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Kinetics studies for removing pharmaceutical pollutants from water by Zinc oxide-based- composites.

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

By

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Acknowledgement & Dedication

Our deepest appreciation goes out to Dr. Babiker Yagoub, our supervisor, for all the support and direction he has given us.

Please accept our sincere appreciation for the chemistry faculty's hard work.

This effort is dedicated to our loved ones, who have always been there for us and encouraged us to keep going.

Figures

Abstract

Water contamination is a problem that affects the ecosystem on a global scale. In this study, a rapid one-pot approach was employed to synthesize composites of ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO. The produced composites were investigated for their efficacy in removing OXTC from water by adsorption. The elimination of OXTC commenced promptly and achieved a state of equilibrium within 60 minutes. Approximately 90% of the quantity (qt) acquired by the three composites was observed to occur within the initial 20-minute period. The ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO samples yielded qt values of 29.36, 47.66, and 64.31 mg g^{-1}, respectively. The findings indicated that the 10%NiO@ZnO-MgO composite exhibited superior sorption properties than the other synthesized materials. The investigation focused on studying the kinetics of OXTC removal using three different sorbents. The investigation focused on determining the rate order of adsorption by employing PSFO and PSSO. The results indicated that the adsorption of OXTC by the synthesized three sorbents followed the pseudo-first-order kinetic model. Furthermore, the rate-control mechanism analysis results suggest that the IP model implementation significantly influences the adsorption of OXTC onto the three sorbents.

الملخص باللغة العربية

يعد تلوث المياه مشكلة تؤثر على النظام البيئي على عالمياً. في هذه الدراسة، تم استخدام نهج سريع بوعاء واحد لتصنيع مركبات ZnO-MgO, 5%NiO@ZnO-MgO, و 10%NiO@ZnO-MgO . تمت دراسة فعالية المركبات المحضرة للتعرف على فعاليتها في إزالة OXTC من الماء عن طريق الامتزاز. بدأ امتزاز OXTCعلى الفور ووصل الى حالة اتزان خلال 60 دقيقة. ولوحظ أن ما يقرب من 90٪ من الكمية (سعة الامتزاز) التي اكتسبتها المركبات الثلاثة حدثت خلال فترة الـ 20 دقيقة الأولية. اظهرت عينات ZnO-MgO و5 %NiO@ZnO-MgOو10 %NiO@ZnO-MgOعن قيم قدرة امتزاز قدرها 29.36 و47.66 و64.31 مجم/ جرام على التوالي. أشارت النتائج إلى أن المركب 10@NiO@ZnO-MgO أظهر مقدرة امتزاز عالية مقارنة بالمركبات الأخرى. ايضاً ركز البحث على دراسة حركية إزالة OXTC باستخدام المواد المازة الثلاثة. تم فحص رتبة معدل الامتزاز باستخدام نموذج التفاعل الكاذب من الرتبة الاولى ()ونموذج الرتبة الثانية (PSSO). أشارت النتائج إلى أن امتزاز OXTC بواسطة المواد الماصة الثلاثة المصنعة يتبع النموذج الحركي من الدرجة الأولى الزائفة. علاوة على ذلك، تشير نتائج تحليل آلية التحكم في المعدل إلى أن تنفيذ نموذج الانتشار داخل حبيبات المواد المازة يتحكم بشكل كبير في امتزاز OXTC على المواد الثلاثة المحضرة في هذه الدراسة

Chapter One

Introduction
and Literature Review

1. Introduction

1.1. Water pollution

The significance of water for the sustenance of human life cannot be overstated, given that the deterioration of water quality poses a threat to the existence of all living organisms. The presence of organic pollutants in water systems on a global scale is a significant issue. The presence of pharmaceuticals and organic dyes in water and sewage infrastructure is notable due to their extensive usage and strong consumer demand [1, 2]. The health of the population has been affected by the quality of their drinking water. Water contamination is often the primary source of waterborne infections, decimating urban populations. Due to this circumstance, individuals are compelled to ingest untreated water for irrigation, resulting in considerable adverse effects [3]. In order to mitigate the presence of harmful substances in the environment and establish a climate conducive to the preservation of ecosystems, it is imperative to get a comprehensive understanding of the sources, interactions, and consequences of water pollutants. The improper disposal of aged pollutants, the decontamination of equipment, and the elimination of commodities that were inadequately manufactured and contaminated with human and animal waste can all lead to the introduction of such pollutants into water systems [4-6]. The vulnerability of water supply systems in nations with industrialized economies is mainly attributed to the presence of dangerous aquatic pollutants. Under the United States, a greater volume of water is present than what is generated by its rivers and lakes. Specific locations may exhibit groundwater that contains various chemical hazards. Various water pollutants such as heavy metals, chlorinated hydrocarbons, organic pigments, industrial metal plating, and bacteria can be identified. The manufacture and utilization of synthetic chemicals have experienced significant growth since the conclusion of World War II. Consequently, the presence of these pollutants has led to the contamination of water supplies. Two examples include the use of pesticides, the discharge of pesticide runoff from agricultural fields, and the improper disposal of industrial trash into water bodies. Moreover, improper chemical waste disposal in landfills, storage lagoons, treatment ponds, and similar facilities can cause groundwater contamination. Despite appearing to be limitless, many global water sources suffer from pollution and inequitable distribution, resulting in their limited usability. Water scarcity is a prevalent issue affecting a substantial number of individuals globally, leading to the emergence of numerous armed conflicts [7]. The baseflow of rivers is heavily influenced by groundwater, which can be obtained through methods such as drilling or excavation or can naturally emerge through springs [8]. Nearly eighty percent of the pollutants in the ocean come from land-based sources, mostly from industrial processes or the indirect dumping of different wastes left over from human activities [9].

1.2. Ocurence of water contaminants

Between 2010 and 2014, a comprehensive monitoring operation was carried out in the Netherlands at a statewide level. This operation's results revealed significantly elevated pesticide concentrations in groundwater wells, which is cause for concern. A study was conducted in the Netherlands and Flanders to analyze shallow groundwater samples for 405 pesticides and 52 metabolites. The results indicated the existence of neonicotinoids, which are known for their high mobility and persistence, at concentrations ranging from 0.12 g/L to 0.01 g/L [10]. The Yangtze River Basin in Hubei Province in Central China had elevated concentrations of organochlorine and organophosphate pesticides [11]. Sixteen groundwater samples from the specified area contained fifteen organochlorine pesticides and four organophosphate pesticides. The mean concentrations of the four organophosphate pesticides investigated were 196.01 ng/L for aldrin, 196.01 ng/L for dieldrin, and 196.01 ng/L for hexachlorocyclohexane. The potability of the water supply failed to fulfill the standards set by the United States Environmental Protection Agency (EPA) [12]. The detection of organochlorine pesticides in the phreatic aquifer located beneath the Pampean region of Argentina serves as evidence for the long-lasting presence of these chemical compounds within the underground water [13]. Multiple studies have indicated that certain places exhibit elevated fluoride levels in their groundwater. It is advisable to refrain from utilizing groundwater containing elevated fluoride concentrations for extended periods. Fluoridation of public water sources is implemented due to the substantiated health benefits associated with fluoride. Nevertheless, excessive fluoride absorption can lead to the development of skeletal and dental fluorosis. The results of this study suggest that young children, specifically newborns and toddlers, are more susceptible to a noncarcinogenic hazard known as dental fluorosis [14]. A recent study in Agra City, India, focused on fluoride in the groundwater and revealed a wide range of fluoride concentrations exceeding the upper WHO threshold of 1.5 mg/L. Fifty-one groundwater samples from the Siddipet Vagu region in India showed an average fluoride concentration of 3.7 parts per million (ppm). A notable proportion of the samples, precisely 51%, had fluoride levels above the safety threshold of 1.5 mg/L established by the World Health Organization. [15]. The study involved the analysis of fifty borehole samples collected from areas of intensive agriculture located on the West Bank of the Nile River in Luxor Governorate, Egypt, which revealed that 62% of the studied region exhibited a moderate vulnerability to groundwater pollution and the remaining 38% demonstrated a high vulnerability. Intensive agricultural practices have contaminated around 52% of the land due to elevated levels of nitrate pollution from nitrogen-based fertilizers [16]. A recent study uncovered that nitrate concentration in Chungcheong Province, South Korea, has been determined to have a mean value of 12.4 mg/L [17]. On a global scale, pharmaceutical contaminants (PhCs) are present in groundwater, oceans, and rivers. It may be beneficial to elucidate humanity's pressing predicament: approximately 50% of Earth's water supplies have been declared contaminated since 1970 [18]. In 1999, the United States of America recognized the issue of water pollution caused by PhCs as a significant concern for public health [19-21]. Similarly, it was reported that over fifty percent of China's population was found to be ingesting contaminated drinking water during the same period. Pharmaceutical compounds (PhCs) are present in several water sources in India, including rivers, groundwater, and water treatment facilities. The quantities of these compounds can reach up to 31.0 mg L-1 [22, 23]. The pollution caused by PhCs is rising due to the increased demand for infectious disease treatments and the need for enhanced production in agricultural, poultry, and livestock farming [24-26]. The set of tetracycline compounds considered the most representative include tigecycline, Chlortetracycline, Oxytetracycline (OXTC), and Doxycycline [27]. The use of tetracyclines (TCs) has increased with antibiotics and food preservatives. Multiple research investigations have documented the dissemination of TCs inside soil and water reservoirs across many regions, including the United States, the United Kingdom, and China [27]. The proliferation of PhCs in marine and freshwater ecosystems, including seas, oceans, rivers, and drinking water sources, proves the inadequacy of standard treatment methods [28-36]. Therefore, it is imperative to adopt novel techniques to prevent the proliferation of PhCs. The emergence of nanomaterials has contributed to the advancement and proliferation of the adsorption process, known for removing non-degradable pollutants in water, such as heavy metals. This process is advantageous due to its simplicity, lower energy consumption, and ability to avoid releasing hazardous fragments [37].

