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Compound**

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Abstract

A Schiff base tin (IV) compound was synthesized by reactions between 2-((E)-(p-tolylimino)methyl)phenol (TIMPH) and butyltin trichloride in 2:1 mole ratio in ethanol at room temperature. $[\text{SnBuCl}_3(\text{TIMPH})_2]$ was characterized by FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectroscopy, elemental analysis, and mass spectrometry. Optimization of Murexide dye from aqueous solution was performed by examining; effect of contact time, initial pH, adsorbent amount, initial dye concentration and temperature on the tin adsorbent. The highest adsorption recovery value of was 98.00% and the adsorption capacity was 248.8 mg/g at the end of 20 minutes at 100 mg/L dye concentration while the temperature was 25 °C and the pH was 3. Langmuir, Freundlich, and Temkin adsorption isotherms were calculated at 25 °C. The highest R^2 value was found 0.099 for the Langmuir isotherm model. The adsorption characteristics of murexide dye showed that adsorption kinetic obeyed the pseudo-second-order kinetics, and the thermodynamic data suggested the spontaneous and exothermic process.

Keywords: Murexide removal, Schiff base, Tin, Langmuir, Kinetics

1. Introduction

Water is one of the main crucial components for life in the world. Unfortunately, with the rapid development of industry, this essential water is being polluted due to the industrial waste released into the environment. For instance, conscious or unconscious discharge of dyes, which are classified as industrial, is one of the reasons, which can be held responsible for the increased the pollution of water [1-3]. Such materials with significant coloring capacity are widely used in many industry areas like textile, food, plastic etc. [1,2]. Most of these dye compounds are toxic to animals, plants, and human beings. In order to find a solution to this issue, removing dyes from the aqueous solution has been studied and as a result, various techniques such as adsorption, chemical precipitation, ion-exchange and membrane systems have been used to remove dyes from aqueous solutions. Among these methods, adsorption is widely preferred in the purification of water because it is efficient, simple and fast and its cost is low as well [4-6]. During the adsorption process, the choice of adsorbent greatly affects the adsorption selectivity and capacity [5,6]. A wide range of compounds was used as an adsorbent to remove dyes from the aqueous solution [7,8]. Some materials, which were frequently used as adsorbents in previous studies, have limited applications due to their poor selectivity and low adsorption capacity [9]. Unlike these, Schiff base metal compounds have better adsorptive properties for removing dyes from aqueous solutions. Therefore, new Schiff base adsorbents containing oxygen and nitrogen atoms have been investigated for the removal of dyes from aqueous solutions because they can easily form a complex with central metal ions [10]. The new nano hybrid material containing Cd (II) semicarbazone Schiff base complex was synthesized by Farhadi et al. [11]. They were tested to remove cationic dyes such as methylene blue (MB), rhodamine B (RhB), and methyl orange (MO) and mentioned that the novel material had an excellent adsorption ability towards these dyes. The removal of methyl orange (MO) from aqueous solution performed by nano-composite containing cobalt (Si/Al-PAEA = SA@Co) was proved in the study of Arshadi [12].

Murexide (MX) is a dye used as an indicator in EDTA titrations and also dyes wool and many textile products. Murexide's chemical formula is $\text{NH}_4\text{C}_8\text{H}_4\text{N}_5\text{O}_6$, ammonium purpurat is another name for this dye. It can be dangerous for eyes, skin and respiratory tract when it is exposed. When Murexide is used a considerable amount of it goes to the wastewater, which is hazardous for the aquatic lives as well as humans and animals [13].

The aim of this study is to understand the murexide dye adsorption from aqueous solution by using Schiff base tin adsorbent. In this work, (TIMPH) ligand was reacted with butyltin trichloride to form a Schiff base tin compound. This tin compound was characterized by a combination of spectroscopic techniques such as $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FT-IR, MS and elemental analysis. A series of batch experiments was conducted to evaluate the effect of Murexide dye adsorption onto the Schiff base tin adsorbent from aqueous solution under the different experimental parameters. Moreover, the isotherms, kinetics, and thermodynamic results of the adsorption process were determined and evaluated.

2. Experimental

2.1. Materials

Salicylaldehyde (98%, Sigma-Aldrich), p-toluidine (99%, Merck), ethyl alcohol absolute (Merck), butyl tin trichloride (95%, Sigma-Aldrich), Murexide (ACS reagent, Merck), and n-hexane (95%, Merck) were used as received. HCl and NaOH were of analytical grade. All glassware was kept in an acidic washing solution for at least one night before being used and then rinsed with deionized water. The deionized water was supplied from the Elga brand with $18.2\ \mu\text{s}$ conductivity.

2.1. Instruments

^1H and $^{13}\text{C-NMR}$ spectra of TIMPH ligand and tin compound were measured on a Bruker 400 MHz NMR spectrometer (100 MHz for ^{13}C and 400 MHz for ^1H). FTIR spectra were recorded between $400\text{-}4000\ \text{cm}^{-1}$ on a Alpha-P Bruker spectrophotometer. LECO CHNS-932 elemental analyzer was employed to determine carbon, hydrogen, and nitrogen amounts in both ligand and tin compound. High-resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G1 MS spectrometer using electrospray ionization (ESI \pm , in the range of 50-1100 Da). The dye absorption after adsorption was measured using a UV-Vis spectrophotometer (T80+UV/VIS Spectrometer PG Instruments Ltd). The pH of dye solutions was measured by Hanna Instruments pH 211 Microprocessor. In the method of adsorption several brands of magnetic stirrers were used.

2.2. Synthesis of 2-((E)-(p-tolylimino)methyl)phenol (TIMPH)

Salicylaldehyde (4.00 g, 0.032 mol) was added to the stirring solution of p-toluidine (3.45 g, 0.032 mol) in 25 mL of ethyl alcohol and the reaction was allowed to react at 80 °C for 3 hours. The resulting mixture was cooled to approximately 20 °C and an orange solid precipitate was obtained. Then, the precipitate was filtered, washed two times with 20 mL ethanol and dried under reduced pressure by a vacuum evaporator as in literature [14]. Elemental analysis of C₁₄H₁₃NO (211.26 g/mol) Calculated: H 6.20, C 79.59, N 6.63%; Found: H 6.28, C 79.35, N 6.42. HRMS (\pm ESI) (m/z): [C₁₄H₁₃NO] = 212.0 (100%) Da. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 2.42 (s, 3H, CH₃); 6.90–7.45 (m, 8 H, Ar); 8.68 (s, 1 H, CH); 13.30 (s, 1 H, OH) ppm. FTIR (cm⁻¹): 3050, 3020, 2860, 1618 (C=C, Ar), 1598 (C=C, Ar), 1576 (C=N), 1510, 1496, 1460, 1416, 1368, 1280 (C-O, phenolic), 1180, 1160, 1120, 1032, 912, 850, 836, 790, 754, 632.

2.3. Synthesis of [SnBuCl₃(TIMPH)₂] compound

The obtained TIMPH ligand (3.0x10⁻³mol, 0.64g) was added to the solution of BuSnCl₃ (1.50x10⁻³mol, 0.45g) compound in 30 mL of ethyl alcohol. This mixture was stirred at ambient temperature for 3 hours and it gave yellow product. Then, a vacuum evaporator was used to remove the solvents from mixture at 35 °C. The resulting compound was then washed two times with 20 mL n-hexane and dried under vacuum. Elemental analysis, (C₃₂H₃₅Cl₃N₂O₂Sn, M_w=704.70 g/mol) Calculated: H 5.01; C 54.54; N 3.98%. Found: H 4.57; C 54.77; N 4.33%. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 0.92 (s, 3H, α -CH₃); 1.27 (m, 2H, γ -CH₂); 1.44 (m, 2H, β -CH₂); 1.86 (t, 2H, α -CH₂); 2.41 (s, 6H, CH₃-Ar); 6.91-7.51 (m, 16H, C₆H₄); 8.52 (s, 2H, CH=N); 9.92 (s, H, OH), 11.0 (s, H, OH). ¹³C-NMR, (100 MHz, CDCl₃), δ (ppm): 13.5 (CH₃); 20.9 (γ -CH₂); 21.2 (CH₃); 25.6 (β -CH₂); 27.1 (α -CH₂); 117.9; 118.8; 120.5; 130.0; 130.4; 133.9; 136.2; 138.6 (=C, Ar); 160.7 (C-OH, Ar), 165.3 (CH=N). FT-IR (cm⁻¹): 3044 (C-H, Ar, sp², asym), 2947 (C-H, sp³, asym str), 2868(C-H, sp³, sym str), 1637 (C=C, Ar), 1601 (C=C, Ar), 1543 (CH=N), 1484 (C-H, sp³, bending), 1379, 1284 (C-O, phenolic), 1244, 1188, 1147, 1016, 897, 817, 790, 754, 686, 623. MALDI-TOF MS (m/z): [C₃₂H₃₅Cl₃N₂O₂Sn+Na]⁺ = 729.01 (100%), 731.02 (90%) and 727.02 (97.8%) Da.

2.4. Adsorption experiments on [SnBuCl₃(TIMPH)₂] compound

The murexide dye adsorption was investigated on different amounts (10-60 mg) of Schiff base tin compound in batch adsorption mode. The experiments were performed in 250 mL Erlenmeyer flasks containing 100 mL of murexide dye solution with different initial concentrations (100-500 mg/L). These solutions were agitated with the magnetic stirrer at 300 rpm, at a different initial temperature (25-65 °C) and in contact times (10-80 min.). The solution's pH (2-10) was adjusted by a pH-meter with a negligible volume of 0.1 M HCl and NaOH before adsorption. At the end of the equilibrium period, the suspension was centrifuged for 3 min at 4000 rpm. The concentration of murexide dye in the filtrate taken by decantation was measured by absorbance in a T80 + UV / VIS spectrophotometer at the maximum wavelength of 525 nm. In equations (1) and (2), the percentage of removal and the amount of equilibrium adsorption capacity were given.

$$\%R = ((C_0 - C_e) / C_0) \times 100 \quad (1)$$

$$q_e = (C_0 - C_e)v / w \quad (2)$$

where C_0 and C_e are the initial dye concentration (mg/L) and the equilibrium dye concentration (mg/L) respectively.

