EurJChem An International Open Access Journal
European Journal of Chemistry
ATLANTA PUBLISHING HOUSE

Check for updates

View Journal Online
View Article Online

Investigation of nigrosine, alizarin, indigo and acid fuchsin removal by modification of CaO derived from eggshell with AgI: Adsorption, kinetic and photocatalytic studies

Ibtighaa Kadhim Radhi, Mouayed Abdulaali Hussein * and Zaki Naser Kadhim

Department of Chemistry, College of Science, University of Basrah, Basrah, 61001, Iraq
ibka7272@yahoo.com (I.K.R.), mouayed_505emar@yahoo.com (M.A.H.), zekinasser99@yahoo.com (Z.N.K.)

* *Corresponding author at: Department of Chemistry, College of Science, University of Basrah, Basrah, 61001, Iraq.*
Tel: +964.40.7727866427 Fax: +964.40.7727866427 e-mail: mouayed_505emar@yahoo.com (M.A. Hussein).

RESEARCH ARTICLE

10.5155/eurjchem.10.1.64-71.1820

Received: 24November 2018
Received in revised form: 22 December 2018
Accepted: 26 December 2018
Published online: 31 March 2019
Printed: 31 March 2019

KEYWORDS

SEM
TEM
Kinetics
Adsorption
Modification
Photocatalytic

ABSTRACT

Successful removal of nigrosine, alizarin, indigo and acid fuchsin dyes from aqueous solutions using modified CaO nanoparticles has been investigated. The CaO was obtained from eggshells and modified with AgI. The adsorbents were characterized using X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy and transmission electron microscopy. The kinetic studies were also investigated, the results showed that the adsorption of alizarin dye follows the pseudo-first-order model, while the adsorption of the nigrosine, indigo, and acid fuchsin follow the pseudo-second-order model onto modified and unmodified CaO. Moreover, the photocatalytic activity of modified adsorbent was tested under sunlight. The modified adsorbent showed a strong photocatalytic activity, a 0.01 g modified adsorbent was sufficient to absorb 100% of acid fuchsin through only 5 min after exposes to sunlight.

Cite this: *Eur. J. Chem.* **2019**, *10(1)*, 64-71 **Journal website**: www.eurjchem.com

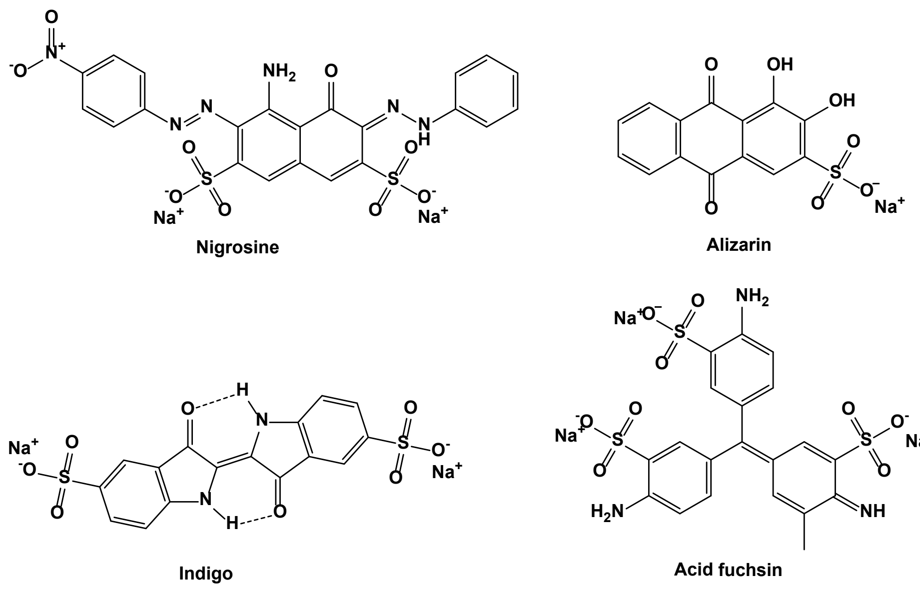
1. Introduction

Dyes extensively used in many industries, such as textiles, papers, rubbers, plastics and cosmetics as well as in the dying and food [1-3]. Dye pollutants from these industries are an important source of environmental pollution [4,5]. More than 7×10^5 tons of synthetic textile dye and other industrial dyes are produced annually [6,7] and, because their high solubility, toxicity and non-biodegradability, dyes are influent source of water pollutants [8]. The removal of dyes from wastewater has been considered much attention by many researchers [9,10]. Many of chemical and biological methods including flocculation [11], ozonation [12], coagulation [13], and adsorption [14] have been used to remove dye pollutants. Adsorption is one of the most effective and comparatively simple and low cost method [15,16]. Despite the activated carbon is one of effective adsorbents for many of pollutants, it is expensive, time consuming and complicated to prepare. Therefore, many attempts have been conducted to improve the cheaper and effective adsorbents for removal of dyes from wastewater [17,18].

