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Adsorption, Kinetic, Equilibrium, Thermodynamic and Photocatalytic Investigations of the Removal of Nigrosin, Alizarin, Indigo and Acid Fuchsin Dyes on Modified CaO Surface

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Authors' contributions

This work was carried out in collaboration among all authors. Author MAA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author IKR managed the analyses of the study. Author ZNK managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Calcium oxide was obtained from eggshell and modified with Sulfur, Nitrogen and, Oxygen. The adsorbents were characterized using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX) and, scanning electron microscopy (SEM). The adsorbents were used for the removing of the dyes of Nigrosin, Alizarin red S, Indigo carmine, and Acid fuchsin from their aqueous solutions. The adsorption isotherm experiments were studied, and the equilibrium adsorption found either obeyed the Langmuir or Freundlich isotherm depending on the Sips isotherm results. Thermodynamic studies showed that the adsorption processes of the studied dyes were spontaneous, endothermic and randomness increases according to their ΔG, ΔH and ΔS values, respectively. The kinetic studies revealed that the pseudo second-order model best represented adsorption kinetics. Moreover, the photocatalytic ability of adsorbents was investigated under the sunlight, the results revealed the adsorbents have a strong photo-catalytic ability to absorb the dyes, particularly that observed for Acid fuchsin.

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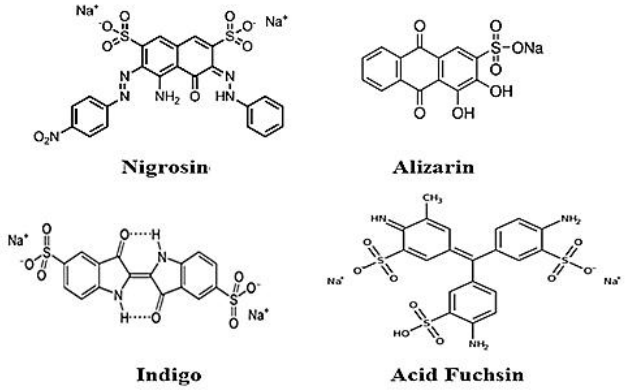
Keywords: Eggshell; modified CaO; adsorption; sips isotherm; kinetics; photocatalytic.

1. INTRODUCTION

Environmental pollution is one of the vast problems facing the world and the efforts need to combine to address and reduces it [1].The concept of water pollution is an undesirable change in qualities, whether chemical, physical or life, resulting in damage to human life and other organisms [2]. About 30% of the dyes used in industrial processes go to industrial wastewater [3]. The dyes have been used for a long time in the industry in the dyeing of paper, pulp, textile, plastic, leather, cosmetics and food industries [4] and most of these substances seep into the environment and pollution, and the presence of dyes in the water affect the nature of water and prevent the entry of sunlight and penetration through the rivers and also reduce the process of photosynthesis, many of them toxic and carcinogenic [5]**.** The removal of dyes from wastewater has been considered much attention [6,7]. Many of chemical and biological methods including flocculation [8], ozonation [9], coagulation [10], and adsorption [11] have been used to remove dye pollutants. These components can be removed largely by adsorption on the surfaces of many porous natural materials dyes are particularly removed using various adsorbents. Many such adsorbents such as orange peel, neem seed, oil cakes, date palm, olive shell and, charcoal have been explored for its removal. The good adsorbent depends upon several parameters such as surface area, porosity, surface charges, mechanical strength and, chemical interaction optimizations are needed while performing and choosing the right adsorbent for metal ion removal. Some studies have been reported that the modification of adsorbent surface improves of adsorption efficiency [12-14]. Adsorbent can be modified to improve desirable physiochemical properties such as surface area, pore-size distribution, pore volume, and surface functional groups. Three well known types modification methods are involve the chemical characteristics, physical characteristics or biological characteristics. Among of these methods, modification with chemical compound has been common employed to increases the adsorption and consequently the removal capacity of an adsorbent as the agents include organic and mineral acids, bases and basic solutions, oxidizing agents, and many other chemical compounds [15,16].

Adsorption takes place when molecules in a liquid bind themselves to the surface of a solid substance. Adsorbents have a very high internal surface area that permits adsorption. Eggshell represents around 10% of hen egg, a vital foodstuff that consumed worldwide for home uses. Large amounts of eggshells are produced by egg industrial processes, and large quantities of these solid residue are disposed as waste, consequently are contribute to environmental pollution [17]. The chicken eggshell is a natural porous make it an interesting adsorbent [18,19]. Eggshell is composed of about 96% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate, organic materials and water [20]. The present study reports the performance and ability of unmodified CaO extracted from eggshell and modified CaO (S, N and O forms) for the adsorptive removal of Nigrosin, Alizarin red S, Indigo carmine, and Acid fuchsin dyes (Scheme 1) from aqueous solutions, along with kinetic, thermodynamic and photocatalytic efficiency studies.



Scheme 1. Chemical structures of dyes

2. MATERIALS AND METHODS

2.1 Adsorbate

The dyes were manufactured by Sigma-Aldrich. Stock solutions were prepared by dissolving an accurately weighed amounts of dyes in distilled water and, any desired concentration can be obtained.

2.2 Adsorbent

Calcium oxide was obtained from eggshells that were collected from domestic places. The collected eggshells have been carefully washed, boiled for 2 hrs, separated the interior membrane and, dried at 120^0C for 2 hrs, then crushed, sieved and, calcined at 700^0C for 4 hrs [21].

S/CaO contains sulfur (5%) was prepared by stirring (1.00 g) of CaO for 15 minutes, mixed with 5 ml of ethanol and 0.0679 g thiourea, as a source for S-dopant compound, the mixture was stirred at room temperature for 12 hr and, dried at 80°C for 36 hr. A white powder of S/CaO was obtained after calcination at 400°C for 4 hrs.