1.3. Aim of the study

This study seeks to prepare a relatively safe sorbent; hence, the ZnO-MgO composite was selected as a base material for the intended triple nanocomposite. In order to make it a simple route, a one-put method will be used. The study aimed to prepare triple nanocomposite using NiO as doping material in ratios of 5.0 and 10.0 w/w%; typically, ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO will be synthesized. The prepared composites will be tested for removing oxytetracycline (OXTC) as an example of harmful pharmaceutical pollutants. The kinetic of adsorping OXTC by the ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO is a primary goal of this study.

Chapter Two

Materials and Methods

2. Materials and methods

2.1 Materials

Oxytetracycline (OXTC) and nickel acetate (Ni-Ac) were provided by Fluka, USA. Zinc acetate dihydrate (Zn-Ac)and magnesium acetate tetrahydrate (Mg-Ac) were supplied from Win-lab, England. Glucose sugar (Gl) was provided from Redl De-Haen, Germany.

2.2. Preparation of ZnO-MgO and its NiO composites

A total of 13.45 g of Zn-Ac, 24.6 g of Mg-Ac, and 5 grams of glucose (Gl) were carefully put into a 600 mL beaker. Approximately 30 milliliters of distilled water was introduced. The combination was heated 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 acquired black product was transformed into a powdered form and then transferred into a porcelain dish. It was then subjected to a calcination process at a temperature of 700°C for 4.0 hours. The procedure was replicated employing the conventional quantities of Zn-Mg, supplemented with an appropriate quantity of $Ni(Ac)_2$, to produce the nanocomposites of 5%NiO@ZnO-MgO and 10%NiO@ZnO-MgO.

2.3. Adsorption of OXTC

A stock solution of OXTC at a concentration of 100 mg L^{-1} was prepared by dissolving 0.1 grams of OXTC in 1.0 L of distilled water with an ultrasonic path. The influence of contact time was examined for adsorbing of OXTC onto ZnO-MgO, 2.5%NiO@ZnO-MgO, 5% NiO@ZnO-MgO, and 10% NiO@ZnO-MgO. A mass of 50 mg was weighed from each sorbent in a 150 mL beaker, and 120 mL OXTC 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 OXTC 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 Three

Results and Discussion

3. Results and discussion

3.1. Contact time study

Using Eq. 1, we determined the concentration of unadsorbed OXTC at each time interval based on the absorbance we measured during the contact time study. Using Eq. 2, we calculated the adsorption capacity (the OXTC milligrams adsorbed onto one gram of sorbent, q_t, mg g^{-1}).

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

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

Figures 1, 2, and 3 demonstrate the performance of ZnO-MgO, 5% NiO@ZnO-MgO, and 10% NiO@ZnO-MgO sorbents in removing OXTC as a function of contact time. The OXTC adsorption progressed fast till it attained equilibrium at minute 60, and about 90% OXTC sorption by the three sorbents was accomplished within the first 20 min. ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO maximum q_t values were 29.36, 47.66, and 64.31 mg g^{-1}, respectively. These results revealed that the 10%NiO@ZnO-MgO composite was the best for removing OXTC from contaminated water (Fig. 4).

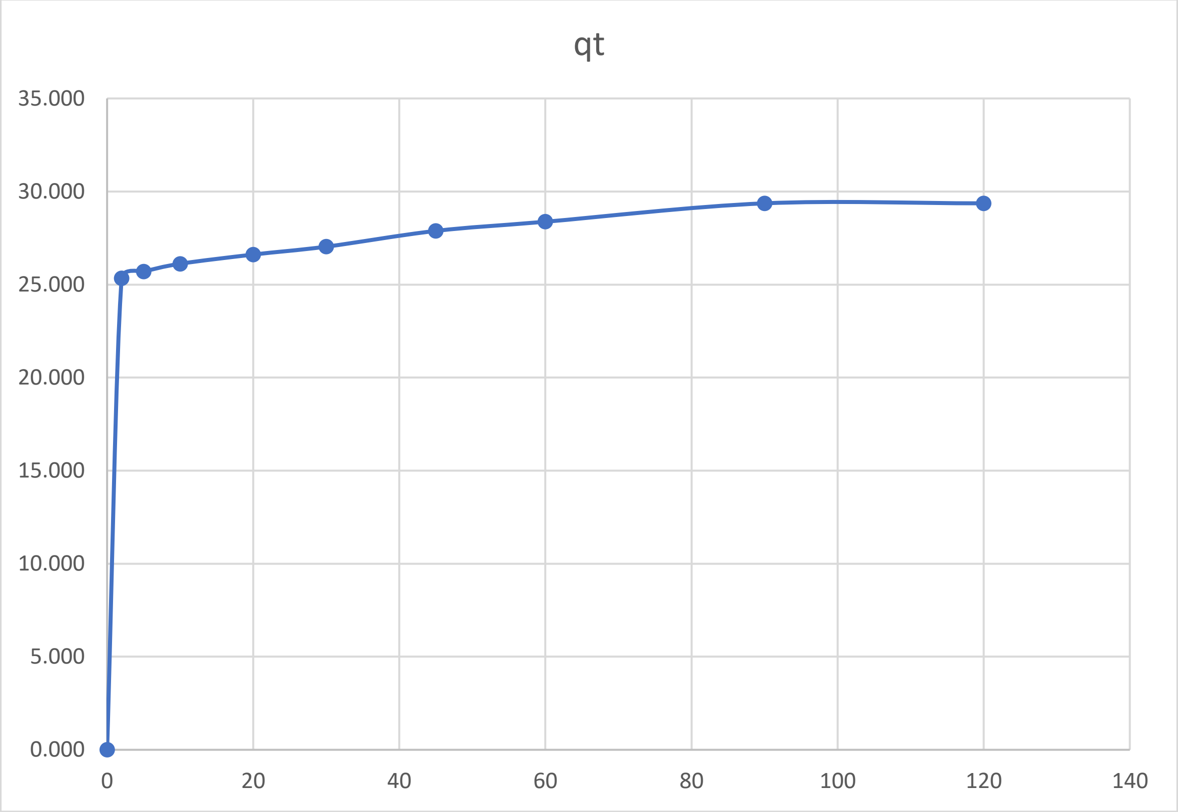

Fig. 1 The contact time study of the OXTC adsorption on ZnO-MgO, nanocomposite.