Some studies have been reported that the modification of adsorbent surface improves of adsorption efficiency [19-21]. 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 [22,23].

Eggshells are waste material discarded from domestic sources. Composition of the eggshells have been found as 94% $CaCO_3$, 1% $MgCO_3$, 1% $Ca_3(PO_4)_2$, and approximately 4% of organic matter [24]. They have porous quality that makes it an interesting adsorbent [25]. In the present study, we reported the preparation of CaO from eggshell modified with AgI to investigate of its adsorption efficiency and photocatalytic activity towards the dyes of nigrosine, alizarin, indigo and acid fuchsin. Scheme 1 shows the chemical structures of the four studied dyes.

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
http://dx.doi.org/10.5155/eurjchem.10.1.64-71.1820



Scheme 1. Chemical structures of dyes.

2. Experimental

2.1. Adsorbate

We used the dyes manufactured by Sigma-Aldrich. Stock solutions were prepared by dissolving accurately weighted amounts of dyes in distilled water and we can obtain any desired concentrations of dye solutions through successive solutions.

2.2. Adsorbent

Calcium oxide was prepared using eggshells, which were collected from domestic places. Eggshells were carefully washed, boiled for 2 h, separated the interior membrane, and dried at 120 °C for 2 h, then crushed, sieved and, calcined at 700 °C for 4 h. AgI/CaO containing Ag 5%wt was prepared by deposition-precipitation method. Briefly, 1.000 g of CaO and 0.296 g of KI were dissolved in 100 mL of H_2O and 1.000 g of CaO was added to this solution, then 0.1515 g of $AgNO_3$ in 1.15 mL of NH_4OH (25 wt% NH_3) was added to the mixture rapidly. The suspension was stirred for 12 h at room temperature. The product was filtered, washed with water, and then dried at 80 °C. The obtained white powder is AgI/CaO nanoparticle.

2.3. Adsorption studies

The residual concentration of dyes have been measured using UV-Visible spectrophotometer (PG Instrument T80) at 573, 520, 610 and 569 nm for nigrosine, alizarin, indigo, and acid fuchsin, respectively. Adsorptive removal of dyes from aqueous solution by AgI/CaO, where 25 mL of dye solution of known initial concentration C_0 (Nigrosine: 0.040 g/L, alizarin: 0.400 g/L, indigo: 0.100 g/L and acid fuchsin: 0.005 g/L) and known amount of adsorbent (0.01 g) were used. The solutions were then shaken at 200 rpm for 24 h at room temperature. The suspensions were then centrifuged and the equilibrium concentration for each dye using UV-Visible spectrophotometer. The amount of adsorbed dye per unit mass of adsorbent (mg/g) at any time (q_t) and at equilibrium (q_e) was calculated using Equations (1) and (2).

$$q_t = \left(C_o - C_t\right) / mv \quad (1)$$

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

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).

$$R\% = \frac{A_o - A}{A_o} 100 \quad (3)$$

where A_o is the initial absorbance of samples.

3. Results and discussion

3.1. XRD and EDX measurements

X-ray diffraction (XRD) patterns of CaO and AgI/CaO adsorbents, shown in Figure 1. The patterns show new peaks are emerged obviously indicate the formation of AgI over CaO. The formation of AgI/CaO has been supported by energy dispersive X-ray spectroscopy (EDX) analysis was clearly assigned to the doping species as shown in Figure 2.

3.2. SEM analysis

The morphology of CaO and AgI/CaO measured by scanning electron microscopy (SEM) are given in Figure 3. SEM visual data of AgI/CaO show totally different morphology that for CaO. Interestingly, the agglomerate surface structure of CaO changes to papillae surface structure when modified with AgI, providing a very large surface area. The SEM image of the papillae surface structure is not familiar and it is rarely obtained by chemical synthesis. Studies reported this structure using SEM images in plants and insects of which called superhydrophobic surface [26].

3.3. TEM analysis

The transmission electron microscopy (TEM) nano-composite images of the AgI-modified CaO are shown in Figure 4. The images reveal the embedded the AgI and CaO (Figure 5a).