2.4. Adsorption isotherms, kinetics, and thermodynamics

2.4.1. Isotherms

The parameters obtained from various isotherm models provide valuable details on the essence of the adsorption process interaction, the surface properties of the adsorbent, and their adsorbent affinity [15]. The isotherms depend on equilibrium conditions at a constant temperature were plotted on graphs. For the newly synthesized adsorbent, the most popular adsorption isotherms (Langmuir, Freundlich, and Temkin isotherms) were investigated for murexide. The three-isotherm equations were shown in [Table 1](#).

Table 1. Isotherm equations

Isotherms	Equations	Plot
Langmiur	$C_e/q_e = (1/K_L Q_{max}) + (C_e/Q_{max})$	C_e/q_e against C_e
Freundlich	$\ln q_e = \ln K_f + 1/n_f(\ln C_e)$	$\ln q_e$ against $\ln C_e$
Temkin	$q_e = B \ln K_T + B \ln C_e$	q_e against $\ln C_e$

By linear form, the Langmuir isotherm model was determined. In [Table 1](#), the maximum monolayer adsorption capacity of the adsorbent is Q_{max} (mg/g), and K_L is the Langmuir adsorption constant (L/mg). The Q_{max} and K_L were calculated from the intercept and slope of the linear plot [\[13-16\]](#). The adsorption properties of heterogeneous surfaces were also represented using the Freundlich isotherm. The Freundlich isothermal constants of adsorption capability and adsorption strengths are K_f (L/mg) and n_f , respectively. From the linear plot equation, these values were determined. Due to the interactions, the Temkin isotherm accepts a linear decrease in the adsorption temperature of all molecules in the layer. Where the Temkin isotherm equilibrium binding constant (L/g) is K_T , and the heat-related constant (J/mol) is B . The values of K_T and B are computed from the plot of q_e against $\ln C_e$ [\[17,18\]](#).

2.4.2. Adsorption kinetics

This study used the pseudo-first-order kinetic model and the pseudo-second-order kinetic model among the several kinetic models to describe the adsorption rate and the adsorption mechanism of Murexide on the Schiff base compound. The coefficients and equations of these kinetic equations were demonstrated in [Table 2](#) below.

Table 2. Kinetic Equations

Pseudo-First-Order Equation	Pseudo-Second-Order Equation
$\log (q_e - qt) = \log q_e - (k_1/2.303) \times t$	$t/q_t = 1/k_2(q_e)^2 + (1/q_e) \times t$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, q_t is the adsorption capacity at time t (mg g^{-1}), t is time (min), k_1 (min^{-1}) and k_2 ($\text{g.mg}^{-1} \text{min}^{-1}$) are the pseudo first-order rate and pseudo second-order rate constants, respectively. From the slope and intercept of the log graph ($q_e - q_t$) against time t , the pseudo-first-order rate constant (k_1) and equilibrium adsorption power (q_e) were determined. The pseudo-second-order rate constant k_2 and the equilibrium adsorption capability (q_e) values were determined from the intercept and the graph slope of t/q_t against time t [19].

2.4.2. Adsorption thermodynamics

One of the other essential considerations for identifying and recognizing the meaning of adsorption is thermodynamic analysis. Van't Hoff equation measures the effect of temperature. The thermodynamic parameters of the equation include the change in Gibbs free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) values were calculated from the equations of 3-4 [20]. These values were used to assess the thermodynamic feasibility of the effect of temperature on the process of adsorption.

$$\ln K_c = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (3)$$

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

here K_c (q_e/C_e) is the thermodynamic equilibrium constant, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature of the solution.

3. Results and Discussion

3.1. Tin adsorbent

Stoichiometric reaction between p-toluidine and salicylaldehyde in 1:1 mole ratio in ethanol at 80°C produced TIMPH ligand as in the literature [14]. The reaction of BuSnCl_3 with TIMPH in the 1:2 mol ratio in ethanol gave the tin compound at room temperature. The formulation of tin compound was based on mass measurements, elemental analysis, the interpretation of ^1H , ^{13}C -NMR, and FT-IR spectra. TIMPH ligands were coordinated to the tin atom at two sites via

both O and N atoms. In the $^1\text{H-NMR}$ spectrum of tin compound, two OH protons were shifted from 13.0 ppm for free ligands to 9.92 (s, H, OH), and 11.0 (s, H, OH) ppm. This shift shows that OH protons were protected in the tin compound and OH groups interacted with the tin atom to a different degree. FT-IR measurement showed that a strong peak was observed at 1576 cm^{-1} in the spectrum of TIMPH ligand for C=N group. After the coordination of TIMPH to tin atom, the C=N peak was shifted to the lower value (1543 cm^{-1}) in the spectrum. It is an expected phenomenon that the bonding of CH=N group to metal atom lowers the double bond character of CH=N group [21]. In the $^{13}\text{C-NMR}$ spectrum of tin compound, the C-OH (160.7 ppm) and CH=N (165.3 ppm) carbons having different values than the peaks of the TIMPH ligand indicate that there was a binding as shown in Fig. 1.

Fig. 1 Structure of $[\text{SnBuCl}_3(\text{TIMPH})_2]$ compound

The spectroscopically proposed structure was also confirmed by mass measurement. The peak at 729.01 (100%), 731.02 (90%), and 727.02 (97.8%) Da on mass spectrum confirmed the proposed structure ($[\text{C}_{32}\text{H}_{35}\text{Cl}_3\text{N}_2\text{O}_2\text{Sn}+\text{Na}]^+$).

3.2. Effect of pH in the removal of murexide

The pH of aqueous solutions is an important parameter that controls the adsorption process [13, 22]. The effect of the initial pH on the percentage removal of murexide in the pH range from 2 to 8 at room temperature (100 mg/L murexide) by using 40 mg of the adsorbent at a contact time of 20 minutes was shown in Fig. 2. It was observed that the maximum percentage removal of murexide on Schiff base was obtained at pH 3.0 and its value was determined to be 99.82%. Maximum adsorption occurred in acidic environment. Therefore, all subsequent studies were carried out at pH 3.

In an acidic environment, adsorbents are protonated, and have a positive charge to attract dye ions on their surface, thereby dye removal increases. However, in the case of neutral pH, the percentage removal was reduced. This was because at high pH, the adsorbent was coated on the surface with negative charges and these charges have the repulsive force for the dye. The reason for the maximum removal of murexide dye used in this study at acidic pH was due to the presence of coordinated covalent bonds between the tin atom of Schiff base compound and the dye ions in addition to attractive forces [23,24].

Fig. 2 Effect of pH on the adsorption of murexide onto $[\text{SnBuCl}_3(\text{TIMPH})_2]$ (temperature: 25°C; initial dye concentration: 100 mg/L; adsorbent dose: 40 mg and time: 20 min)

3.3. Effect of initial dye concentration on adsorption

The initial dye concentration may have different effects on adsorption. Therefore, in this study the effect of initial dye concentration on adsorption was investigated. Adsorption of murexide onto $[\text{SnBuCl}_3(\text{TIMPH})_2]$ was carried out at different initial dye concentration ranged from 100 to 600 mg/L, and other conditions such as time (20 min), pH (3), temperature (25 °C), and amount of adsorbent (40 mg) were kept constant. Fig. 3 showed the effect of initial murexide dye concentration on dye removal percentage. The maximum adsorption removal percentage was 98.52% for 100 mg/L concentration of dye solution. The high percentage of dye removal at a low concentration of dye could be attributed to the presence of active sites in the adsorbent. And the rise in the initial concentration of dye could be caused by a reduction in the driving force of the concentration gradient [25,26].

Fig. 3 Effect of initial dye concentration on adsorption (adsorbent dose: 40 mg; temperature: 25°C; pH: 3; and time: 20 min)

3.4. Effect of adsorbent amount

By preparing an adsorbent-adsorbate solution, the effect of the amount of adsorbent on the adsorption process can be achieved by applying a different amount of adsorbent to the solution at a constant initial dye concentration and shaking it until equilibrium time [27,28]. The effect of different adsorbent amounts on murexide adsorption was investigated. Fig. 4 represents the results. It was found that as the adsorbent dose increased, the adsorption value increased. The maximum adsorption value for the 60 mg dose was 99.5%. This is due to an increase in the active surface area of the adsorbent and the increased adsorption areas when the amount of adsorbent is increased [29]. 40 mg of $[\text{SnBuCl}_3(\text{TIMPH})_2]$ was selected as the optimum amount of adsorbent.

Fig. 4 Effect of adsorbent amount (dye concentration: 100 mg/L; temperature: 25°C; pH: 3; and time: 20 min)

3.5. Effect of temperature

The experimental findings indicate that the temperature is a critical factor that greatly affects the adsorption process. To establish whether the continuous adsorption process was endothermic or exothermic in the dye adsorption process, dye adsorption experiments were performed at temperatures of 25-65 °C for 100 mL of 100 mg/L murexide, pH 3, 40 mg adsorbent dosage, and 20 min contact time. **Fig. 5** indicates that the maximum percentage removal of murexide at 35 °C was 99.5%. At higher temperatures, the adsorption capacity can increase or decrease, depending on the nature of the reaction and other controlling variables. Adsorption can increase at higher temperatures if the reaction process is endothermic. Increased surface coverage at higher temperatures, as well as the expansion and formation of reactive and active sites, may explain this. When a reaction is exothermic, the amount of adsorption decreases as the temperature rises. [30, 31].