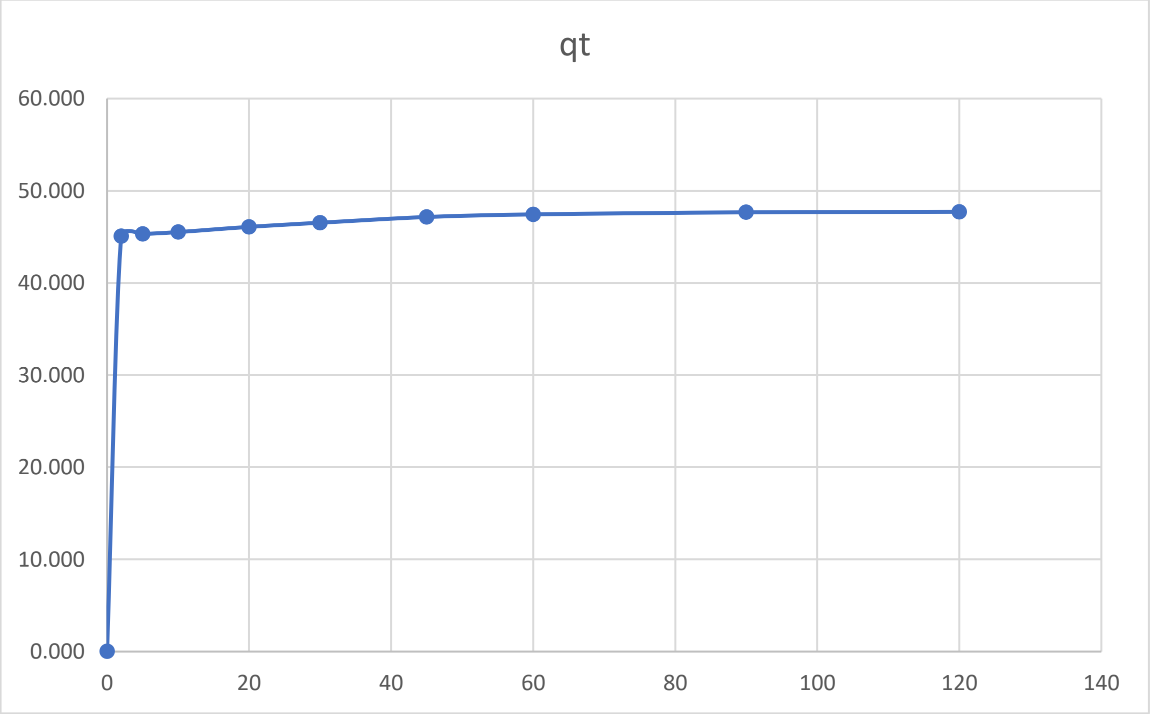

Fig. 2 The contact time study of the OXTC adsorption on 5%NiO@ZnO-MgO nanocomposite.

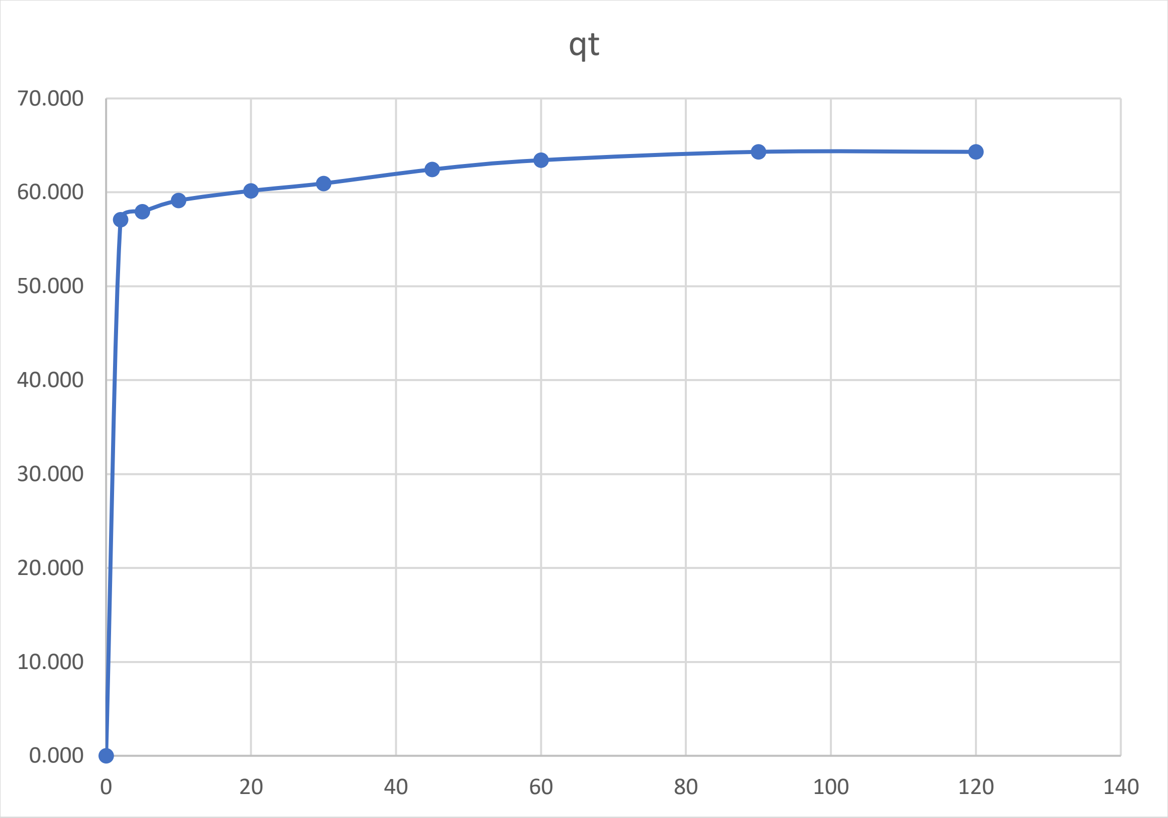

Fig. 3 The contact time study of the OXTC adsorption on 10%NiO@ZnO-MgO nanocomposite.

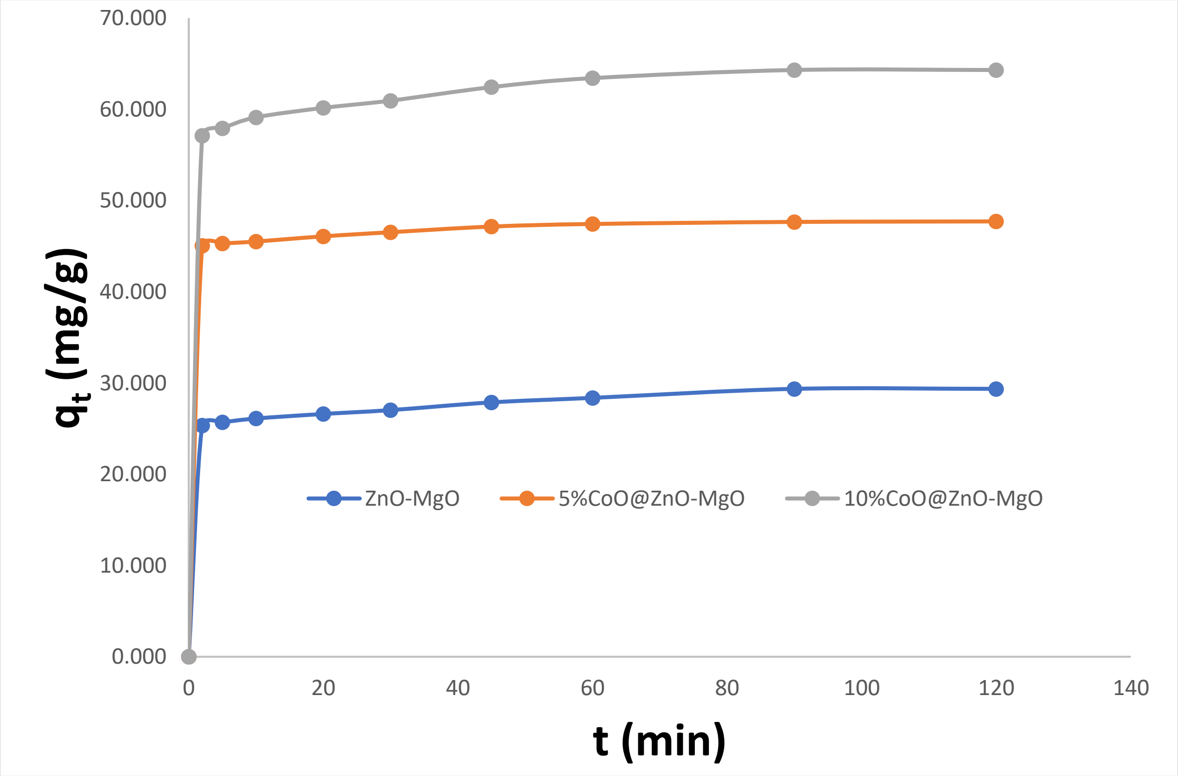

Fig. 4 Comparing the performance of ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO composites in removing OXTC from water.