N/CaO contains nitrogen (5%) was prepared by stirring (1.00 g) of CaO for 15 minutes, mixed with 5 ml of ethanol, 1.5 ml nitric acid and 5 ml ammonia, as a source for N-dopant compound, the mixture was stirred at room temperature for 12 hr and, dried at 80°C for 36 hr. A white powder of N/CaO was obtained [15].

O/CaO contains oxygen (5%) was prepared by stirring (1.00 g) of CaO for 15 minutes, mixed with 5 ml of ethanol and 0.0535 g urea, as a source for O-dopant compound, the mixture was stirred at room temperature for 12 hr and, dried at 80°C for 36 hr. A white powder of O/CaO was obtained after calcination at 400°C for 4 hrs.

2.3 Adsorption Studies

The adsorption experiments were carried out using a 25 ml of dye solution with a known initial concentration C_o (Nigrosine: 0.05 g/L, Alizarin: 0.4 g/L, Indigo carmine and Acid fuchsin 0.1 g/L) and a known amount of adsorbent (0.01 g). The concentrations of dyes have been recorded on UV-Visible spectrophotometer (PG Instrument T80) at 573, 520, 610 and 569 nm for Nigrosin (NG), Alizarin (AR), Indigo (IC), and Acid fuchsin (AF), respectively. Adsorptive removal of dyes from aqueous solution onto S/CaO, N/CaO and O/CaO were performed using a 25 ml of dye solution with certain initial concentrations (C_o), that where for; Nigrosin: (0.01, 0.020, 0.030, 0,040, 0.050) g/L, Alizarin: (0.100, 0.200, 0.300, 0.400, 0.500) g/L, Indigo and Acid Fuchsin: 0.040, 0.060, 0.080, 0.100, 0.120) g/L, and a fixed amount of adsorbent (0.01 g) was used. The solutions were shaken at 200 rpm for 24 h at room temperature, the obtained suspensions were centrifuged and the equilibrium concentration of each dye were determined using a UV-Visible spectrophotometer. The amount of adsorbed dye (mg) per unit mass of adsorbent (g) at any time (q_t) and at equilibrium (q_e) was calculated using Equations (1) and (2).

$$q_t = \frac{C_o - C_t}{m} v \quad (1)$$

$$q_e = \frac{C_o - C_e}{m} v \quad (2)$$

Where,

C_o, C_e and C_t are the initial concentration, equilibrium concentration and at any time dye concentration, respectively, m and v are the adsorbent mass (g) and the solution volume (L), respectively. The removal percentage was calculated using Equation (3).

$$R\% = \frac{C_o - C_e}{C_o} * 100 \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 XRD and EDX Measurements

The S, N, and O modified CaO were characterized by XRD technique. The XRD pattern of S modified CaO (Fig. 1A) show the emergence two new broad diffraction peaks at 2θ range of 28-30□ and 46-48□, indicating the presence of new crystalline form of S modified CaO compared to unmodified CaO content. Unlike the S/CaO, the XRD patterns of N and O modified CaO (Fig. 1B, 1C) shown no significant changes, indicating that the amorphous content of CaO content remained unchanged during modified with N and O.

Energy dispersive X-ray analysis (EDX) were recorded at room temperature in the range of 0-80 keV (Fig. 2), have confirmed that the modified surfaces are highly pure and have well assigned the doping species. EDX results revealed the presence of 4.97% S, 5.46% N and 78.79% O, which are consistent with standard practical results.