Fig. 5 Effect of temperature (dye concentration: 100 mg/L; pH: 3; and time: 20 min)

3.6. Effect of time

The effect of contact time on the percentage removal of murexide dye with an initial concentration of 100 mg/L was tested at pH 3 at 25°C. It has been observed that the removal of dye increased on [SnBuCl₃(TIMPH)₂] adsorbent with increasing contact time and achieved the highest value (**Fig. 6**). It is almost constant with an increase in contact time after 20 min depending on the findings [32].

Fig. 6 Effect of time (dye concentration: 100 mg/L; temperature: 25°C; pH: 3; and adsorbent dose: 40 mg)

3.7. Adsorption isotherms

Adsorption isotherms are very important because they can explain the interactions between the dye molecules and adsorbents. In this study, the suitability of experimental data to Langmuir, Freundlich and Temkin isotherm models was investigated to determine the adsorption mechanism between dye molecules and adsorbent. In Fig. 7, three isotherms plotted and the values calculated from the isotherm equations were presented in Table 3.

Table 3. Adsorption isotherm results for murexide onto [SnBuCl₃(TIMPH)₂].

	Langmuir Constant			Freundlich Constant			Temkin Constant		
	R ²	Q _{max} (mg/g)	K _L (L/mg)	R ²	K _F (mg/g)	1/n	R ²	K _t (L/g)	B
Murexide	0.98	200	37.04	0.95	4.76	0.29	0.77	216.4	133.4

Fig. 7 Langmuir, Freundlich, and Temkin isotherms on [SnBuCl₃(TIMPH)₂] for murexide at temperature: 25°C; pH: 3; and adsorbent dose: 40 mg)

The equilibrium data better matched the isotherms of Langmuir adsorption than the isotherms of Temkin. R² (correlation coefficient) value of linear equation was 0.98, which clearly suggested that Langmuir isotherm was good to explain adsorption of murexide on [SnBuCl₃(TIMPH)₂]. In a monolayer and by chemisorption, there has been an adsorption of murexide dye on [SnBuCl₃(TIMPH)₂] adsorbent [33]. The calculated maximum adsorption capacity of murexide dye on [SnBuCl₃(TIMPH)₂] adsorbent was about 200 mg/g and this value was not far from our experimental maximum adsorption capacity value which was 248.8 mg/g.

The Freundlich adsorption isotherms R² value was 0.95, and the adsorption favorability and high adsorption preference of murexide dye onto [SnBuCl₃(TIMPH)₂] adsorbent was shown to be 1/n (0.29) [17,22].

3.8. Adsorption kinetics

The murexide dye adsorption control rate mechanism on [SnBuCl₃(TIMPH)₂] compound was investigated by fitting pseudo-first-order and pseudo-second-order models. In order to gain

knowledge about the character of adsorption, kinetic studies were carried out. The linear plots of the pseudo-first and second-order models were shown in Fig. 8, and the results of the kinetic parameters were shown in Table 4, according to the results of experiments performed at 100 mg/L murexide dye concentrations.

Table 4. Kinetic parameters for murexide adsorption on [SnBuCl₃(TIMPH)₂].

Dye concentration(mg/L)	First-Order Pseudo Kinetic			Second-Order Pseudo Kinetic		
	R ²	k ₁ (1/min)	q _e (mg/g)	R ²	k ₂ (g/mg.min)	q _e (mg/g)
Murexide (200)	0.478	0.16	175.9	0.998	0.11	142.9

Fig. 8 Pseudo-first and second-order models kinetic equation for adsorption of metal ions

The correlation coefficient value R² of pseudo-second-order kinetic equation was 0.99 suggesting that the adsorption reaction may be chemisorption supported by interaction between the dye and the adsorbent surface [34,35]. Murexide dye contains nitrogen and oxygen atoms, each of which has a lone pair and can serve as a Lewis base against to acidic center. Therefore, both atoms can coordinate to tin atom. The other bonding occurs by replacing the ammonium ion (NH₄⁺) with the tin ion (C₄H₉SnCl₂⁺) as seen in Fig. 9.

Fig. 9 The bonding between murexide dye and tin compound

3.9. Thermodynamic parameters of adsorption

To determine the thermodynamic feasibility and spontaneous existence of the process, the thermodynamic constants of the adsorption systems, such as change in Gibb's free energy (ΔG°), the change in entropy (ΔS°) and the change in enthalpy (ΔH°), were measured.

Table 5. Thermodynamic parameters at different temperatures

T (°C)	ΔG° (j/mol)	ΔH° (Kj/mol)	ΔS° (Kj.mol/K)	R ²
25	-56.48	-0.045	0.189	0.980
35	-58.37			

45	-60.27
55	-62.16
65	-64.06

Table 5 gives the results of the thermodynamic parameters. In addition, negative values of ΔH° indicated the exothermic presence of the adsorption process and positive ΔS° values indicated an increase in the concentration of the adsorbate in the solid phase and an increase in randomness [36,37]. Negative free energy values ΔG° confirmed the spontaneous existence and feasibility of the adsorption process [38,39].

As a result of this study, it was observed that the newly synthesized Schiff base compound has a high adsorption capacity for murexide dye in a very short time at room temperature. **Table 6** shows the comparison of adsorption capacities of several adsorbents including Schiff base tin adsorbent.

Table 6. Comparison of adsorption capacities of various adsorbents for murexide dye.

Adsorbent	Murexide (mg/g)	Reference
Tin oxide nanoparticles loaded on activated carbon (SnO ₂ -NP-AC)	67.00	[13]
Formalin treated Pisum sativum peels	11.04	[23]
Rice husk	15.06	[25]
Activated Carbon	12.88	[36]
Calcined egg-shell powder	12.64	[37]
HNO ₃ treated Pomegranate bark	1.700	[38]
Lignocellulosic sorbent	15.60	[39]
Cellulosic sorbent	11.80	
(TIMPH) ₂ SnCl ₃ Bu	248.8	This Study

As can be seen from the [Table 6](#), the $[\text{SnBuCl}_3(\text{TIMPH})_2]$ compound appears to be a more effective adsorbent for Murexide dye.

Conclusion

In this study, novel Schiff base tin(IV) compound $[\text{SnBuCl}_3(\text{TIMPH})_2]$ was synthesized, characterized and used as an effective adsorbent for removal murexide dye from aqueous solutions for the first time. Optimization was performed by studying the effects of contact time, initial pH, amount of adsorbent, initial dye concentration and temperature on $[\text{SnBuCl}_3(\text{TIMPH})_2]$. The maximum removal percentage (98%) and adsorption capacity (248.8 mg/g) were obtained from the results of optimization at pH 3 in 20 min. while 100 mg/g murexide dye concentration at 25°C. Adsorption equilibrium isotherms were determined and the equilibrium data fitted very well with Langmuir isotherms. The kinetic study of murexide onto $[\text{SnBuCl}_3(\text{TIMPH})_2]$ compound was performed based on pseudo-first-order and pseudo-second-order. The data indicated that the adsorption kinetics follows the pseudo-second-order rate. The determination of the thermodynamic parameters (ΔG° , ΔH° , ΔS°) indicated the spontaneous and exothermic nature of the adsorption process. The present study shows that $[\text{SnBuCl}_3(\text{TIMPH})_2]$ compound can be employed as a low cost and simply synthesized adsorbent for dye removal. Finally, $[\text{SnBuCl}_3(\text{TIMPH})_2]$ compound with high adsorption capacity and removal percentage in rapid time with easy adsorption process is an alternative applicable industrial application for the removal of dyes.

Disclosure statement

The authors reported no potential conflict of interest.

References

- [1] S. Karayunlu Bozbas, Y. Boz, *Desalin. Water Treat.* 57, 7040 (2016)
<https://doi.org/10.1080/19443994.2015.1012122>.
- [2] P.A. Carneiro, R.F.P. Nogueira, M.V.B. Zanoni, *Dyes Pigm.* 74, 127 (2007).
<https://doi.org/10.1016/j.dyepig.2006.01.022>.
- [3] L. Huang, M. He, B. Chen, B. Hu, *Chemosphere* 199:435-444 (2018)
<https://doi.org/10.1016/j.chemosphere.2018.02.019>.
- [4] D. Bingol, S. Karayunlu, *Spectrosc. Lett.* 45, 324 (2012).
<https://doi.org/10.1080/00387010.2012.666697>.
- [5] S. Karayunlu Bozbas, and M. Karabulut, (2021). *Int. J. Environ. Anal. Chem.*

DOI: 10.1080/03067319.2021.1873312 .

[6] S. Karayunlu Bozbas, U. Ay, and A. Kayan, *Desal. Water Treat.* 51(37-39):7208-7015 (2013).

<https://doi.org/10.1080/19443994.2013.793500>.

[7] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, *J. Hazard. Mater.* 177, 70 (2010).

<https://doi.org/10.1016/j.jhazmat.2009.12.047>.

[8] V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, *Water Res.* 35(14):3357-3366 (2001).

[https://doi.org/10.1016/S0043-1354\(01\)00056-2](https://doi.org/10.1016/S0043-1354(01)00056-2).

[9] R. Zein, R. Suhaili, F. Earnestly, E. Munaf, *J. Hazard. Mater.* 181(1-3):52-56 (2010).

<https://doi.org/10.1016/j.jhazmat.2010.04.076>.

[10] A. Naz, S. Arun, S.S. Narvi, M.S. Alam, A. Singh, P. Bhartiya, P.K. Dutta, *Inter. J. Biol. Macromol.* 110:215-226 (2018).

<https://doi.org/10.1016/j.ijbiomac.2017.11.112>.