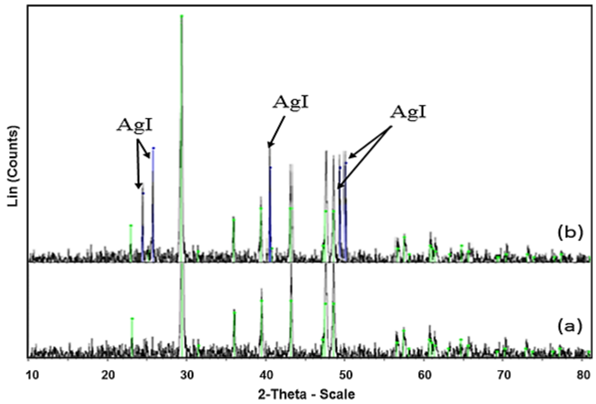


Figure 1. XRD patterns (a) CaO and (b) AgI/CaO.

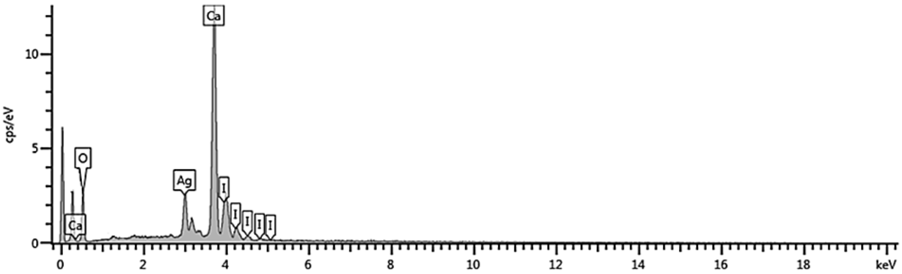


Figure 2. EDX analysis of AgI/CaO.

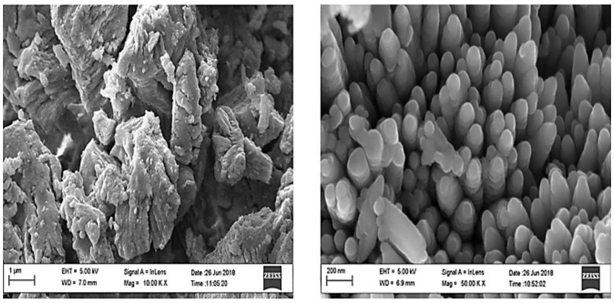


Figure 3. SEM images of CaO (left) and AgI/CaO (right).

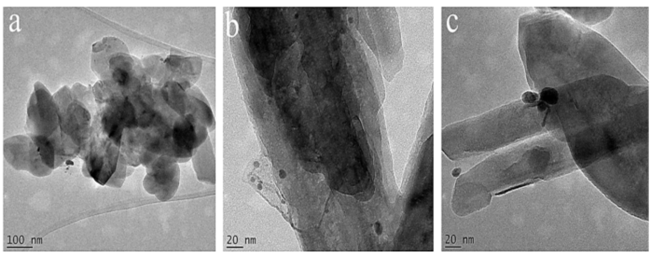


Figure 4. TEM images of AgI/CaO in different formations a, b and c.

A layer of AgI is surrounding the CaO, with shaped like a pit (Figure 5b). Moreover, the TEM nanocomposite images of AgI/CaO had a good degree of crystallinity (Figure 5c).

3.4. Equilibrium studies

Equilibrium data were applied using the Langmuir, Freundlich and Sips adsorption isotherms to design the basic of adsorption systems and optimizing the use of adsorbents. The Langmuir isotherm has been usually used for many adsorpion systems of homogeneous surfaces. It can be expressed using Equation (4).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

where C_e 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.