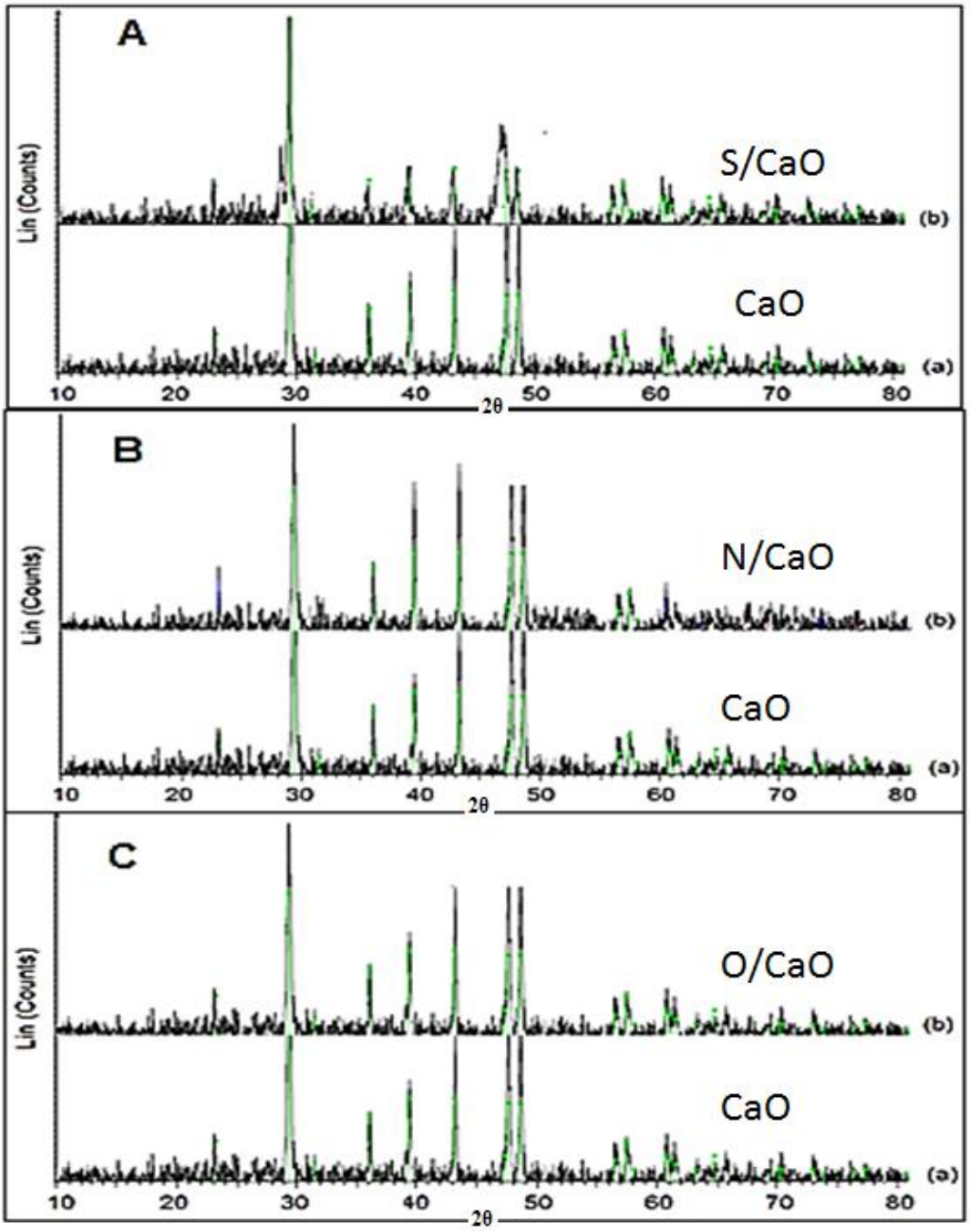


Fig. 1. X-ray diffraction of (a) CaO and (b) S/CaO (A), N/CaO (B) and O/CaO (C)

3.2 SEM Analysis

SEM visual data of modified CaO show totally different morphology from that for CaO. The SEM image of CaO (Fig. 3A) shows the presence of many irregularly distributed cracks and openings that providing good adsorption properties for CaO surface [21]. An irregular distribution changes to regular distribution when CaO surface modified with S, N and, O. Interestingly, the SEM image of CaO modified with S reveals crystalline morphology more than the CaO, and SEM image shows a filled surface with internal cracked fractures (Fig. 3B).

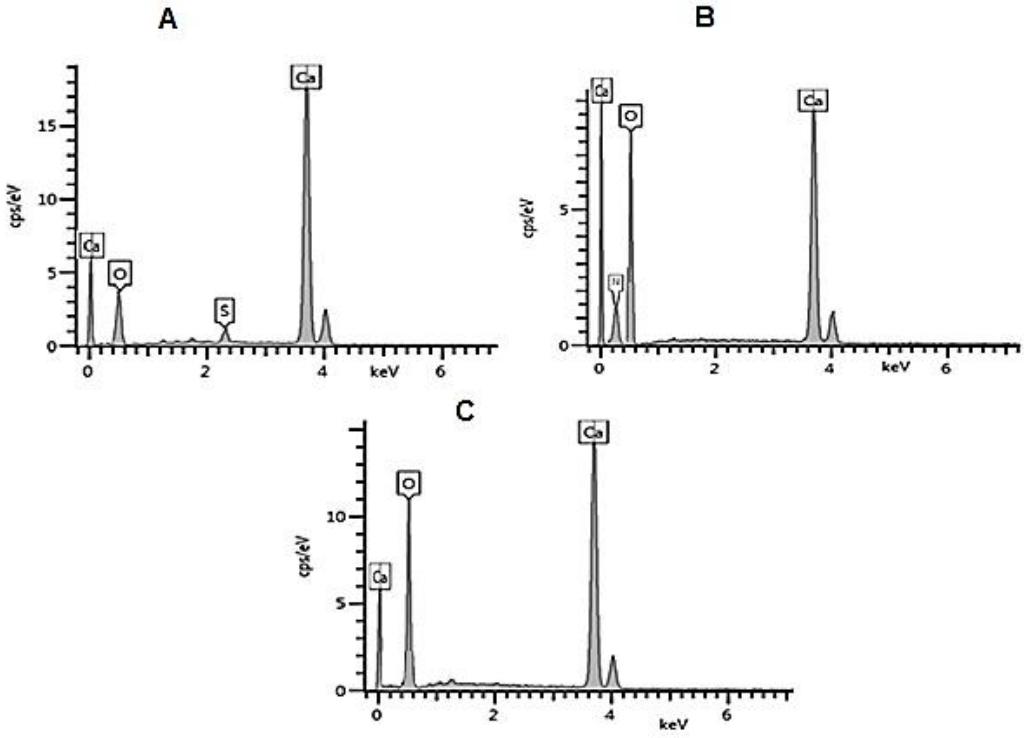


Fig. 2. EDX analysis of S/CaO (A), N/CaO (B) and O/CaO (C)