[11] S. Farhadi, M.M. Amini, M. Dusek, M. Kucerakova, F. Mahmoudi, *J. Mol. Struct.* 1130, 592 (2017).

<https://doi.org/10.1016/j.molstruc.2016.10.081>.

[12] M. Arshadi, *J. Mol. Liq.* 211, 899 (2015).

<https://doi.org/10.1016/j.molliq.2015.08.027>.

[13] S. Davoodi, F. Marahel, M. Ghaedi, M. Roosta, A. Hekmati, A. Jah, *Desal. Water Treat.* 52:7282–7292 (2014).

<https://doi.org/10.1080/19443994.2013.831781>.

[14] A. Kayan, *J. Turk. Chem. Soc. Sec. A: Chem.* 4(1):59-80 (2017).

<https://doi.org/10.18596/jotcsa.14346>.

[15] C.S. Araújo, I.L. Almeida, H.C. Rezende, S.M. Marcionilio, J.J. Léon, T.N. de Matos, *Microchem. J.* 137:348-354. (2018).

<https://doi.org/10.1016/j.microc.2017.11.009>.

[16] M.R. Awual, M.M. Hasan, M.M. Rahman, & A.M. Asiri, *J. Mol. Liq.* 283 772-780 (2019).

<https://doi.org/10.1016/j.molliq.2019.03.141>.

[17] A.A. Edathil, I. Shittu, J.H. Zain, F. Banat, M.A. Haija, *J. Environ. Chem. Eng.* 6(2), 2390 (2018).

<https://doi.org/10.1016/j.jece.2018.03.041>.

[18] R. Lafi, A.B. Fradj, A. Hafiane, B. Hameed, *Korean J. Chem. Eng.* 31, 2198 (2014).

<https://doi.org/10.1007/s11814-014-0171-7>.

- [19] B. Adane, K. Siraj, N. Meka, *Green Chem. Lett. Rev.* 8, 1 (2015).
<https://doi.org/10.1080/17518253.2015.1065348>.
- [20] A. Kayan, M.O. Arican, Y. Boz, Ü. Ay, S. Karayunlu Bozbas, *J. Environ. Chem. Eng.* 2:935-942 (2014).
<https://doi.org/10.1016/j.jece.2014.03.008>
- [21] B.C. Yildiz, and A. Kayan, *Sustain. Chem. Pharm.* 21:100416 (2021).
<https://doi.org/10.1016/j.scp.2021.100416>
- [22] N. Dharmaraj, P. Viswanathamurthi, K. Natarajan, *Transit. Met. Chem.* 26(1):105-109 (2001) <https://doi.org/10.1023/A:1007132408648>.
- [23] R. Rehman, T. Mahmud, A. Arshad, *Asian J. Chem.* 27(5) 1593 (2015).
<https://doi.org/10.14233/ajchem.2015.17383>.
- [24] S.S. Nawar, H.S. Doma, *Sci. Total Environ.* 79, 270 (1989).
[http://dx.doi.org/10.1016/0048-9697\(89\)90342-2](http://dx.doi.org/10.1016/0048-9697(89)90342-2).
- [25] R. Rehman, J. Anwar, T. Mahmud, M. Salman, U. Shafique, W. Zaman, *J. Chem. Soc. Pak.* 33(4), 598 (2011). [ISSN 0253-5106](https://doi.org/10.1016/S0253-5106).
- [26] C. Demirebalek, C. Özdemir Dinç, *Desalin. Water Treat.*, 57(15), 6884 (2016).
<https://doi.org/10.1080/19443994.2015.1013506>.
- [27] S. Mam, D.K. Mahmoud, W.A. Karim, A. Irdi, *Desalin. Water Treat.* 280, 1 (2011).
<https://doi.org/10.1016/j.desal.2011.07.019>.
- [28] K. Bharathi S. Ramesh, *Appl. Water Sci.* 3, 773 (2013).
<https://doi.org/10.1007/s13201-013-0117-y>.
- [29] V.K. Garg, R. Gupta, A.B. R. Yadav, Kumar, *Bioresour. Technol.* 8:121–124 (2003).
[https://doi.org/10.1016/S0960-8524\(03\)00058-0](https://doi.org/10.1016/S0960-8524(03)00058-0)
- [30] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, *Sep. Purif. Technol.* 53, 97 (2007).
<https://doi.org/10.1016/j.seppur.2006.06.018>.
- [31] C.S. Lu, Y.L. Chung, K.F. Chang, *J. Hazard. Mater.* 138, 304 (2006).
<https://doi.org/10.1016/j.jhazmat.2006.05.076>.
- [32] M. Özdemir, Ö. Durmuş, Ö. Şahin, C. Saka, *Desalin. Water Treat.* 57(38), 18038 (2015).
<https://doi.org/10.1080/19443994.2015.1085916>.
- [33] M.W. Ashraf, N. Abulibdeh, A. Salam, *Int. J. Chem. Eng.* 1, (2019).
<https://doi.org/10.1155/2019/9728156>.
- [34] A. Salama, *J. Colloid Interface Sci.* 487, 348 (2017).
<https://doi.org/10.1016/j.jcis.2016.10.034>.
- [35] A. Kayan, *Adv. Compos. Hybrid. Mater.*(1) 34 (2019).

<https://doi.org/10.1007/s42114-018-0073-y>.

[36] A. Shokrollahi, M. Ghaedi, M. Ranjbar, A. Alizadeh, J. Iran. Chem. Soc., 3, 219 (2010).

http://jicr.iau-arak.ac.ir/article_518337.html.

[37] A.V. Borhade, A.S. Kale, Appl. Water Sci. 7, 4255 (2017).

<https://doi.org/10.1007/s13201-017-0558-9>.

[38] M. Ishaq, K. Saeed, M. Shakirullah, I. Ahmad, & S. Sultan, (2012) Journal of the Chemical Society of Pakistan, vol. 34, no. 6, 2012. Gale Academic OneFile, Accessed 11 Apr. 2021.

[39] V. Halysh, O. Sevastyanova, A.V. Riazanova, et al. Cellulose 25, 4729 (2018).

<https://doi.org/10.1007/s10570-018-1896-y>.