3.2 Adsorption rate order

The adsorption rate order was studied for the OXTC removal by ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO sorbents. The pseudo-first-order (PSFO, Eq. 3) and pseudo-second-order (PSSO, Eq. 4) kinetic models were employed.

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

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

The equilibrium adsorption capacity is denoted by qe (mg g^{-1}), where m, v, C_t, and C_o are the sorbent's mass in grams, the solution's volume in milliliters, and its concentration in milligrams per liter at time t, respectively. Both the PFO and PSO constants are time-based, with the former denoted by k_1 (min^{-1}) and the latter by k_2 (g mg^{-1} min^{-1}). The linear plots of the PSFO result for the adsorption of OXTC on ZnO-MgO, 5% NiO@ZnO-MgO, and 10% NiO@ZnO-MgO composites are depicted in Figures 5, 6, and 7, respectively. Figures 8, 9, and 10 also show the PSSO plots for removing OXTC by ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO, respectively. The rate order findings in Table 1 showed that OXTC adsorption by ZnO-MgO, 2.5%NiO@ZnO-MgO fitted the PFO, while OXTC sorption onto 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO followed the PSO.

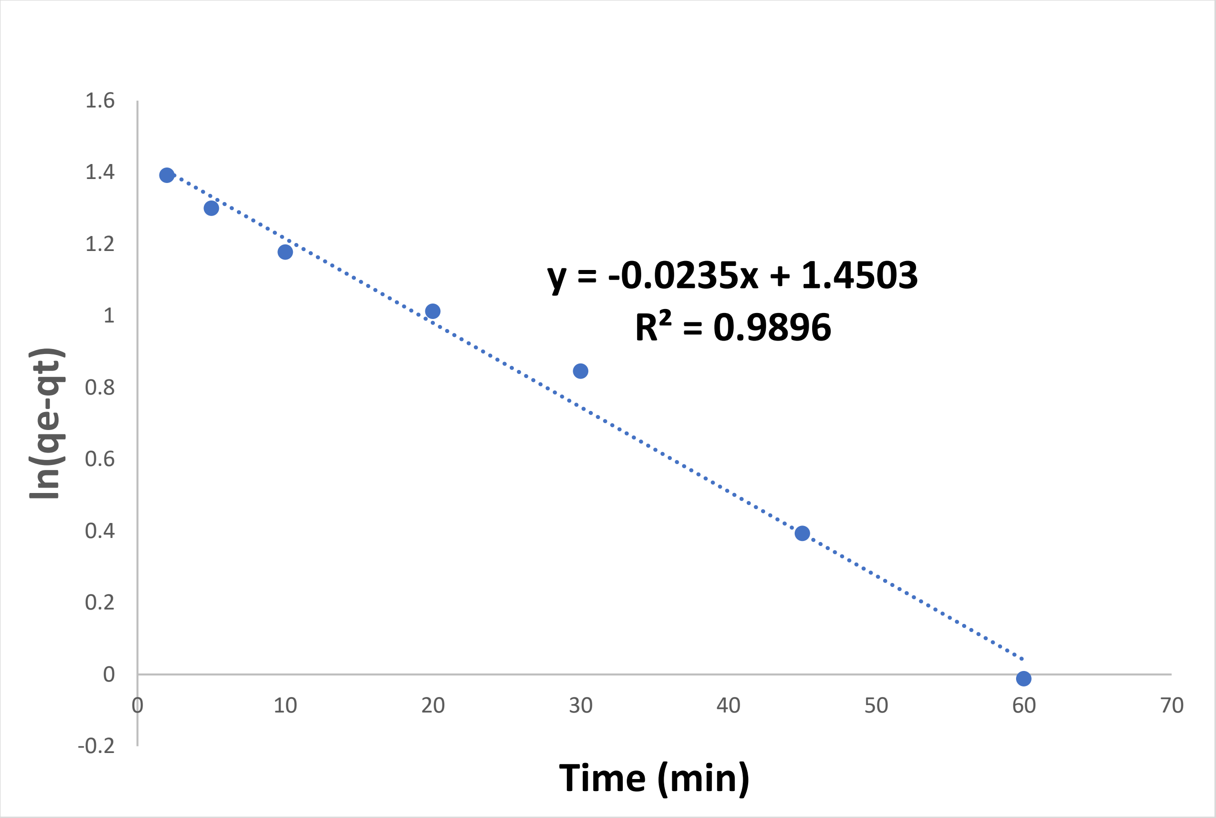

Fig. 5 The PSFO investigation for OXTC adsorption onto ZnO-MgO nanocomposite.

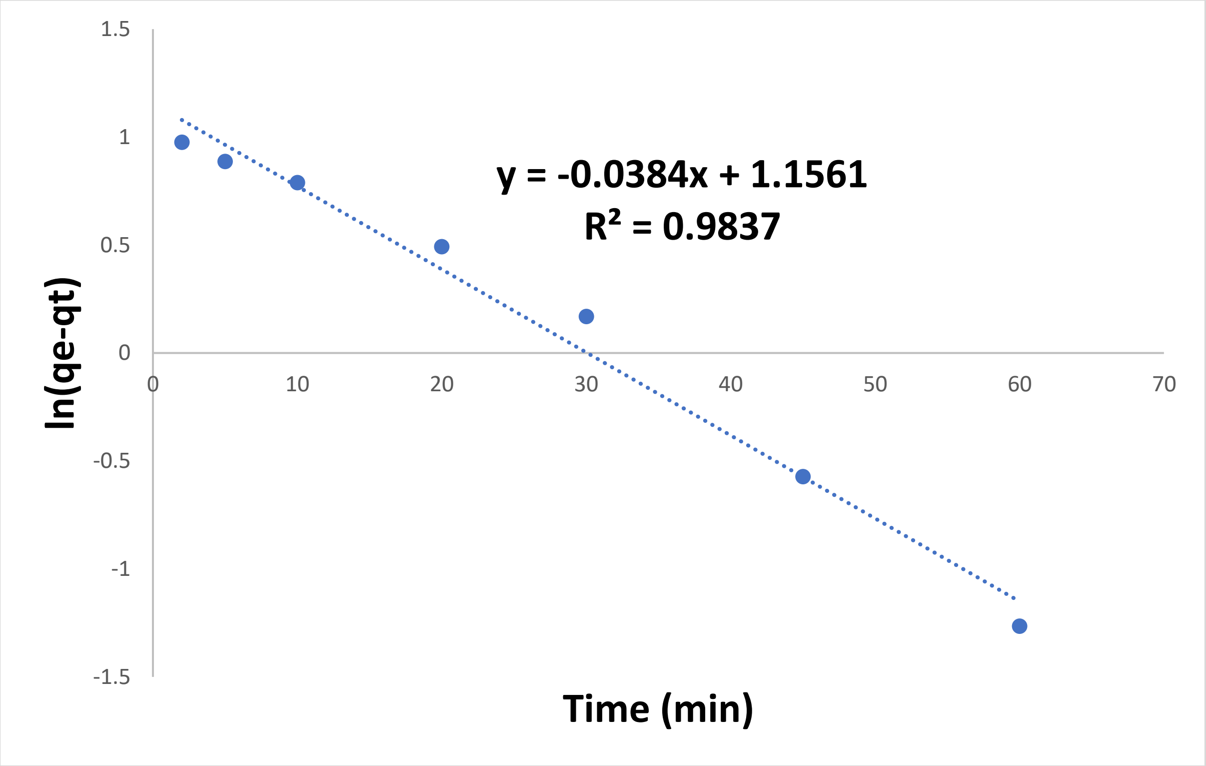

Fig. 6 The PSFO investigation for OXTC adsorption onto 5%NiO@ZnO-MgO nanocomposite.

