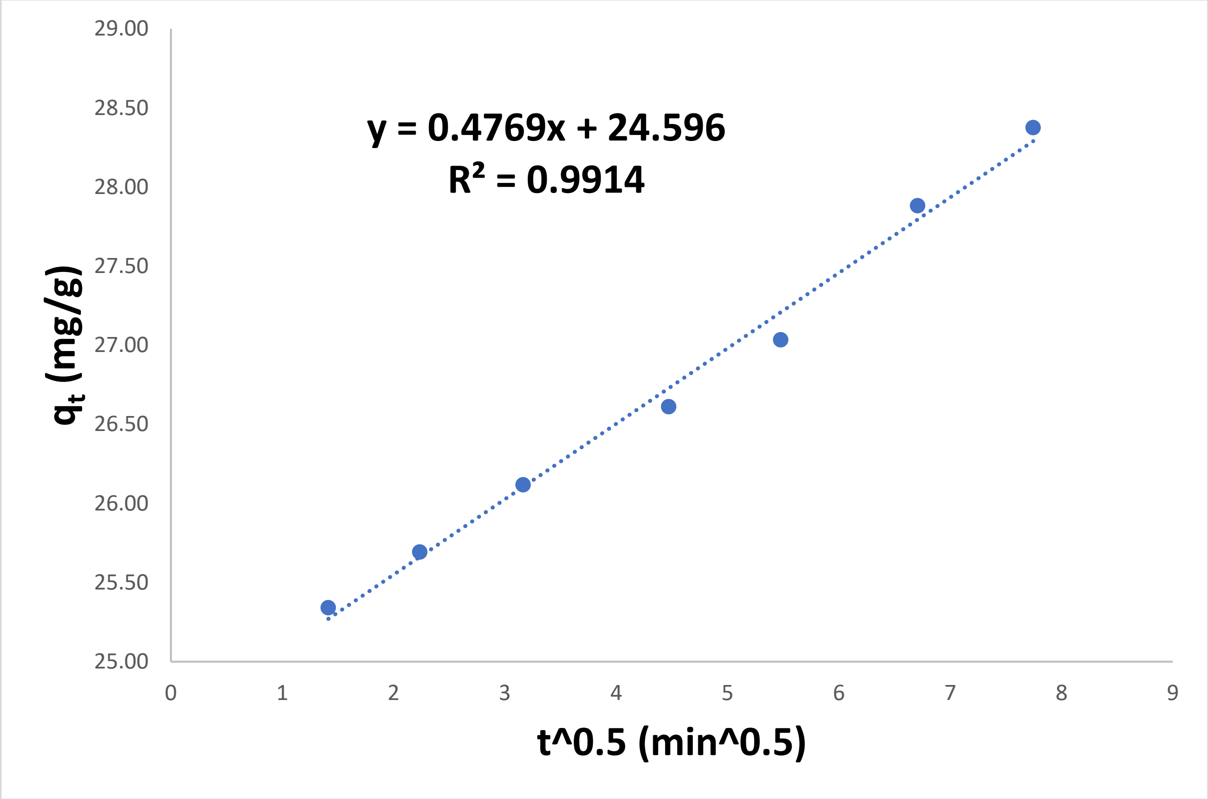

Fig. 18 The IPD study of OTC adsorption on ZnO-MgO nanocomposite.