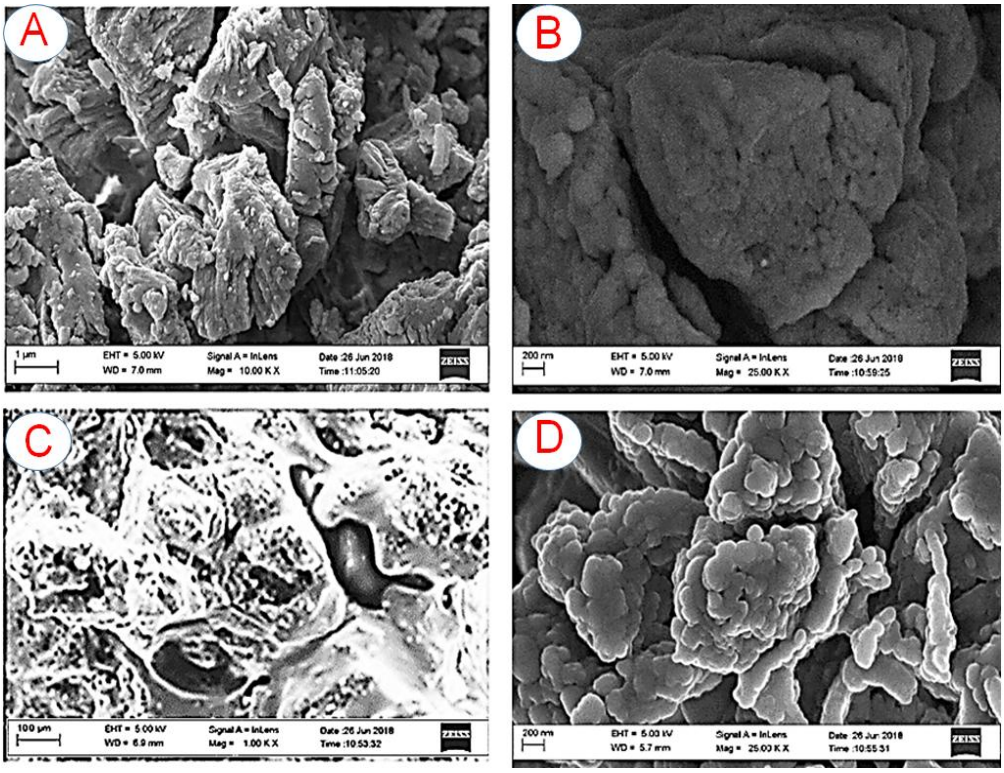


Fig. 3. SEM images of CaO (A), S/CaO (B), N/CaO (C) and O/CaO (D)

The SEM image of CaO modified with N seems like river lines with pits like the ponds (Fig. 3C), whereas the agglomerate surface structure of CaO becomes like clouds when modified with O, as shown in (Fig. 3D).

The new morphology of CaO surface due to its modification leads to the emergence of; new crystalline properties, new sizes of pores and new surface area. Consequently, these factors are practiced different influences on the adsorption capacity of dyes.

3.3 Equilibrium Studies

Equilibrium data were applied using the Langmuir, Freundlich and Sips adsorption isotherms.

The Langmuir isotherm has been usually used for many adsorpion systems of homogeneous surfaces [22]. It can be expressed using equation (4):

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad (4)$$

Where,

Ce is the equilibrium concentration of dye (mg/L), q_m is the adsorption capacity required to complete monolayer on the adsorbent surface (mg/g), q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g), and K_L is Langmuir constant. The K_L and q_m vaues obtained from the plot of *Ce*/ q_e versus *Ce* that gives a straight line with an intercept 1/ K_L q_m and a slope 1/ q_m.

The Freundlich isotherm is valid for heterogeneous surfaces [23], and it follows the equation (5):

$$q_e = K_F C_e^{\,1/n} \quad (5)$$

Where,

K_F and n are the Freundlich constants concerning the capacity and intensity of adsorption, respectively. In contrast to the Langmuir model, provides no information about the monolayer adsorption capacity. The K_F and *n* vaues obtained from the plot of *ln* q_e versus *ln Ce* that gives a straight line with an intercept *ln* K_F and a slope 1/ *n*.

The Langmuir-Freundlich (Sips) isotherm, is a combination of the Langmuir and Freundlich isotherms [24], and it follows equation (6).

$$q_e = \frac{q_m K_S C_e^{1/n}}{1+ K_S C_e^{1/n}} \quad (6)$$

Where,

Ks (L/mg) is the adsorption Sips constant and *n* describes the system's heterogeneity between 0 and 1 [25]. When the value of *n* is equal to 1, the equation 6 becomes a Langmuir equation, also when *n* approaches to 0, the Sips isotherm effectively reduces to Freundlich isotherm [26].

The correlation coefficients (r^2), adsorption capacity (q_m) and heterogeneity factor (*n*), as well as the constants of the isotherm models of Langmuir K_L, Freundlich K_F and Sips K_S are provided in Table 1.

The equilibrium isotherm is determined via the Sips isotherm model in which provides the highest value of correlation coefficients (r^2) for modified and unmodified CaO. Sips isotherm model gives a good idea about which isotherm the adsorption is followed, depending on the Sips model exponent (*1/n*) where n values are limited between 0 and 1 ($0 \leq n \geq 1$). When *1/n* approaches a low value the C_e approaches a low value, the Sips isotherm strongly reduces to Freundlich isotherm and, When *1/n* approaches a high value the C_e approaches a high value, the Sips isotherm predicts the Langmuir monolayer adsorption characteristic.

The isotherm parameters of Nigrosine dye listed in Table 1 show the *n* parameter of Sips isotherm is approximately 1 and the best fit values of correlation coefficients (r^2), onto CaO modified S, O, and N, indicating that the adsorption of the nigrosine follows the Langmuir isotherm onto these surfaces. Moreover, the Sips model data show a significant amount of adsorption capacities onto CaO/S .

The *n* parameter of Sips isotherm and the correlation coefficients (r^2) values refer to the best fit adsorption onto CaO modified S and N indicating that the adsorption of the nigrosine follows the Langmuir isotherm onto these surfaces. Furthermore, the Sips model data show a significant amount of adsorption capacities on CaO/S with low values for *Ks*.

The *n* parameter of Sips isotherm and the correlation coefficients (r^2) values that tabulated in Table 1 reveal that the adsorption of Indigo carmin follow the langmuir isotherm, and best fit adsorption shown onto CaO modified S and N. The results show a significant amount of adsorption capacities on S/CaO.