Figures

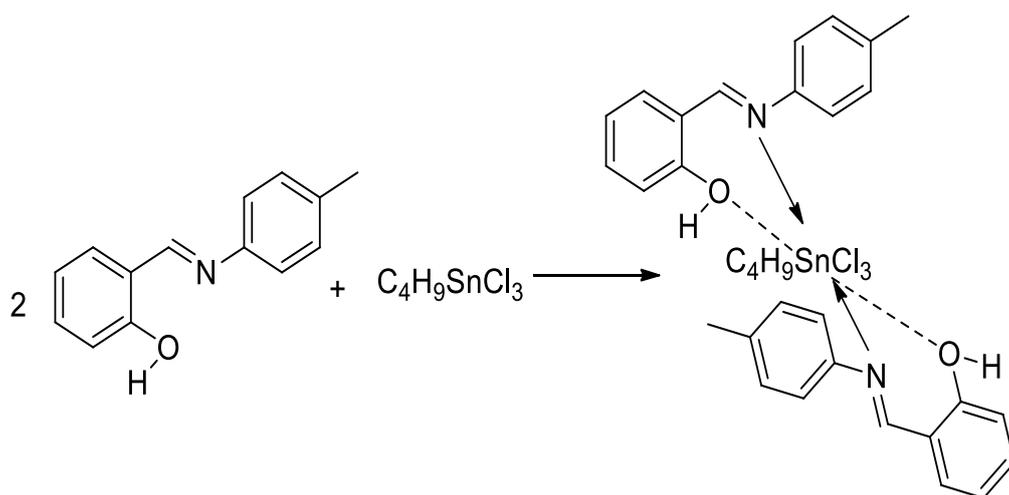


Fig. 1

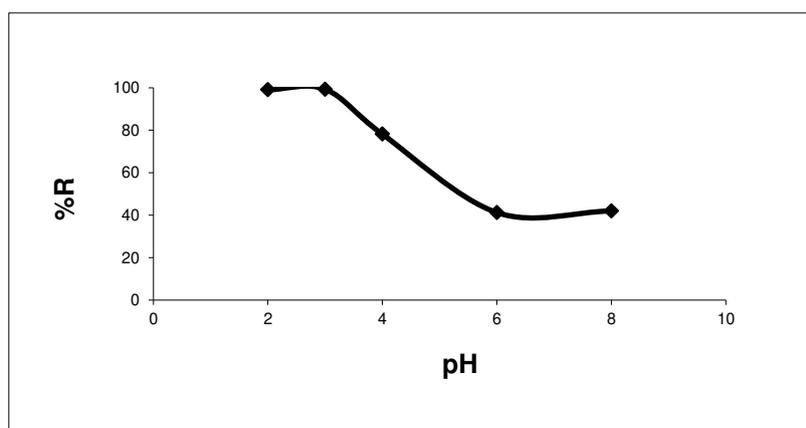


Fig. 2

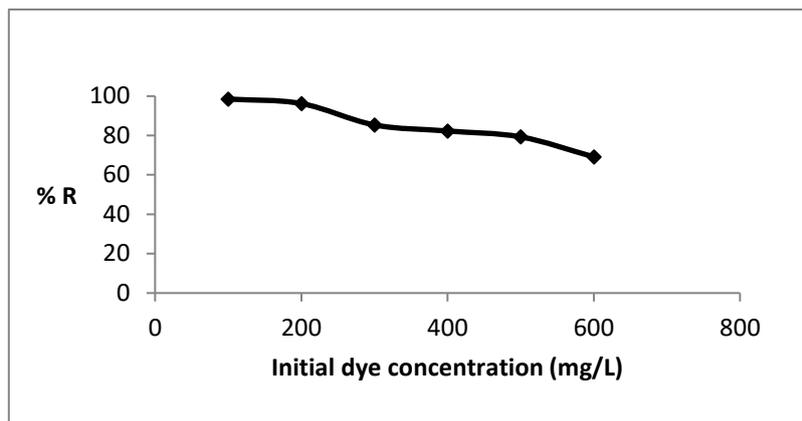


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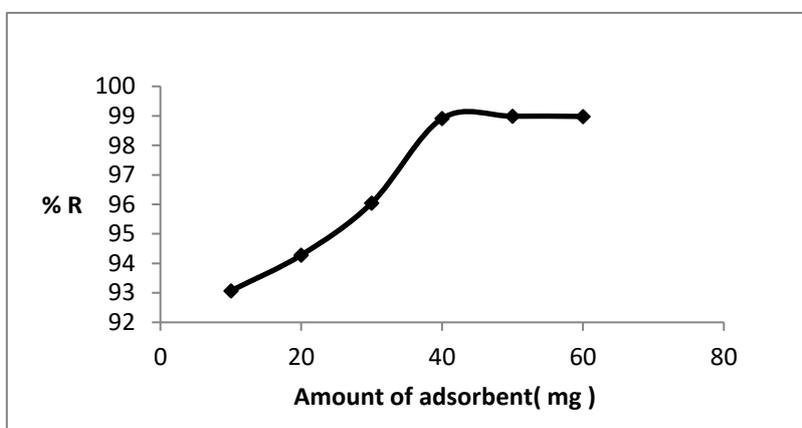


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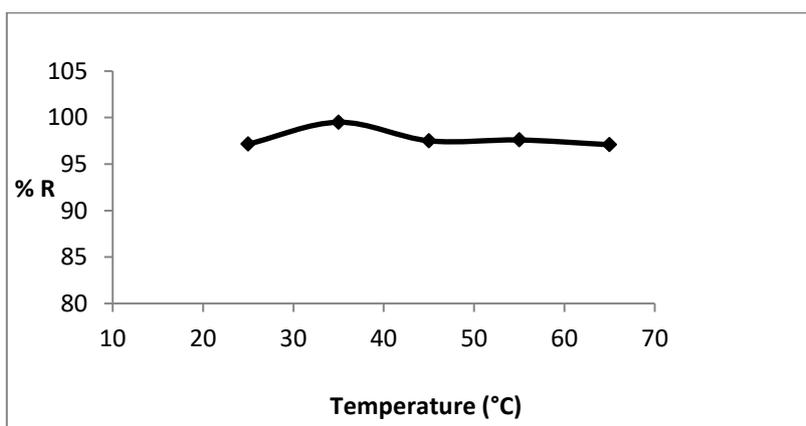


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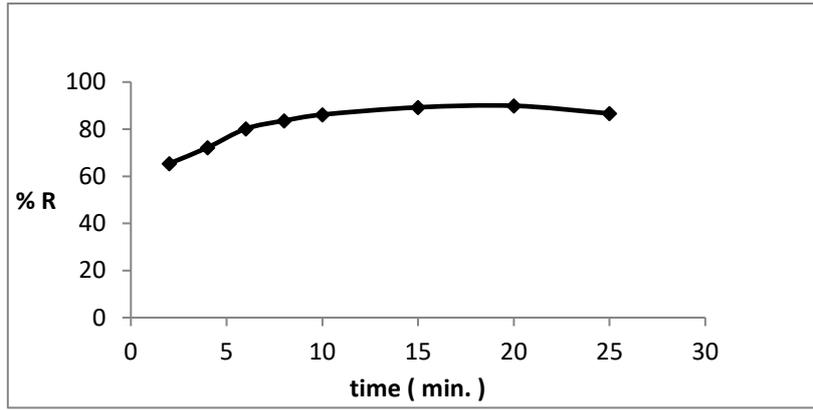


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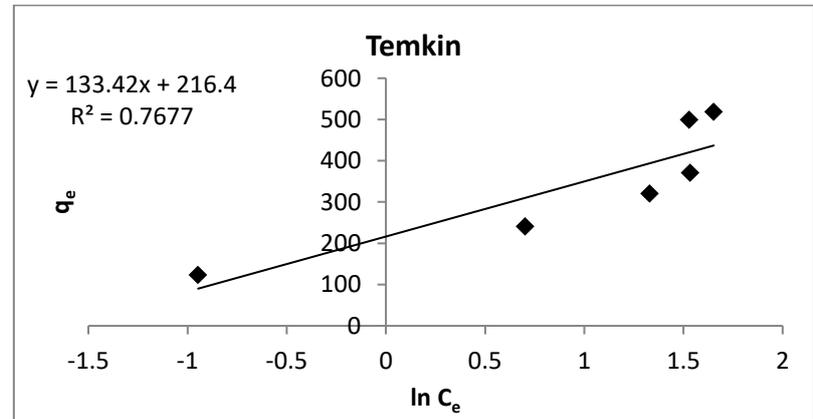
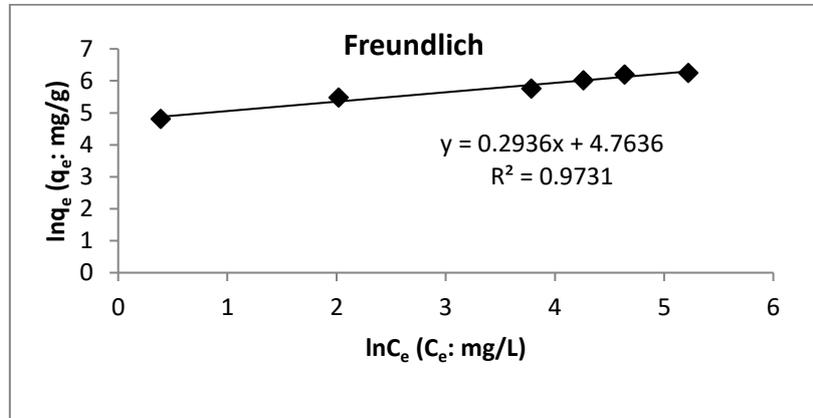
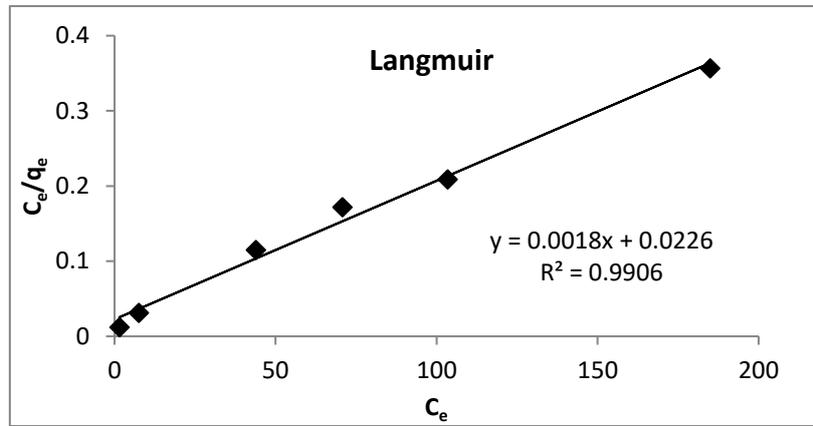


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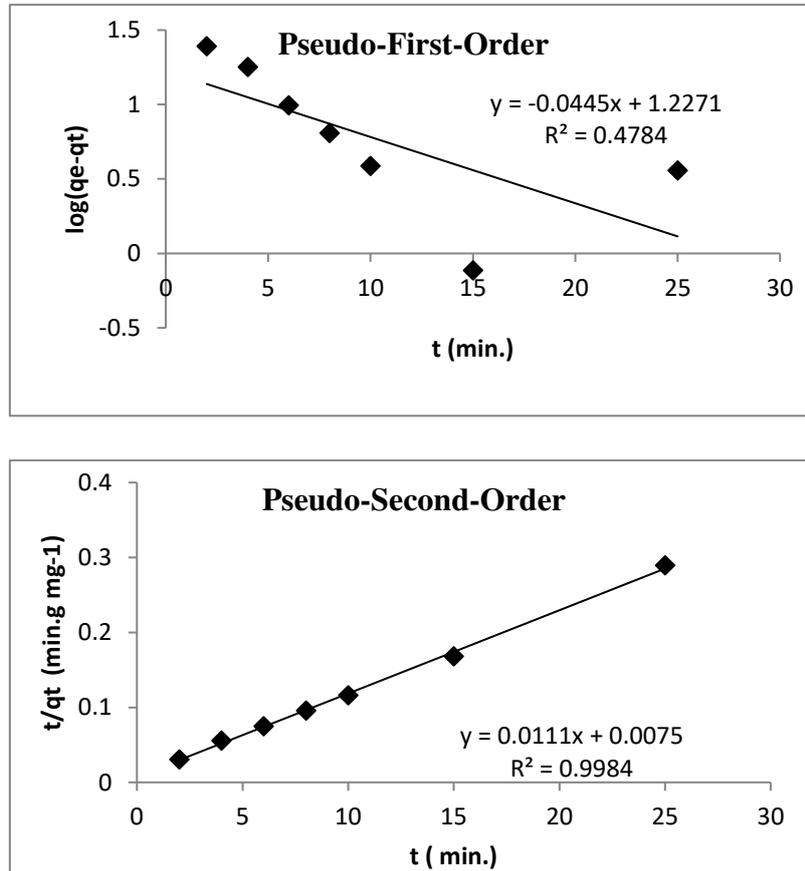