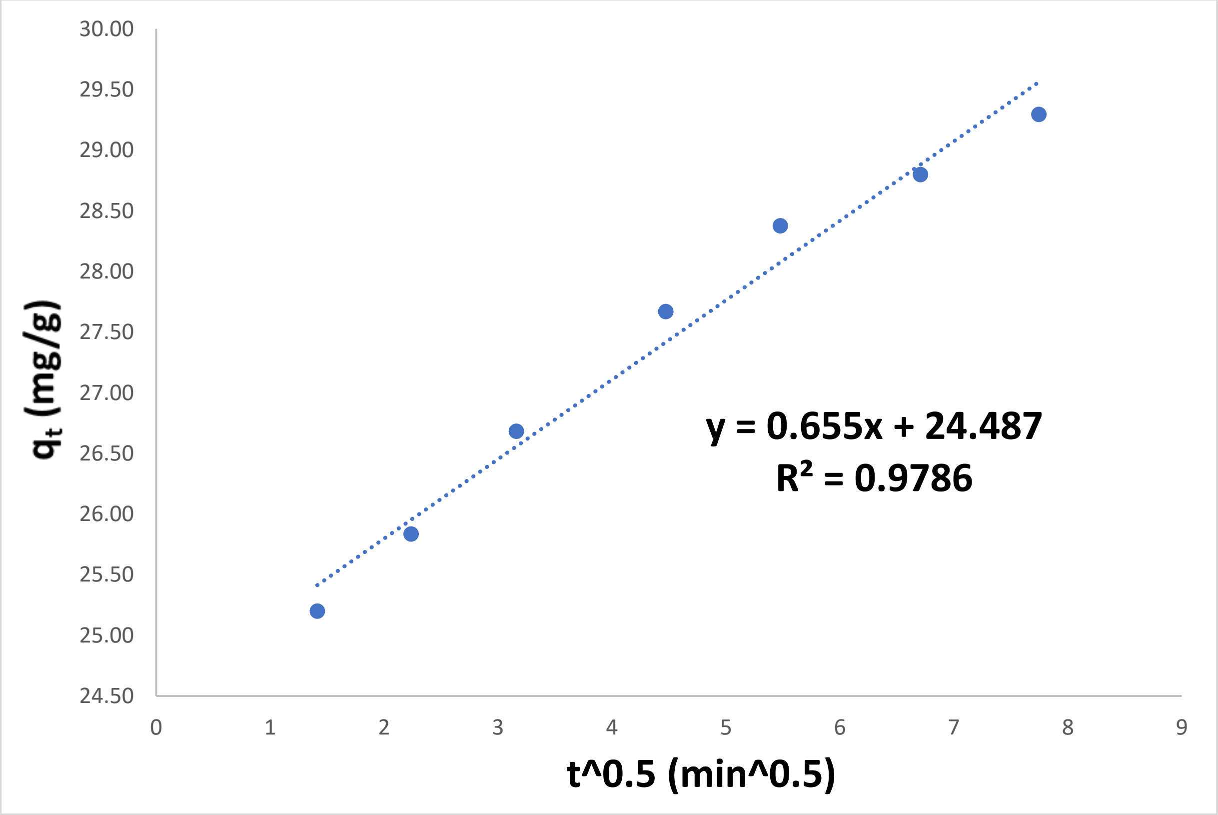

Fig. 19 The IPD study of OTC adsorption on 2.5%CoO@ZnO-MgO nanocomposite.