The isotherm parameters of Acid fuchsin dye show the *n* parameter of Sips isotherm is 1 and the best fit values of correlation coefficients (r^2), onto CaO modified N, indicating that the adsorption of the acid fuchsin is strongly followed the Langmuir isotherm onto this surface.

These results indicate that adsorption that changes surface charge and crystallinity depends on the strong affinity attraction between molecular dyes and applied adsorbents [27].

3.4 Kinetic Studies

The adsorption kinetic behavior of dyes onto S, N and O modified CaO were carried out at 25 ^oC. A known concentrations of dye were prepared in 25 ml H_2O; NG (40 mg/L), AR (400 mg/L), IC (120 mg/L) and AF (120 mg/L), and constant amount of adsorbent (0.1 g). The measurements were carried out at different times intervals; (5, 10, 15 and 30 min) for NG, (30, 60, 90 and 120 min) for AR, (5, 10, 15, 30, 60 and 90 min) for IC, and (3, 5, 10 and 15 min) for AF. A plot of the adsorption capacity (q_t) versus time is shown in Fig 6. The results show that for S/CaO, adsorption of NG and IC are initially very faster and reached to the maximum value after 30 and 20 minutes, respectively. Interestingly, the results that observed for AF dye onto S/CaO and O/CaO, the adsorption reaches to the maximum after only four minutes with q_t amounts of 580 and 600 $mg/g_{ads.}$ of S/CaO and O/CaO, respectively.

The kinetic data were analyzed using the most common models, that of pseudo first order and pseudo second order [28]. The first-order rate equation (7) is one of the most widely used for the sorption of solute from a liquid solution that describes the variation of adsorbed concentration with respect to the time, as follows:

$$ln\left(\frac{q_e-q_t}{q_e}\right) = -K_1 t \quad (7)$$

Where,

q_e is the equilibrium value of q_t (mg/g) and K_1 (min^{-1}) is the rate constants of pseudo first order model. A plot of q_e - q_t versus *t* (min.) gives a linear line, where the correlation coefficient (r^2) determined and the K_1 and q_t calculated from the slope and the intercept.

Table 1. Adsorption isotherm parameters of dyes onto S/CaO, N/CaO and O/CaO

Dye	Langmuir								
	S/CaO			N/CaO			O/CaO		
	K_L	q_m	r^2	K_L	q_m	r^2	K_L	q_m	r^2
Nigrosin	0.5318	59.88	0.9969	0.0192	102.04	0.9602	0.2071	57.471	0.9951
Alizarin	0.0038	5000	0.9067	0.0048	769.23	0.9933	0.0007	1111.1	0.8434
Indigo	0.0177	769.23	0.9631	0.0218	59.524	0.9762	0.0565	188.68	0.9968
Acid Fuchsin	1.667	1000	0.887	0.035	5000	0.93	8.00	625	0.814

Dye	Freundlich								
	S/CaO			N/CaO			O/CaO		
	K_F	n	r^2	K_F	n	r^2	K_F	n	r^2
Nigrosin	23.552	3.3715	0.7752	2.7273	1.2952	0.9973	14.062	2.5094	0.9296
Alizarin	24.582	1.1326	0.999	11.922	1.5352	0.9794	1.2589	1.8804	0.9983
Indigo	15.258	1.1476	0.9971	3.5417	1.8339	0.9902	29.338	2.5056	0.9953
Acid Fuchsin	685.3	1.675	0.982	144.5	1.065	0.999	217.3	1.304	0.998

Dye	Sips											
	S/CaO				N/CaO				O/CaO			
	K_S	q_m	n	r^2	K_S	q_m	n	r^2	K_S	q_m	n	r^2
Nigrosin	0.2446	54.945	0.45	0.9995	0.0213	94.34	0.999	0.9993	0.1766	60.241	0.999	0.9954
Alizarin	0.0058	3333.3	0.999	0.9984	0.0027	666.67	0.84	0.9999	0.0047	769.23	0.999	0.9965
Indigo	0.0162	833.33	0.999	0.9998	0.028	52.356	0.999	0.978	0.0555	169.49	0.999	0.9895
Acid Fuchsin	3.5	714.3	0.999	0.952	0.029	5000	0.999	1.00	1.00	1667	0.999	0.995

The model of pseudo-second-order model equation (8) shows the rate based on the sorption equilibrium capacity in the adsorbent and not on the concentration of the adsorbate [29].

$$\frac{t}{q_t} = \frac{1}{K_2\, {q_e}^2} + \frac{t}{q_e} \quad (8)$$

Where,

K_2 is the pseudo second order model. A plot of t/q_t versus t (min.) gives a linear line. The results fitting the Equations (7) and (8) are listed in Table 2.

Based on the obtained correlation coefficient values r^2 as well as the experimental and calculated values of q_e, the adsorption kinetics was determined, depending on whether the experimental q_e is consistent with the calculated q_e that obtained from the pseudo-first-order model or with the calculated q_e that obtained from the pseudo-second-order model.