Fig. 8

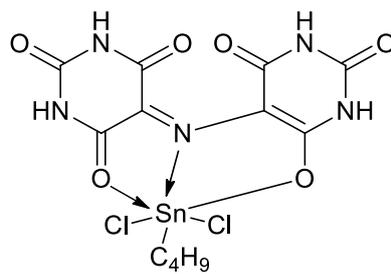


Fig. 9

Figures

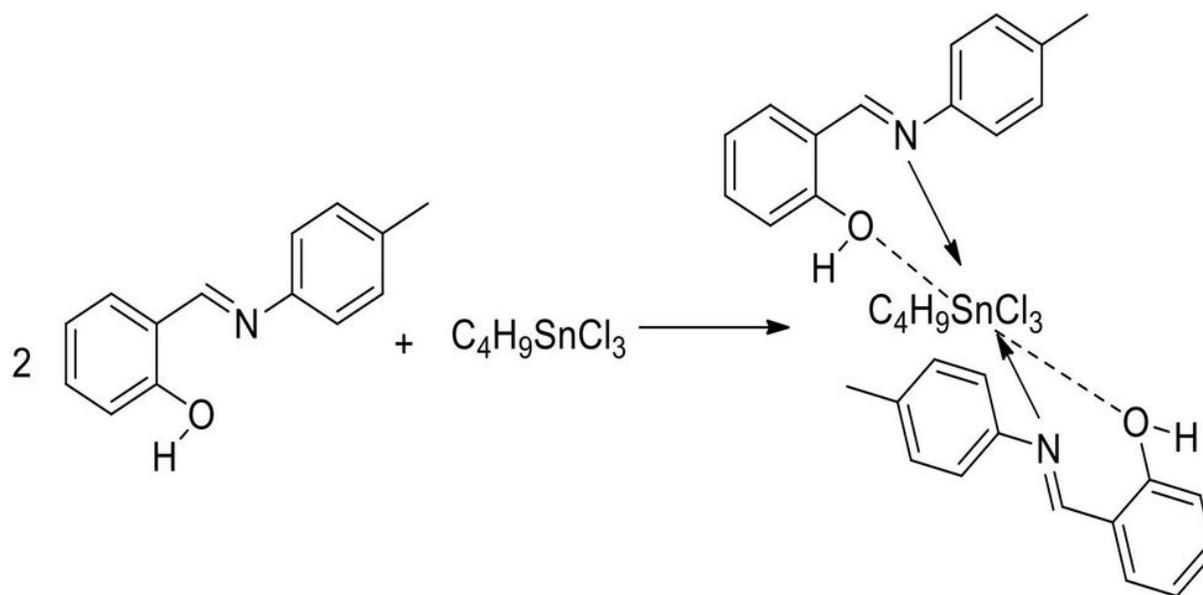


Fig. 1

Figure 1

Structure of $[SnBuCl_3(TIMPH)_2]$ compound

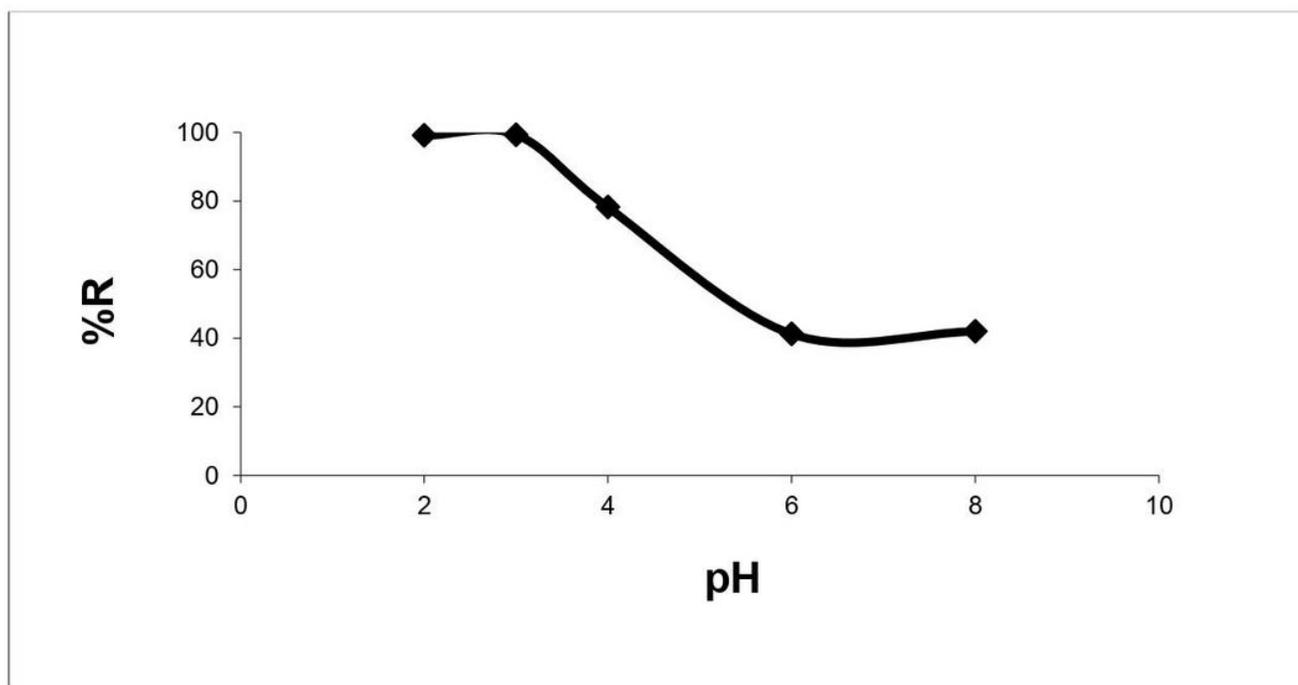


Fig. 2

Figure 2

Effect of pH on the adsorption of murexide onto $[\text{SnBuCl}_3(\text{TIMPH})_2]$ (temperature: 25°C; initial dye concentration: 100 mg/L; adsorbent dose: 40 mg and time: 20 min)

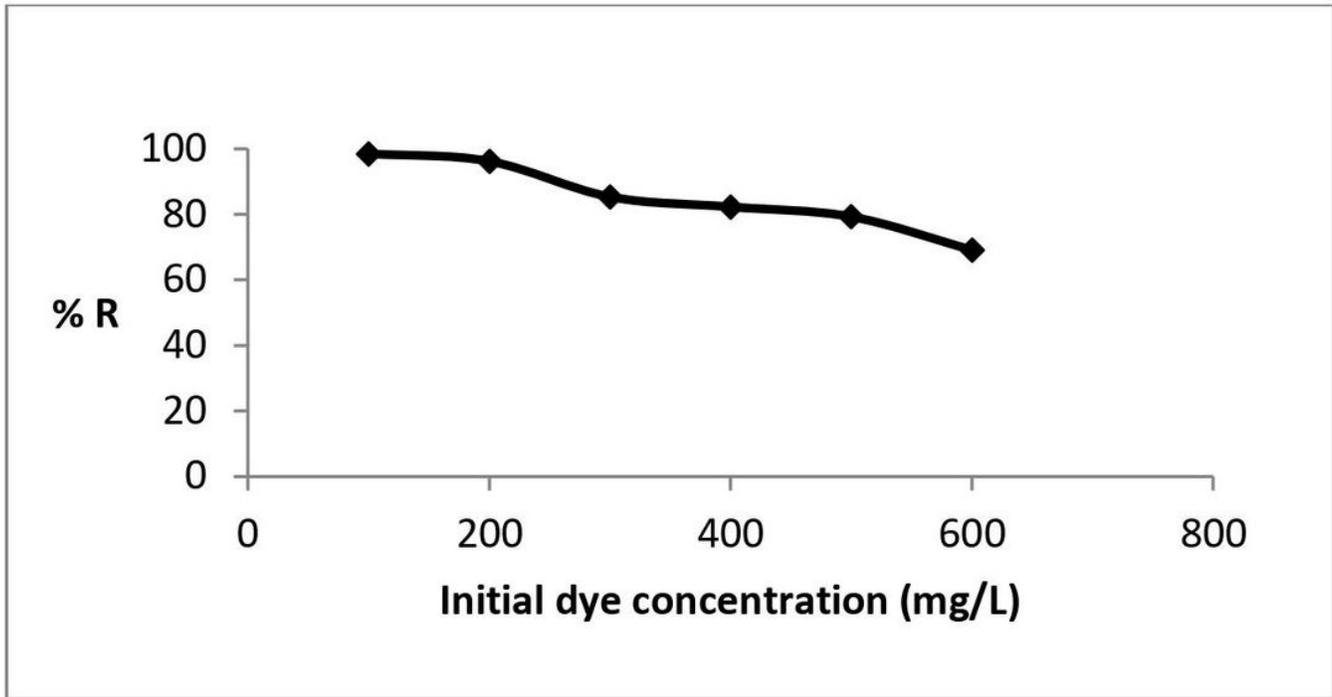


Fig. 3.