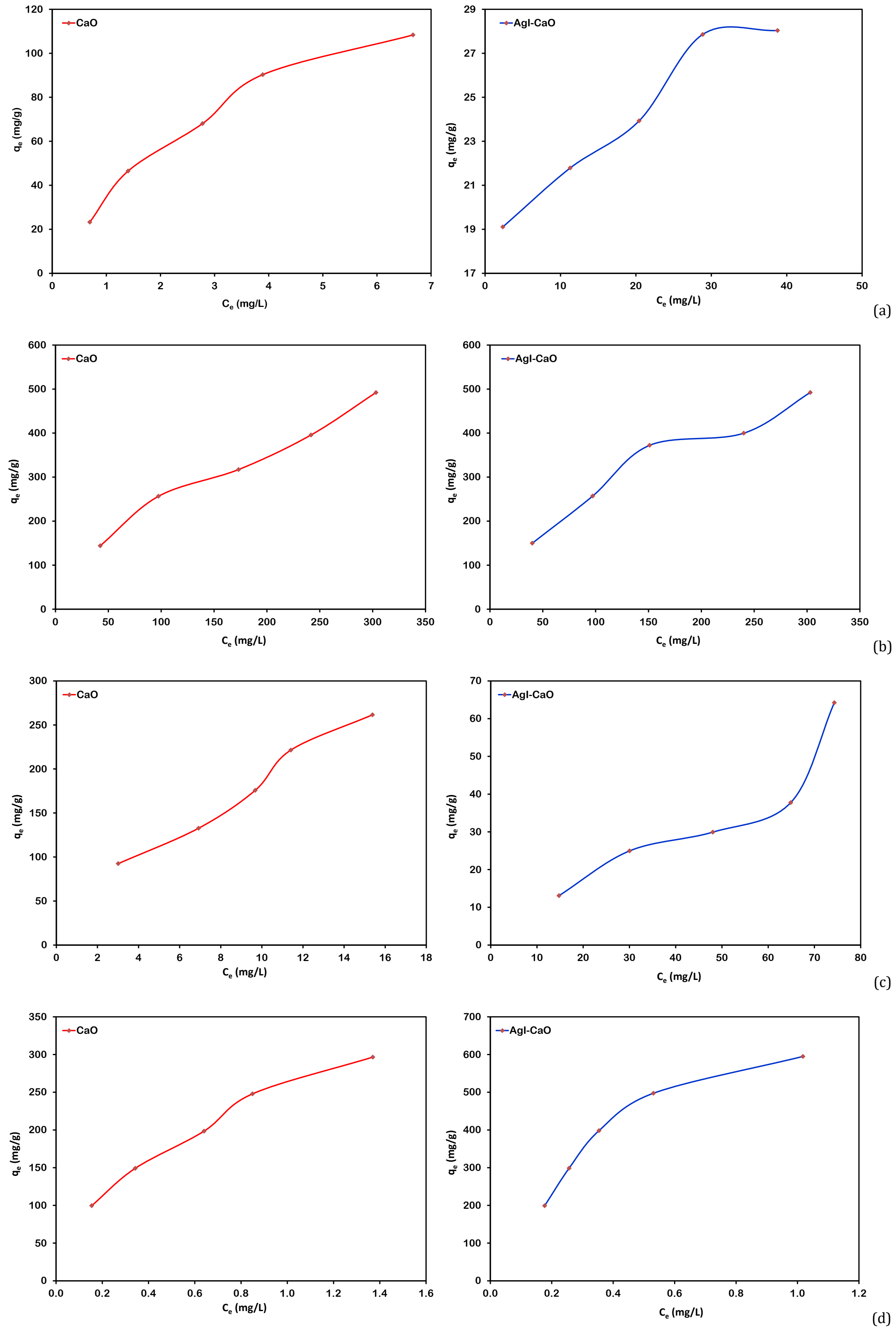


Figure 5. Equilibrium data onto CaO and AgI/CaO of nigrosine (a), alizarin (b), indigo (c) and acid fuchsin (d).

The Freundlich isotherm is valid for heterogeneous surfaces, and it follows the Equation (5).

$$q_e = K_F \times C_e^{1/n} \tag{5}$$

where K_F and n are the Freundlich constants concerning the capacity and intensity of adsorption, respectively. In contrast to the Langmuir model, the Freundlich model provides no information about the monolayer adsorption capacity.

Table 1. Adsorption isotherm constants of dyes onto CaO and AgI/CaO.

Dye	Langmuir							
	CaO				AgI-CaO			
	K_L	q_m		r^2	K_L	q_m		r^2
Nigrosine	0.2170	185.18		0.977	0.3380	29.760		0.988
Alizarin	0.0049	769.23		0.919	0.0062	714.280		0.955
Indigo	0.0580	526.31		0.741	0.0144	76.923		0.937
Acid Fuchsin	1.7140	416.66		0.974	1.6660	1.000		0.947
	Freundlich							
	CaO				AgI-CaO			
	K_F		n	r^2	K_F		n	r^2
Nigrosine	33.082		1.46	0.972	16.42		7.10	0.905
Alizarin	15.980		1.69	0.986	18.46		1.73	0.976
Indigo	42.540		1.54	0.960	1.312		1.18	0.913
Acid Fuchsin	256.870		1.97	0.995	663.740		1.63	0.917
	Sips							
	CaO				AgI-CaO			
	K_S	q_m	n	r^2	K_S	q_m	n	r^2
Nigrosine	0.1750	217.390	0.990	0.993	0.9900	0.163	0.001	0.930
Alizarin	0.0078	1250.000	0.750	0.992	0.0081	1111.110	0.800	0.990
Indigo	0.9960	0.224	0.001	0.988	0.0110	158.730	0.100	0.971
Acid Fuchsin	0.0220	11111.110	0.500	0.997	1.0000	1428.570	0.990	0.970

The Langmuir-Freundlich (Sips) isotherm, is a combination of the Langmuir and Freundlich isotherms, and it can follow the Equation (6) [27].