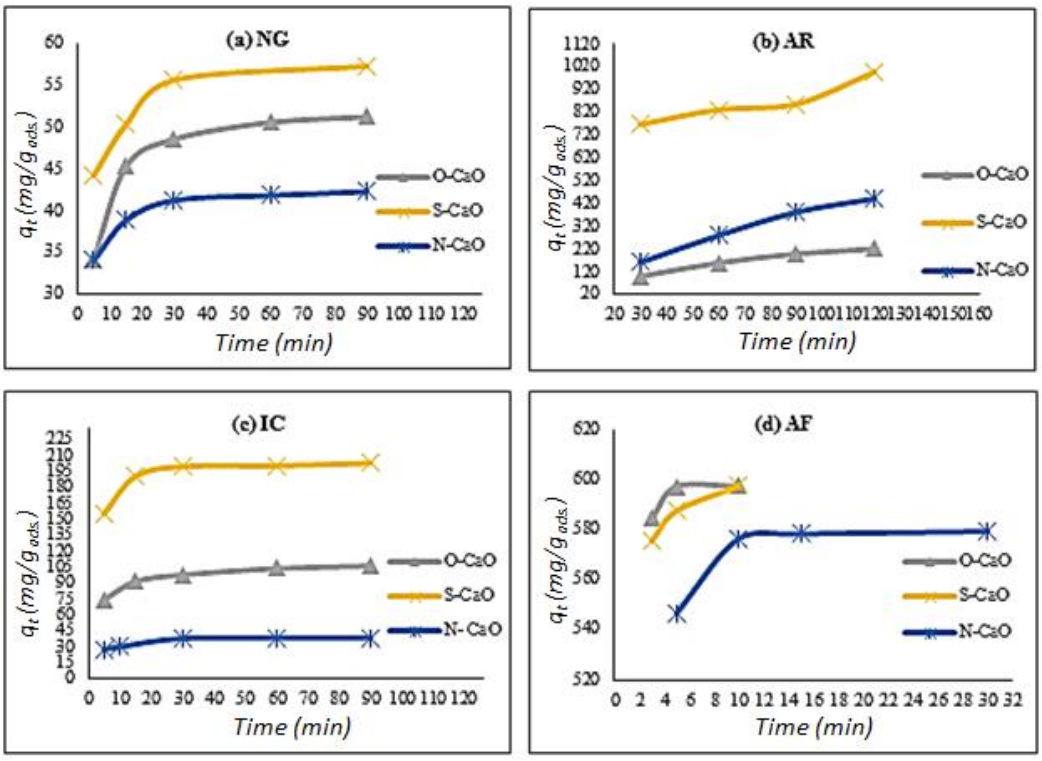


Fig. 4. Adsorption of (a) NG, (b) AR, (c) IC, and (d) AF as a function of time

Table 2. The obtained constants of adsorption kinetic models

Dye	Adsorbent		Pseudo first order			Pseudo second order		
		q_e (exp.) (mg/g)	q_e (Cal.) (mg/g)	K_1 (min^{-1})	r^2	q_e (Cal.)(mg/g)	K_2 (min^{-1})	r^2
Nigrosin	S/CaO	55.7024	18.617	0.0895	0.984	59.172	0.0078	0.998
	N/CaO	41.272	13.166	0.1154	0.998	43.29	0.0148	0.999
	O/CaO	48.6041	23.674	0.1123	0.961	534.76	0.0006	0.999
Alizarin	S/CaO	222.015	338.83	0.0428	0.989	909.09	0.0002	1.00
	N/CaO	129.271	401.29	0.0086	0.998	555.56	1E-05	0.979
	O/CaO	59.6515	209.75	0.0212	0.894	400	3E-05	0.997
Indigo	S/CaO	202.885	129.28	0.1813	0.989	212.77	0.0024	0.999
	N/CaO	62.8594	14.998	0.0534	0.846	42.194	0.0057	0.980
	O/CaO	106.41	50.411	0.1406	0.991	105.26	0.0043	0.999
Acid Fuchsin	S/CaO	499.91	3.0756	6.196	1.00	909.09	0.0003	0.987
	N/CaO	481.71	553.13	0.574	1.00	588.24	0.0041	1.00
	O/CaO	498.84	490.73	1.21	1.00	500	0.02	1.00

Accordingly, the results recorded in Table 2 reveal that the pseudo-first-order model describes the adsorption of the alizarin dye, whereas, the experimental q_e is mostly consistent with the calculated q_e that obtained from the pseudo-first-order model.

From the other hand, the pseudo-second-order model describes the adsorption of the Nigrosin, Indigo and Acid fuchsin, whereas, the experimental q_e is mostly consistent with the calculated q_e that obtained from the pseudo-second-order model.

3.5 Thermodynamic Functions of Adsorption Process

The effect of temperature on the distribution coefficient values of the dyes was studied at a constant dye concentration of NG (50 mg/l), AR (400 mg/l) and, IC as well as AF (100 mg/l) in (25 ml). Temperature effect on sorption processes was analyzed by Van't Hoff plots, based on equation (9), [30].

$$ln\ Kd = (\Delta S°)/R - (\Delta H°)/RT \quad (9)$$

Where *Kd* is the distribution coefficient ($Kd = q_e/Ce$) , T is the absolute temperature, ΔS^o is the entropy change (J/mol), and ΔH^o is the enthalpy change (kJ/mol). ΔG^o values were computed for each temperature by the Helmholtz relations (10 and 11), [31].

$$\Delta G^o = -RT\ ln\ Kd \quad (10)$$
$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (11)$$

Thermodynamic functions ΔG^o, ΔH^o, and ΔS^o calculated from the above equations are shown in Fig. 5, and listed in Table 3.

The results revealed that the adsorption process has positive values of ΔH^o and ΔS^o for all the dyes on all the adsorbents, indicating the endothermic process and the increase in the disorder and randomness at the solid-solution interface during the adsorption of the dyes on the adsorbent surface, the negative values of $\Delta G°$ indicates the spontaneous nature of adsorption [32,33]. As the temperature increases, the $\Delta G°$ values increases, indicating the more driving force and hence resulting in greater adsorption capacity at higher temperatures.