Figure 3

Effect of initial dye concentration on adsorption (adsorbent dose: 40 mg; temperature: 25°C; pH: 3; and time: 20 min)

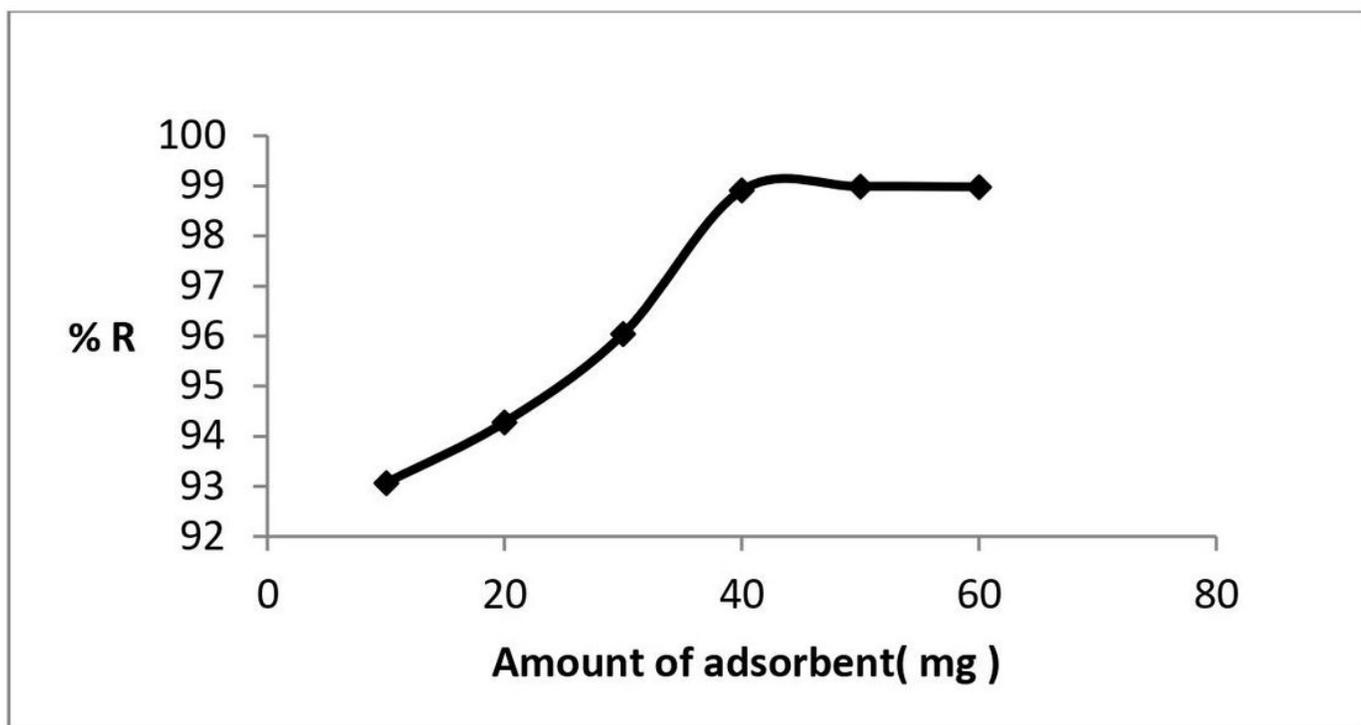


Fig. 4.

Figure 4

Effect of adsorbent amount (dye concentration: 100 mg/L; temperature: 25°C; pH: 3; and time: 20 min)

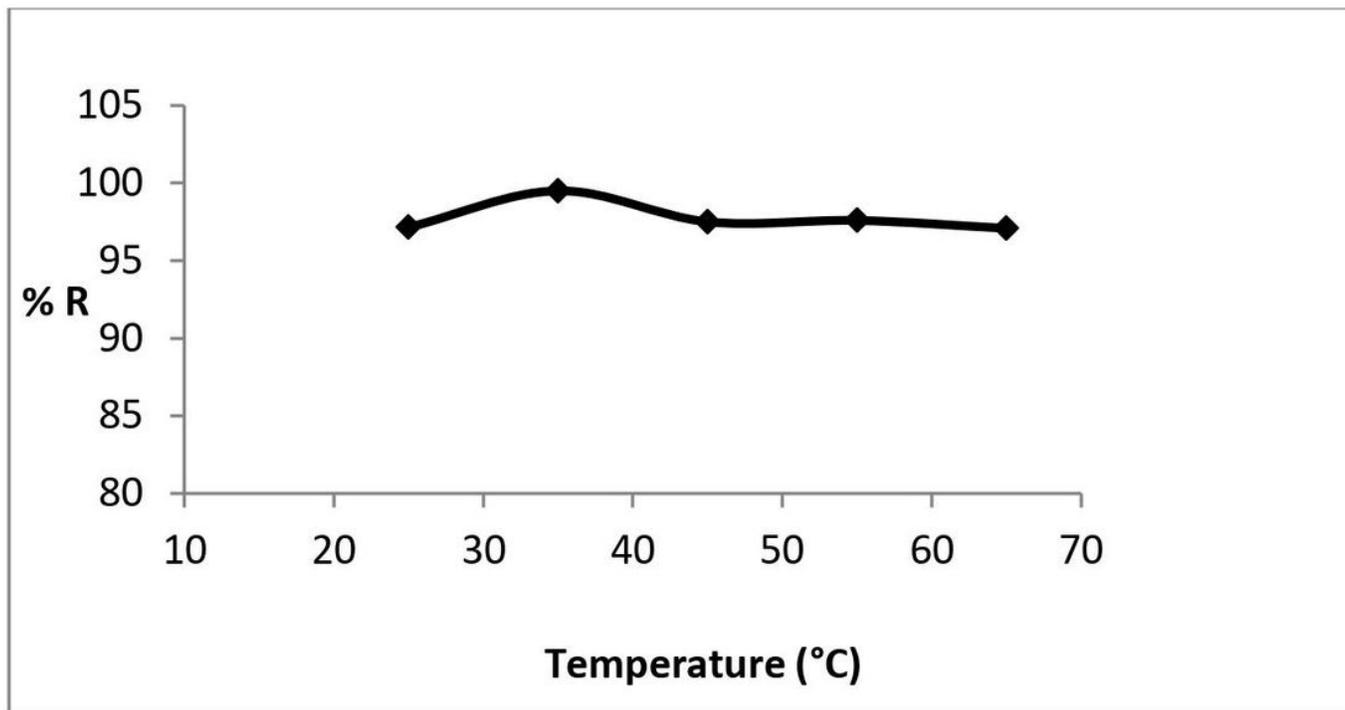


Fig. 5.

Figure 5

Effect of temperature (dye concentration: 100 mg/L; pH: 3; and time: 20 min)

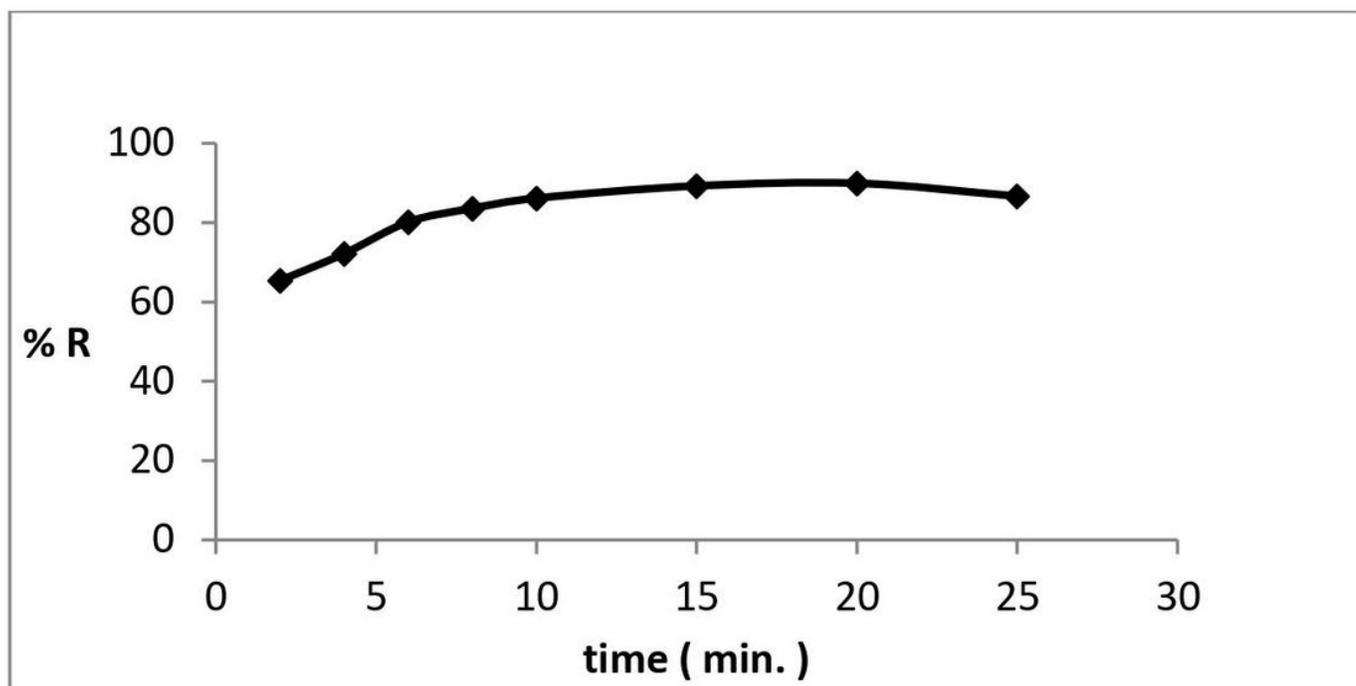


Fig. 6.