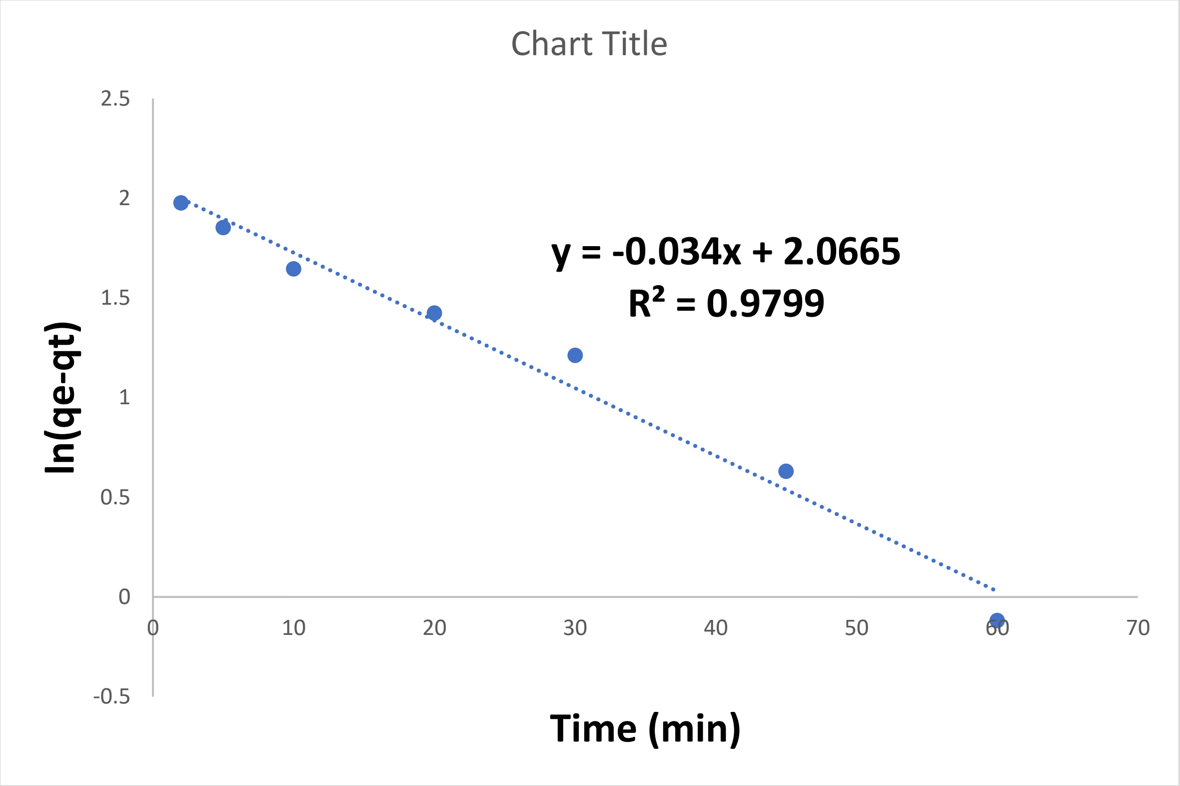

Fig. 7 The PSFO investigation for OXTC adsorption onto 10%NiO@ZnO-MgO nanocomposite.

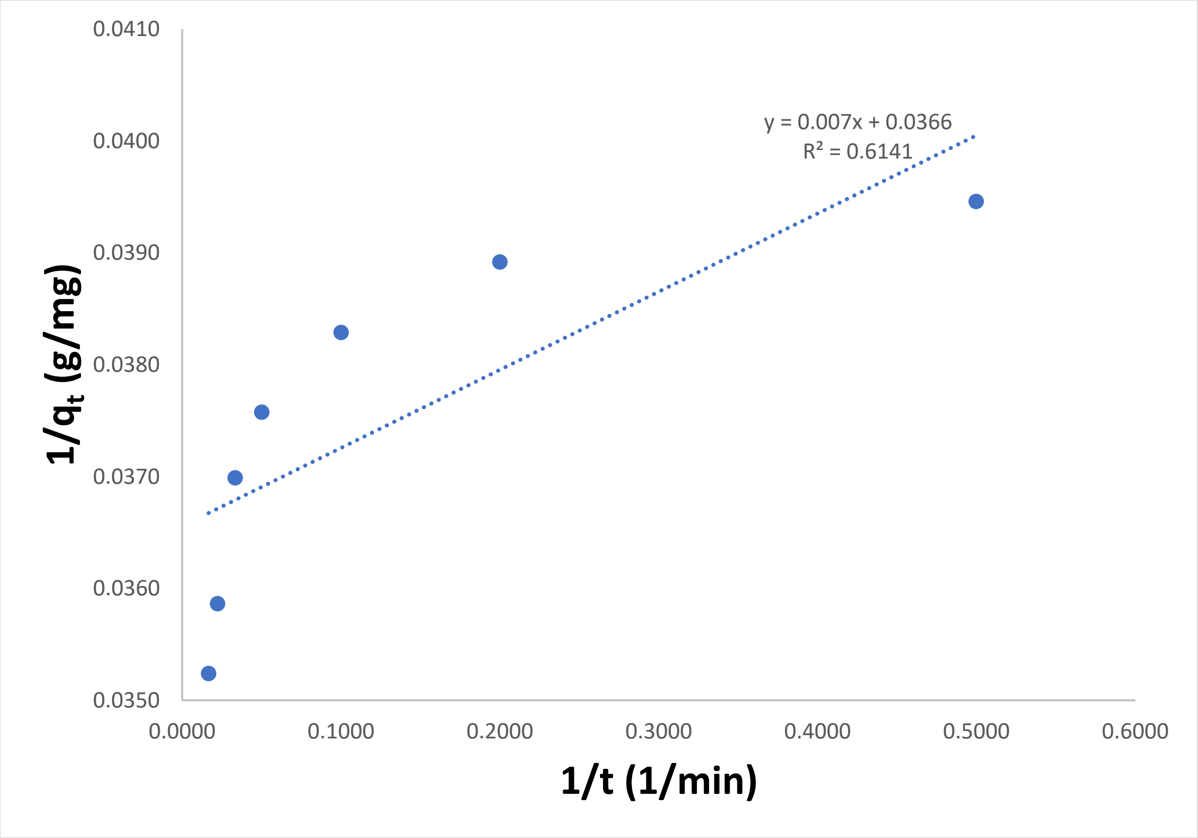

Fig. 8 The PSSO investigation for OXTC adsorption onto ZnO-MgO nanocomposite.

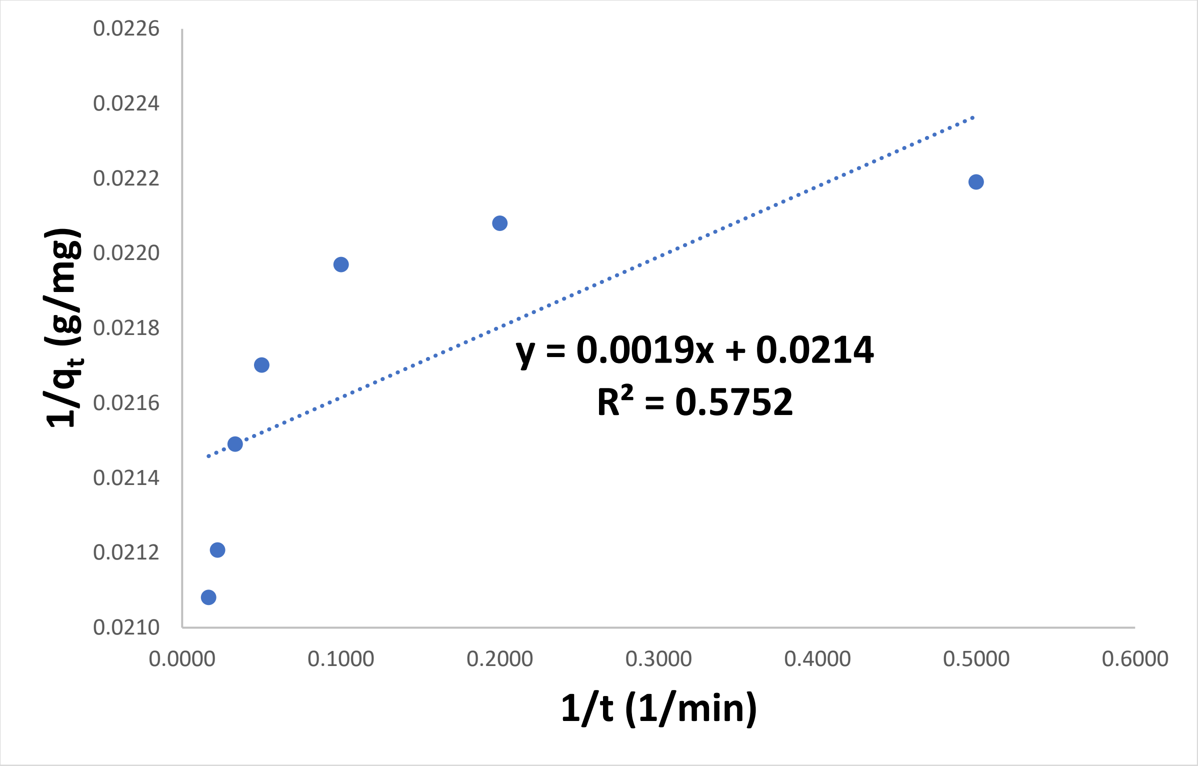

Fig. 9 The PSSO investigation for OXTC adsorption onto 5%NiO@ZnO-MgO nanocomposite.