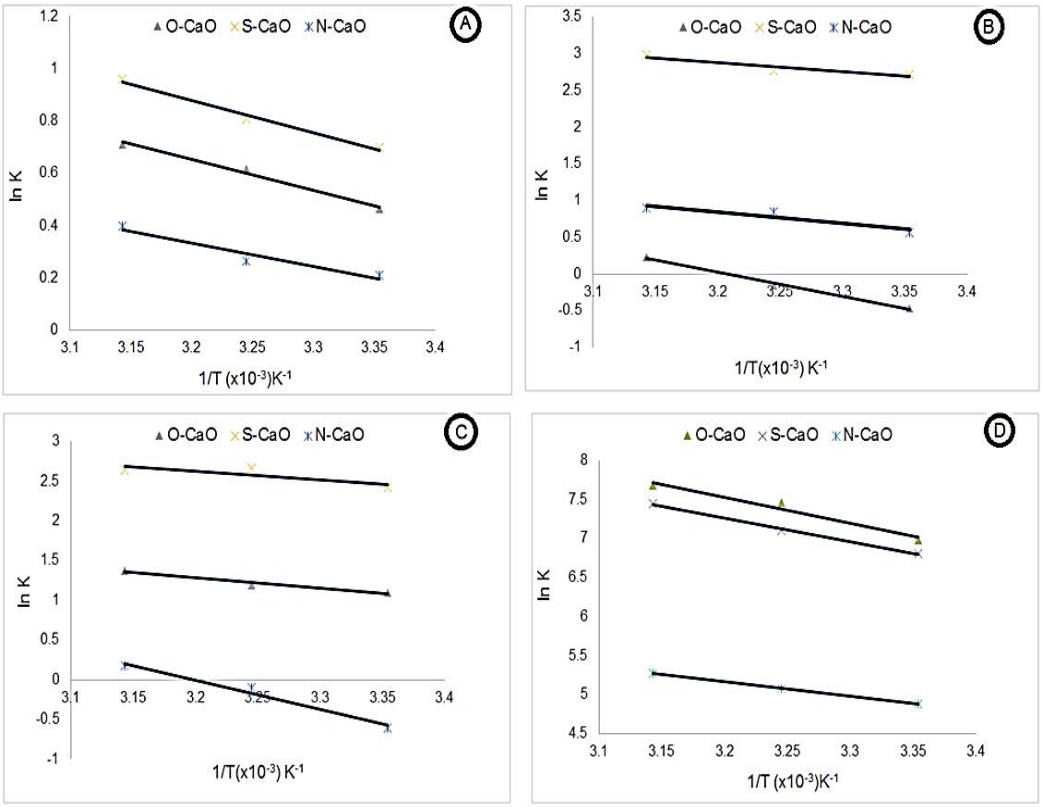


Fig. 5. ln K vs. 1/T for adsorption of (A) Nigrosin (B) Alizarin Red S (C) Indigo carmin and (D) Acid Fuchsin dye on adsorbents surface

Table 3. Thermodynamic functions of adsorption of Nigrosin, of Alizarin Red S, Indigo carmin and Acid Fuchsin on CaO and modified CaO surface

Dyes	Adsorbent	ΔG(KJ.mol^{-1})			ΔH (KJ.mol^{-1})	ΔS (J.mol^{-1})
		298.15K	308.15K	318.15K		
Nigrosin	S/CaO	-1.729975	-2.063197	-2.53353	10.22622	40.029416
	N/CaO	- 0.51787	- 0.67274	-1.053218	7.4253165	26.523323
	O/CaO	-1.150341	-1.577059	-1.87932	9.7373568	36.583263
Alizarin Red S	S/CaO	- 6.73695	-7.094257	-7.887014	10.335133	57.032377
	N/CaO	-1.407435	-2.158122	-2.376744	13.131132	49.04096
	O/CaO	1.165054	0.4001172	- 0.603429	27.48941	88.16997
Indigo carmin	S/CaO	-5.985116	- 6.810849	- 6.982067	8.9857712	50.55494
	N/CaO	1.5018916	0.2753157	- 0.455475	30.763463	98.404504
	O/CaO	-2.717435	-3.054855	-3.631122	10.863072	45.425202
Acid Fuchsin	S/CaO	-16.87447	-18.19932	-19.68303	24.966942	140.25718
	N/CaO	-12.0983	-13.01639	-13.93215	15.239562	91.695106
	O/CaO	-17.30523	-19.09424	-20.30565	27.51934	150.64137