Figure 6

Effect of time (dye concentration: 100 mg/L; temperature: 25°C; pH: 3; and adsorbent dose: 40 mg)

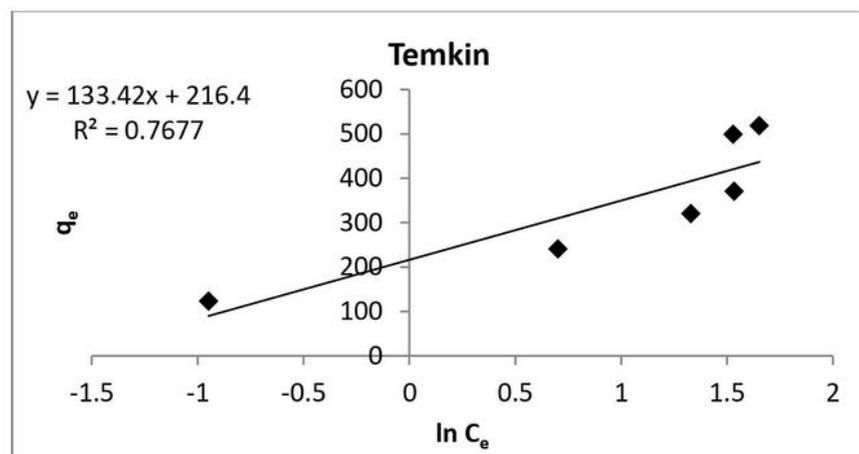
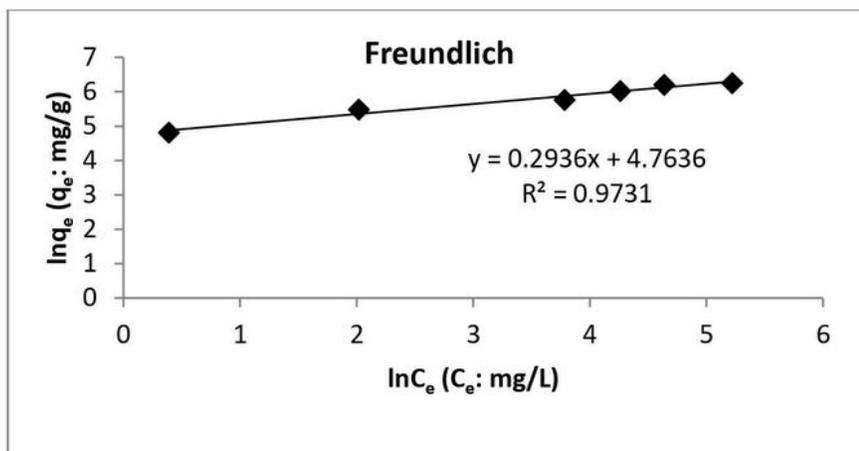
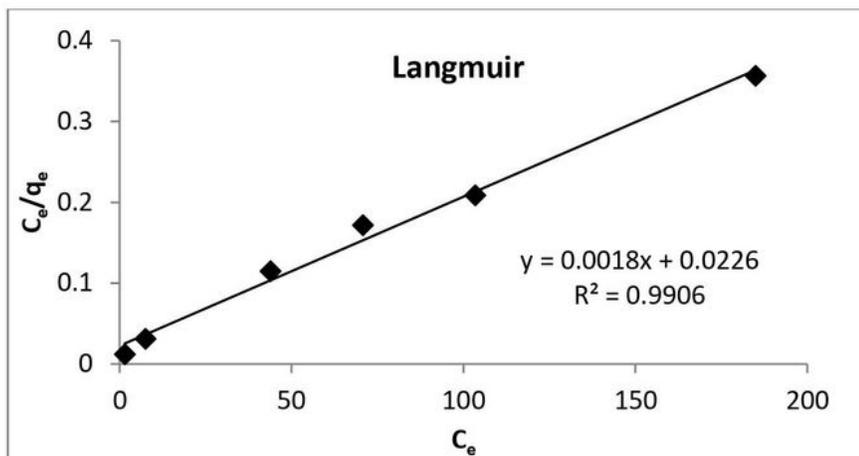


Figure 7

Langmuir, Freundlich, and Temkin isotherms on [SnBuCl₃(TIMPH)₂] for murexide at temperature: 25°C; pH: 3; and adsorbent dose: 40 mg)

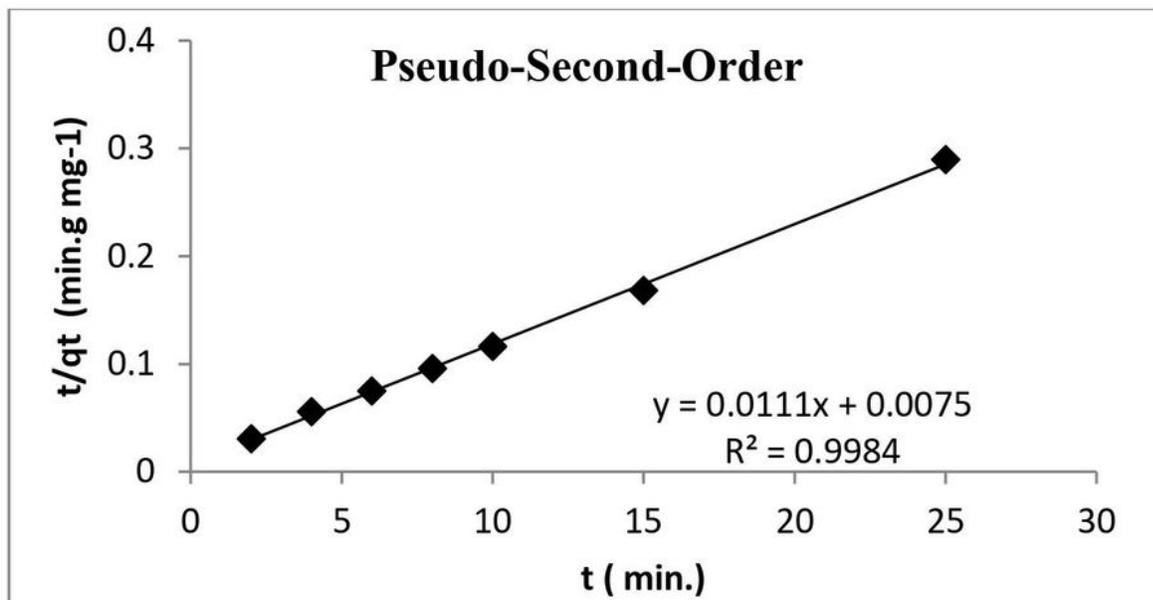
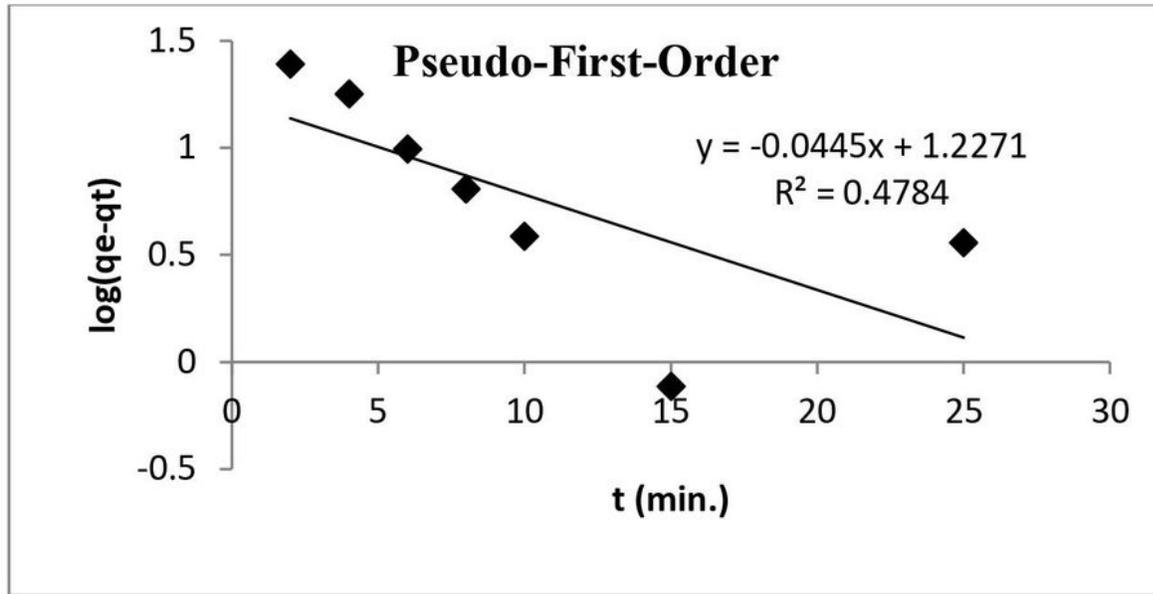


Fig. 8

Figure 8

Pseudo-first and second-order models kinetic equation for adsorption of metal ions

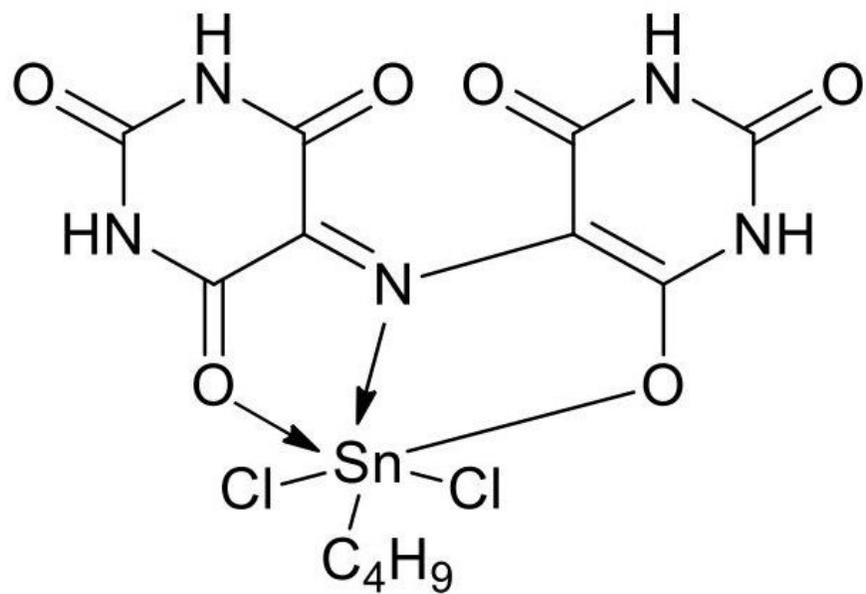


Figure 9

The bonding between murexide dye and tin compound