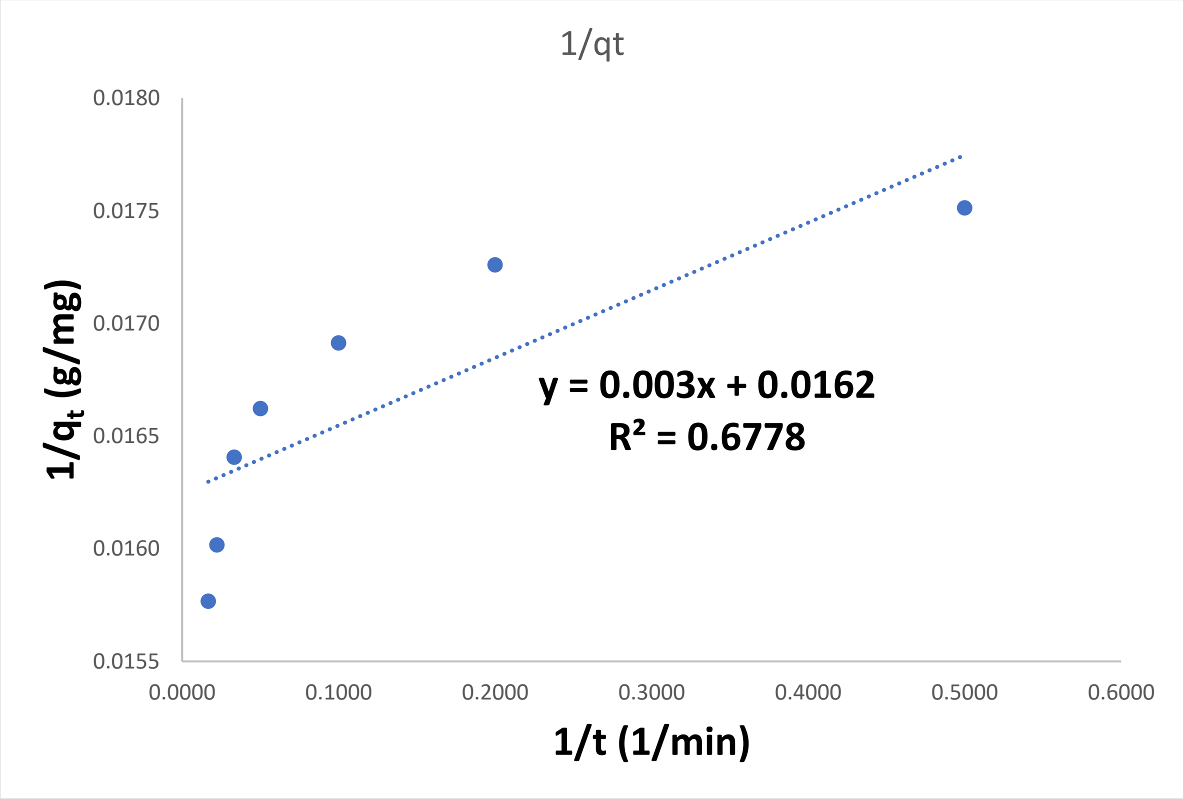

Fig. 10 The PSSO investigation for OXTC adsorption onto 10%NiO@ZnO-MgO nanocomposite.

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

		PFO		***PSO***	
adsorbent	**qe exp. (mg g^{-1})**	**R^2**	**k_1**	**R^2**	**k_2**
ZnO-MgO	**29.36**	**0.9896**	**0.0235**	**0.614**	**0.191**
5%NiO@ZnO-MgO	**47.72**	**0.9837**	**0.0384**	**0.575**	**0.244**
10%NiO@ZnO-MgO	**64.31**	**0.9799**	**0.0340**	**0.678**	**0.088**

3.3 Adsorption control mechanism

Adsorption is thought to occur in two stages, the first of which involves transporting adsorbate molecules from the liquid to the solid sorbent surface. In the second stage, the sorbate molecules must penetrate deep into the solid sorbent. The slowest sorption step, known as the rate control mechanism, governs the adsorption rate. The rate-control mechanism for OXTC adsorption on ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO was investigated using the intraparticle (IP, Eq. 5) and the liquid-film (LF, Eq. 6) diffusion model [29].

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

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

The IP constant is denoted by K_{IP} (mg g^{-1} $min^{-1/2}$), and the LF constant is designated by K_{LF} (min-1). C_i: the boundary layer factor, expressed as mg g^{-1}. The linear LF plots for the OXTC adsorption onto ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO nanocomposites were monitored in Fig. 11, 12, and 13. The IP plots are shown in Fig. 14, 15, and 16, respectively. The results of LF and IP are illustrated in Table 2. The rate control investigation outcomes revealed that both LF and IP models shared controlling the OXTC adsorption onto the four sorbents.

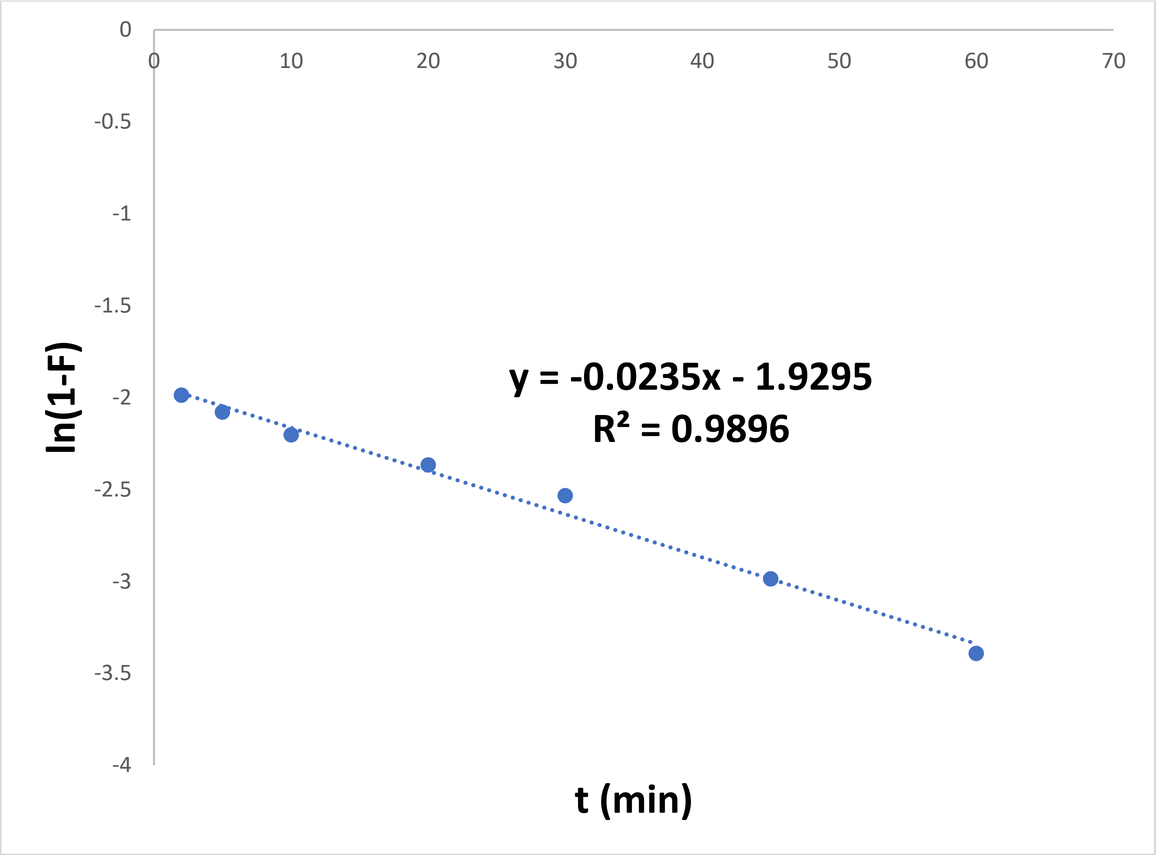

Fig. 11 The LF study of OXTC adsorption on ZnO-MgO nanocomposite.