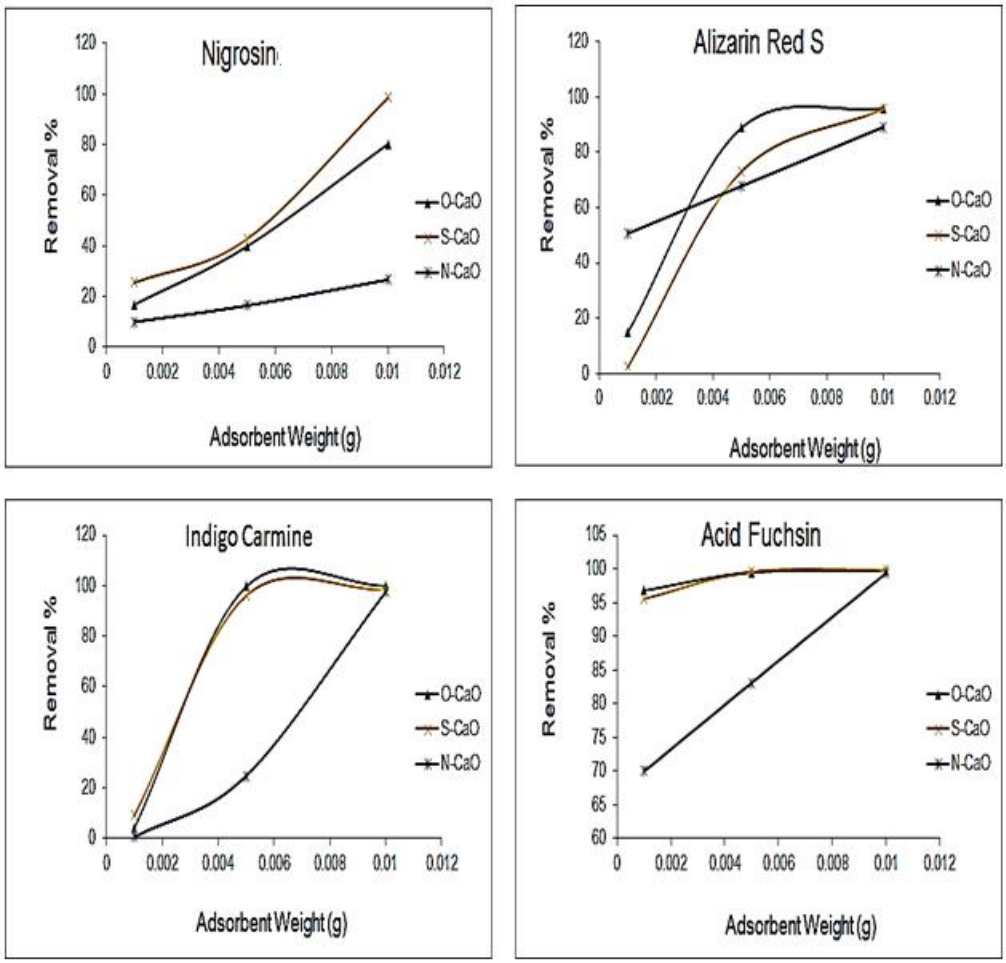


Fig. 6. Relationship removal percentage of dyes(a) Nigrosin (b) Alizarin red S (c) Indigo carmine and (c) Acid fuchsin onto S, N and O/CaO after exposed to sunlight

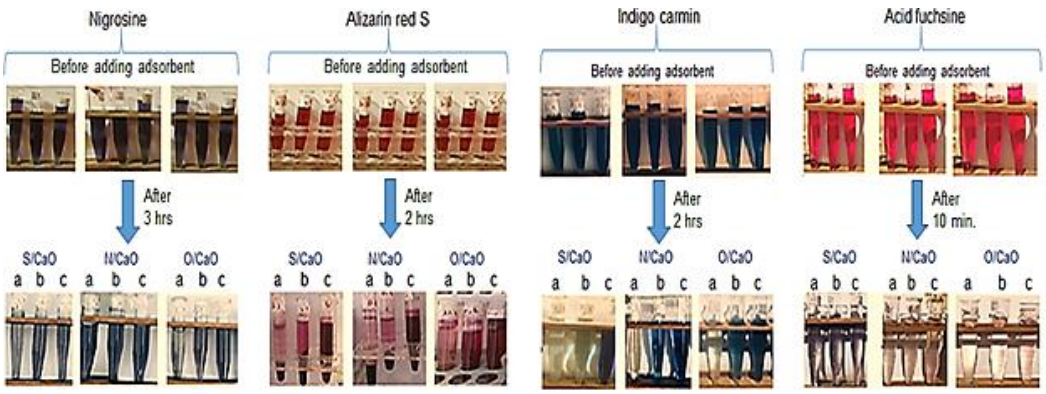


Fig. 7. Color changes of dyes onto 0.01 g (a), 0.005 g (b) and 0.001 g (c) of S/CaO, N/CaO and O/CaO before and after exposed to sunlight

3.6 Photoactivity of S/CaO, N/CaO and O/CaO

The photoactivity was investigated by contact a constant amount of dyes; NG (50 mg/L), AR (400 mg/L), IC (100 mg/L), and AF (120 mg/L) to different amounts (0.001g, 0.005g and 0.01g) of adsorbents. The suspensions were brought in 10 ml tubes. The tubes were closed and well shaking, then exposed to sunlight at different times. The separated aquatic sample was analyzed by UV-Visible technique to determine the residual concentration of the dye using equation (1). The removal percentage and the photocatalytic decomposition of the studied dyes on modified CaO are shown in Figs. 6 and 7, respectively.

The S/CaO showed a strong photocatalytic activity. Only 0.01 g from it, removes 98.5611% of the Nigrosin dye through 180 min. as well as, 0.01g of O/CaO removes 80.2877% of Nigrosin after 180 min. under the sunlight.

The removal percentage on 0.01 g of S/CaO, O/CaO, and N/CaO reaches to 95.5981, 95.9367 and 89.1083% of Alizarin Red S after 120 min. under the sunlight.

Interestingly, the photocatalytic ability shown for the modified surfaces of 0.001g of O/CaO and S/CaO removes 96.7770, 95.5574% of Acid fuchsin after 10 min, respectively under the sunlight.

The exposure of adsorbent to sunlight will increase the negative nature of the surface that may be due to the formation of the free radicals, thus, a very amount (0.001 g) of all the adsorbents removes more than 95% of Acid fuchsin dye because the presence of three NH_2 groups in its structure, which increase the interaction and then adsorption on the adsorbents surfaces. The presence of two NH_2 and one NH_2 on Indigo and Nigrosin make them less adsorption compared to Acid fuchsin.

4. CONCLUSION

Modified CaO with S, N and O surfaces were used to remove the dyes of Nigrosin, Alizarin, Indigo, and Acid fuchsin from aqueous solutions. The results revealed high adsorption efficiency and high ability removal capacity of treatment the anionic dyes. The equilibrium obeys the Sips isotherm. Therefore, it can be concluded that CaO modified S, N and O provide a heterogeneous surface for adsorption of dyes. The kinetic results revealed that the pseudo-first-order model describes the adsorption of the alizarin dye, whereas, the pseudo-second-order model describes the adsorption of the Nigrosin, Indigo and Acid fuchsin. The calculations of ΔH^o and ΔG^o indicate that the adsorption of dyes is endothermic and spontaneous. The study displayed that the modified adsorbents are good potency photocatalysts.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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