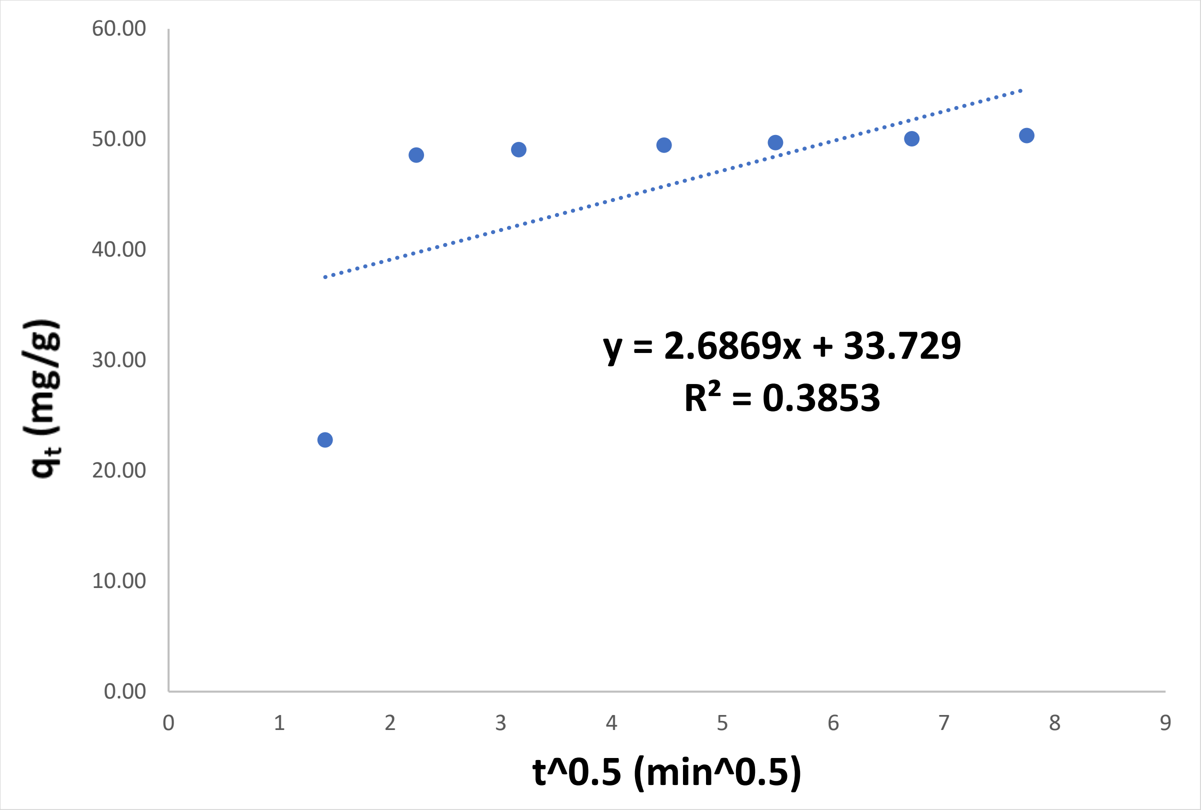

Fig. 20 The IPD study of OTC adsorption on 5%CoO@ZnO-MgO **nanocomposite.**

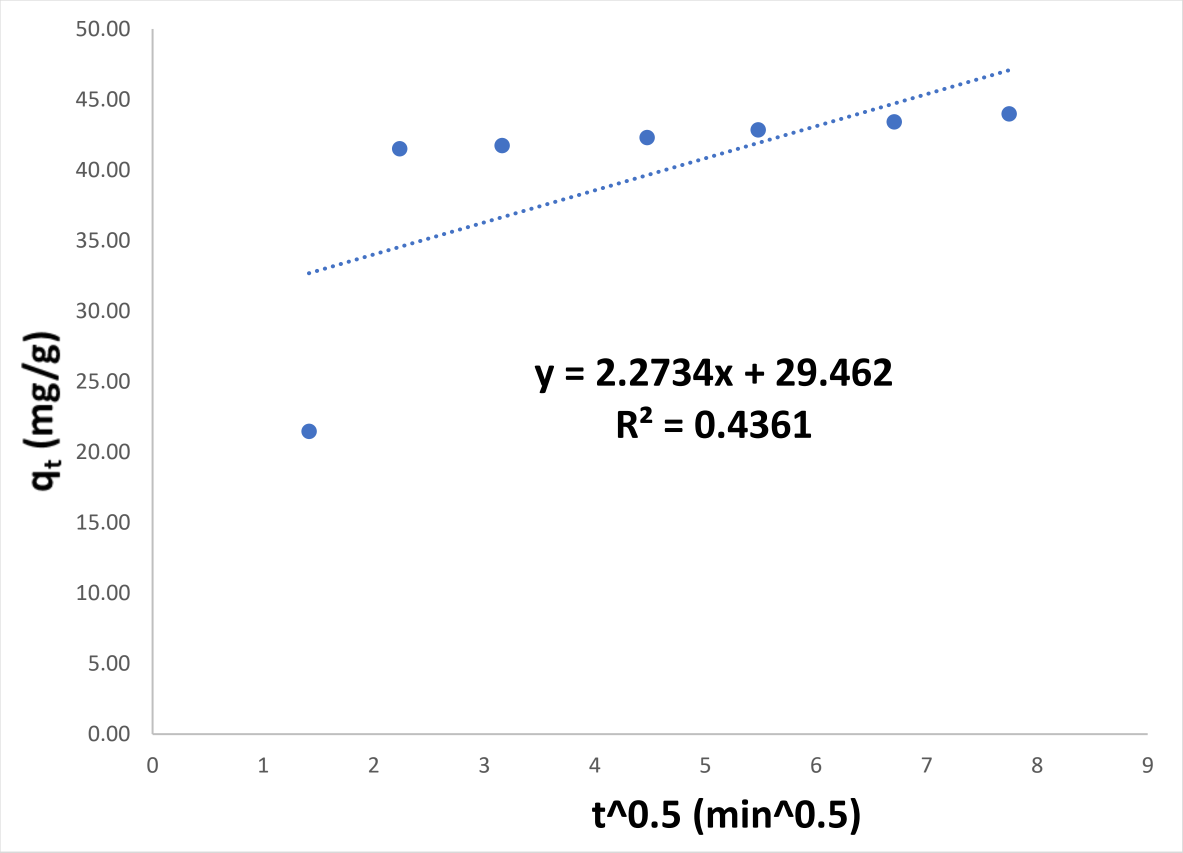

Fig. 21 The IPD study of OTC adsorption on 10%CoO@ZnO-MgO **nanocomposite.**

Table 2 The adsorption rate-control-mechanism results for the removal of OTC by ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO.

Sorbent	***LFDM***		***IPDM***	
	K_{LF} (min^{-1})	***R^2***	**K_{IP} ($mg\ g^{-1}\ min^{0.5}$)**	***R^2***
ZnO-MgO	**0.023**	**0.990**	**0.477**	**0.991**
2.5%CoO@ZnO-MgO	**0.021**	**0.970**	**0.706**	**0.983**
5%CoO@ZnO-MgO	**0.054**	**0.653**	**3.487**	**0.416**
10%CoO@ZnO-MgO	**0.040**	**0.668**	**2.861**	**0.451**

4. Conclusion

In this study, a one-put fast method was used to prepare ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO composites. The synthesized composites were studied for removing OTC from water via adsorption. The removal of OTC started quickly and reached the equilibrium within 60 minutes. About 90% of the q_t by the four composites was accomplished within the first 20 min. A q_t values of 28.8, 29.4, 50.2, and 44.3 mg g^{-1} were obtained by ZnO-MgO, 2.5%CoO@ZnO-MgO, 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO, respectively. These results nominated the 5%CoO@ZnO-MgO composite as the best sorbent among the prepared materials. The kinetics of adsorbing OTC by the four sorbents was studied. The adsorption rate order was studied using PFO and PSO. The obtaining showed that OTC adsorption by ZnO-MgO, 2.5%CoO@ZnO-MgO fitted the PFO, while OTC sorption onto 5%CoO@ZnO-MgO, and 10%CoO@ZnO-MgO followed the PSO. Additionally, the rate control mechanism outcomes revealed that both LFD and IPD models shared controlling the OTC adsorption onto the four sorbents.

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