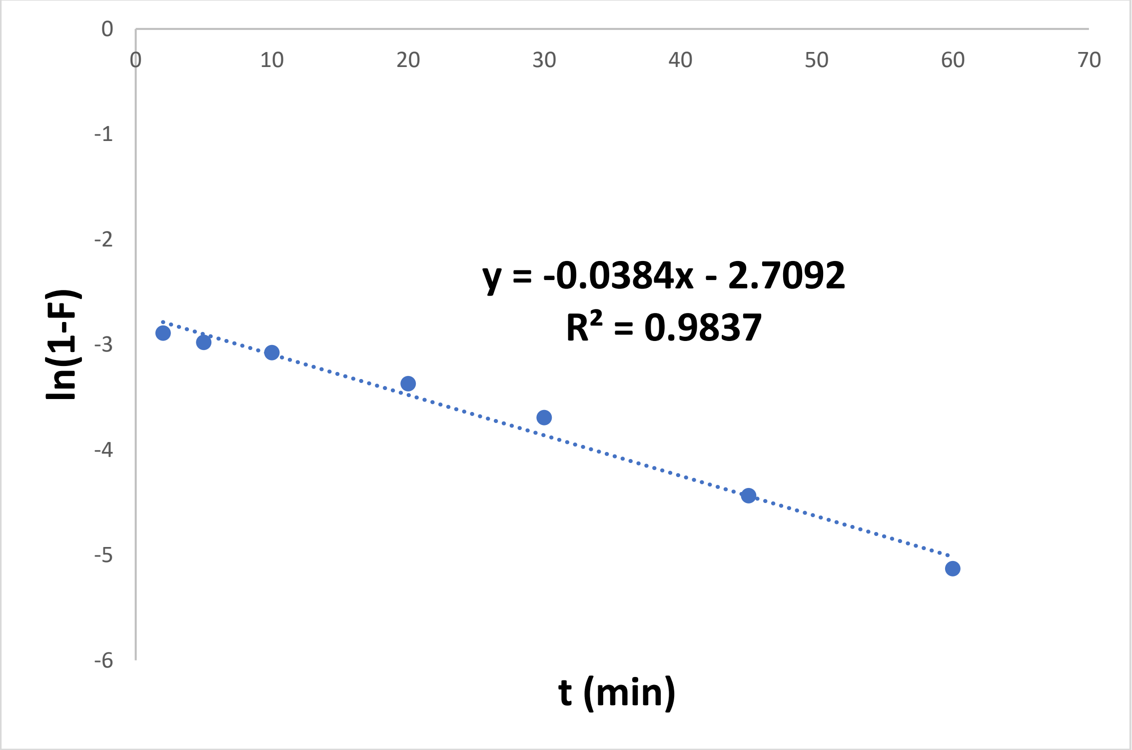

Fig. 12 The LF study of OXTC adsorption on 5%NiO@ZnO-MgO nanocomposite.

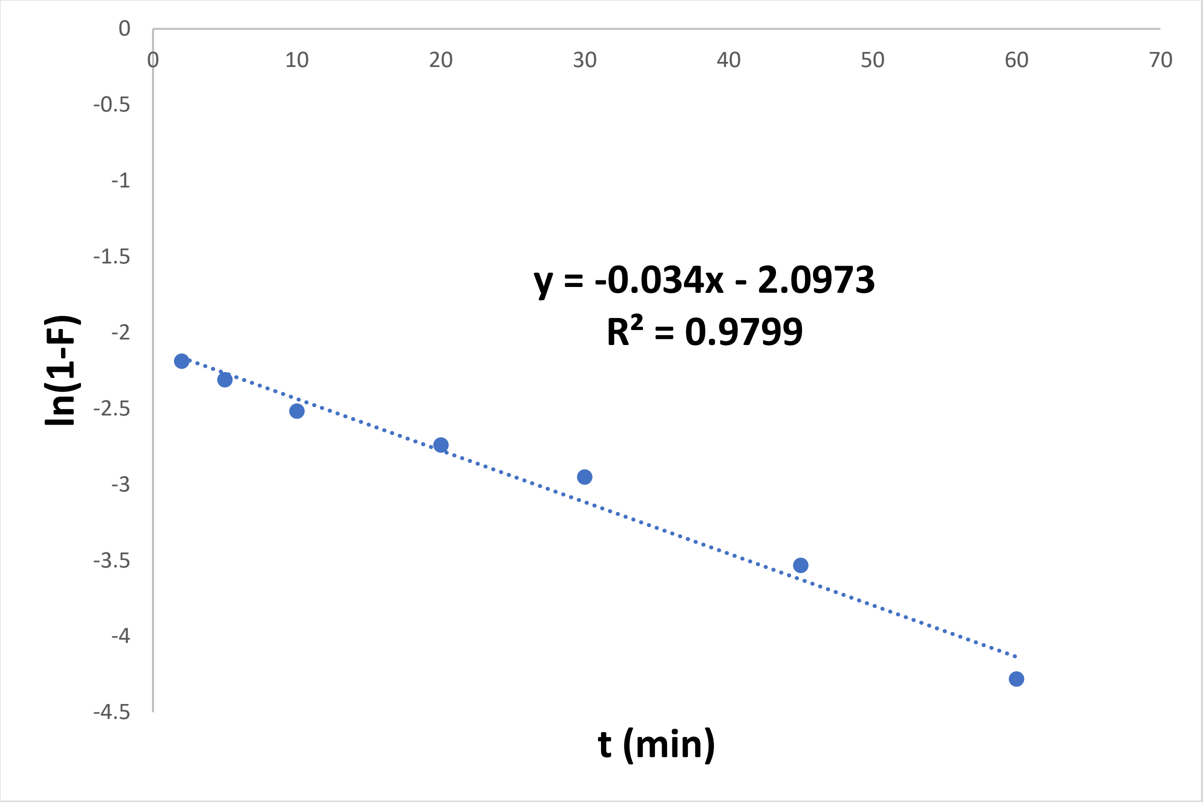

Fig. 13 The LF study of OXTC adsorption on 10%NiO@ZnO-MgO nanocomposite.

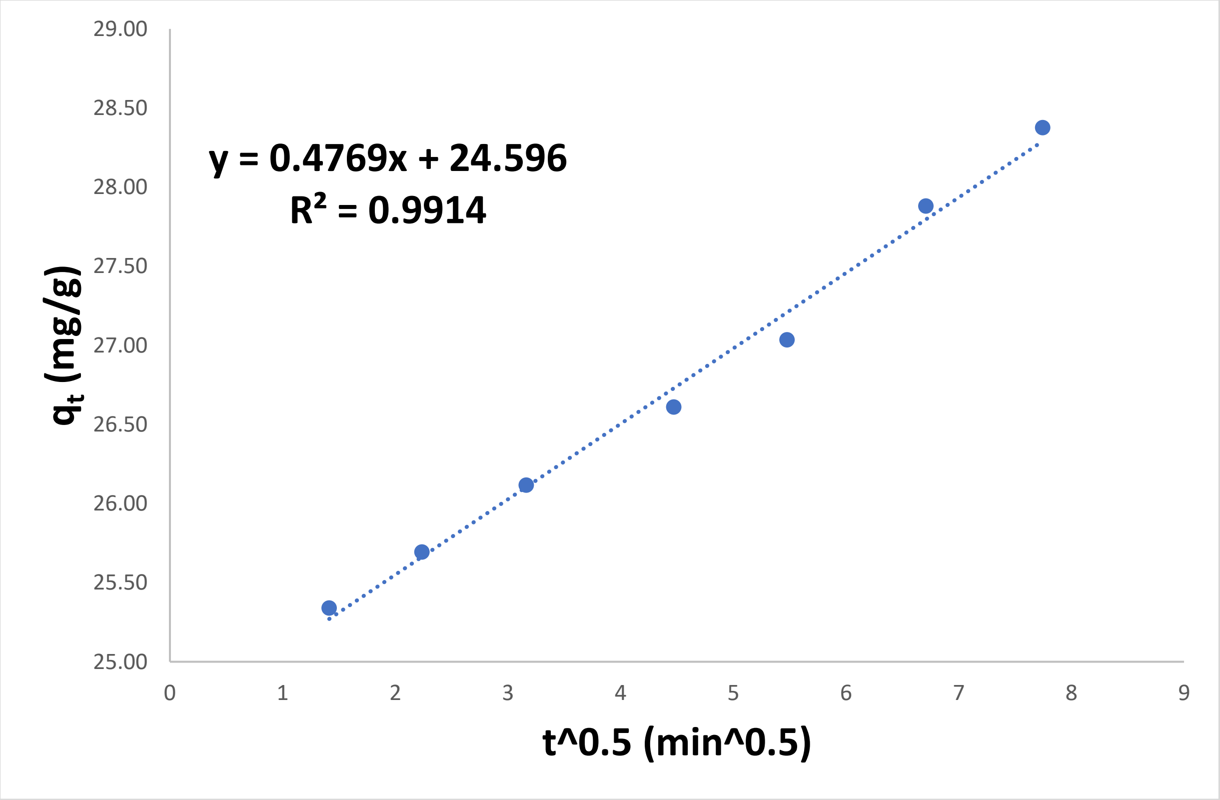

Fig. 14 The IP study of OXTC adsorption on ZnO-MgO nanocomposite.

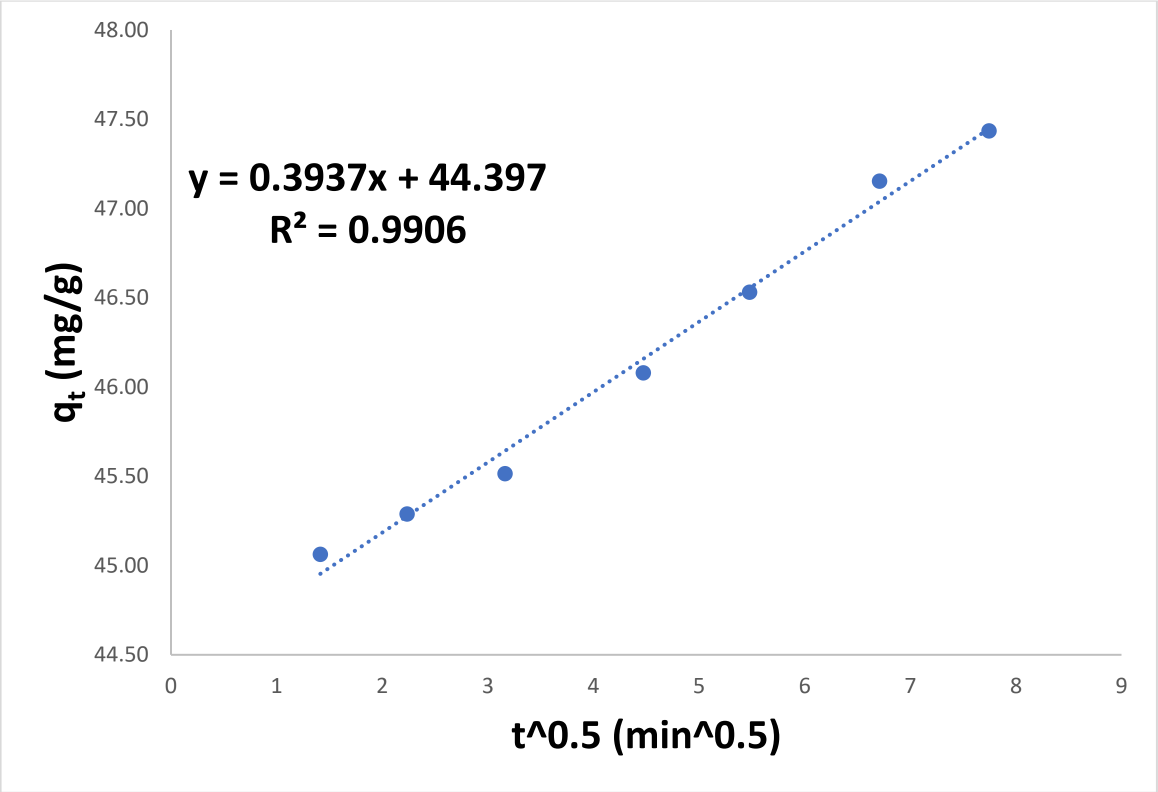

Fig. 15 The IP study of OXTC adsorption on 5%NiO@ZnO-MgO **nanocomposite.**

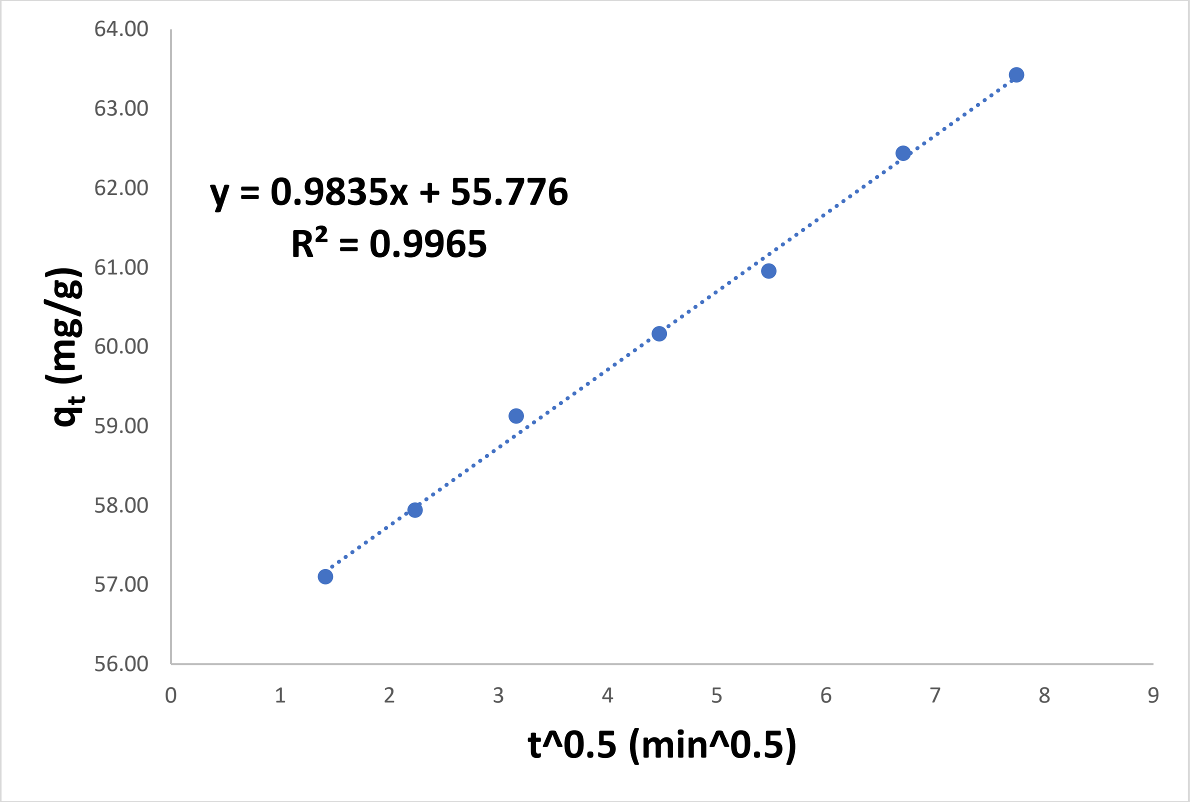

Fig. 16 The IP study of OXTC adsorption on 10%NiO@ZnO-MgO **nanocomposite.**

Table 2 The adsorption rate-control-mechanism results for removing OXTC by ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@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**
5%NiO@ZnO-MgO	**0.038**	**0.984**	**0.396**	**0.985**
10%NiO@ZnO-MgO	**0.034**	**0.980**	**0.978**	**0.994**

3.4. Conclusion

This study used a one-put fast method to prepare ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO composites. The synthesized composites were studied for removing OXTC from water via adsorption. The removal of OXTC started quickly and reached the equilibrium within 60 minutes. About 90% of the q_t by the three composites was accomplished within the first 20 min. A q_t values of 29.36, 47.66, and 64.31 mg g^{-1} were obtained by ZnO-MgO, 5%NiO@ZnO-MgO, and 10%NiO@ZnO-MgO, respectively. These results nominated the 10%NiO@ZnO-MgO composite as the best sorbent among the prepared materials. The kinetics of removing OXTC by the three sorbents was investigated. The adsorption rate-order was examined using PSFO and PSSO. The obtaining showed that OXTC adsorption by the three prepared sorbents followed the PSFO. Additionally, the rate-control-mechanism outcomes revealed that the IP model has much control over the OXTC adsorption onto the three sorbents.

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