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

where K_s (L/mg) is the adsorption Sips constant. Sips model is valid for topical adsorption without adsorbate-adsorbate interaction, proper for predicting the adsorption on the heterogeneous surfaces and characterized by the dimensionless heterogeneity factor, n, which describes the system's heterogeneity between 0 and 1 [28]. When the value of n is equal to 1, the Equation (6) becomes a Langmuir equation, also when C_e approaches to 0, the Sips isotherm effectively reduces to Freundlich isotherm [29]. The adsorption data using the above three isotherms are provided in supplementary materials (Figures S1-3).

The equilibrium data of dyes onto CaO and AgI/CaO are shown in Figure 5. The correlation coefficients and the constants of Langmuir, Freundlich and Sips isotherm models are provided in Table 1. The data display that the amount of adsorbent species (q_0) increases as the dye concentration (C_0) increases. The experimental data of the three above stated equilibrium isotherms that the Sips (Freundlich-Langmuir) isotherm model provided the highest correlation coefficients (r^2) values for modified and unmodified CaO. Sips isotherm model gives an a good idea about which isotherm the adsorption is follow, depend 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 predict the Langmuir monolayer adsorption chracteristic. Therefore, the adsorption of the dyes follows the Freundlich isotherm except of the adsorption of the nigrosine and acid fuchsin that follows the Langmuir isotherm onto CaO and AgI/CaO, respectively. Moreover, the Sips model data show a significant amount of adsorption capacities for acid fuchsin and indigo having the lowest Sips constants K_s on CaO and AgI/CaO, respectively. These results indicate that adsorption through changed surface charge and crystallinity depends on the strong affinity attraction between molecular dyes and applied adsorbents.

3.5. Kinetic studies

The adsorption kinetic of the dyes were also studied. The results shown in Figure 6 display different kinetic behaviour of adsorption onto AgI/CaO and CaO. The adsorption of alizarin and acid fuchsin is faster on AgI/CaO than CaO. During the period of 30 to 60 min, the adsorbed amount q_t of alizarin dye on AgI/CaO is about 60 mg/g compared to 50 mg/g on CaO, and after 2 h the maximum adsorption capacity on AgI/CaO is higher than on CaO. Whereas, during the period of 5 to 10 min, the adsorbed amount of acid fuchsin dye is about 5 mg/g and 3 mg/g on AgI/CaO and CaO, respectively. The modified surface need only a quarter an hour to adsorb 498 mg/g of acid fuchsin compared to 248 mg/g on unmodified surface at the same time.

On the hand, the results show that the adsorption of indigo dye is faster on CaO than on AgI/CaO. Whereas, no main difference was observed for the adsorption of nigrosine on AgI/CaO and CaO.

The kinetic data (Supplementary materials, Figures S4 and 5) were analyzed using the most common equations of pseudo first order and pseudo second order models [30]. The linear forms of two models follow the Equations (7) and (8).

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

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

where q_e is the equilibrium value of q_t, K_1 and K_2 are the rate constants of pseudo first order model and pseudo second order model, respectively. The results fitting the Equations (7) and (8) are listed in Table 2. Based on the experimental and calculated values of q_e and, the obtained correlation coefficient values r^2, the results show that the pseudo-first-order model describes the adsorption of the alizarin dye, while the pseudo-second-order model describes the adsorption of the nigrosine, indigo and acid fuchsin, onto modified and unmodified CaO.

3.6. Photoactivity of AgI/CaO

The photoactivity of AgI/CaO was investigated by contact a constant amount of dye, nigrosine (8.1104×10^{-6} mM), alizarin (1.4608×10^{-5} mM), indigo (1.072×10^{-5} mM) and, acid fuchsin (8.5391×10^{-6} mM), and different amounts of 0.001, 0.005 and 0.010 g of photocatalyst of AgI/CaO. The suspensions were brought in 10 mL, shaken at room temperature, stirred under dark conditions for 10 h to reach the adsorption equilibrium, and then exposed to sunlight at different times. The suspension was centrifuged and the separated aquatic sample was analyzed by UV-Visible technique to determine the residual concentration of the dye using Equation (3).

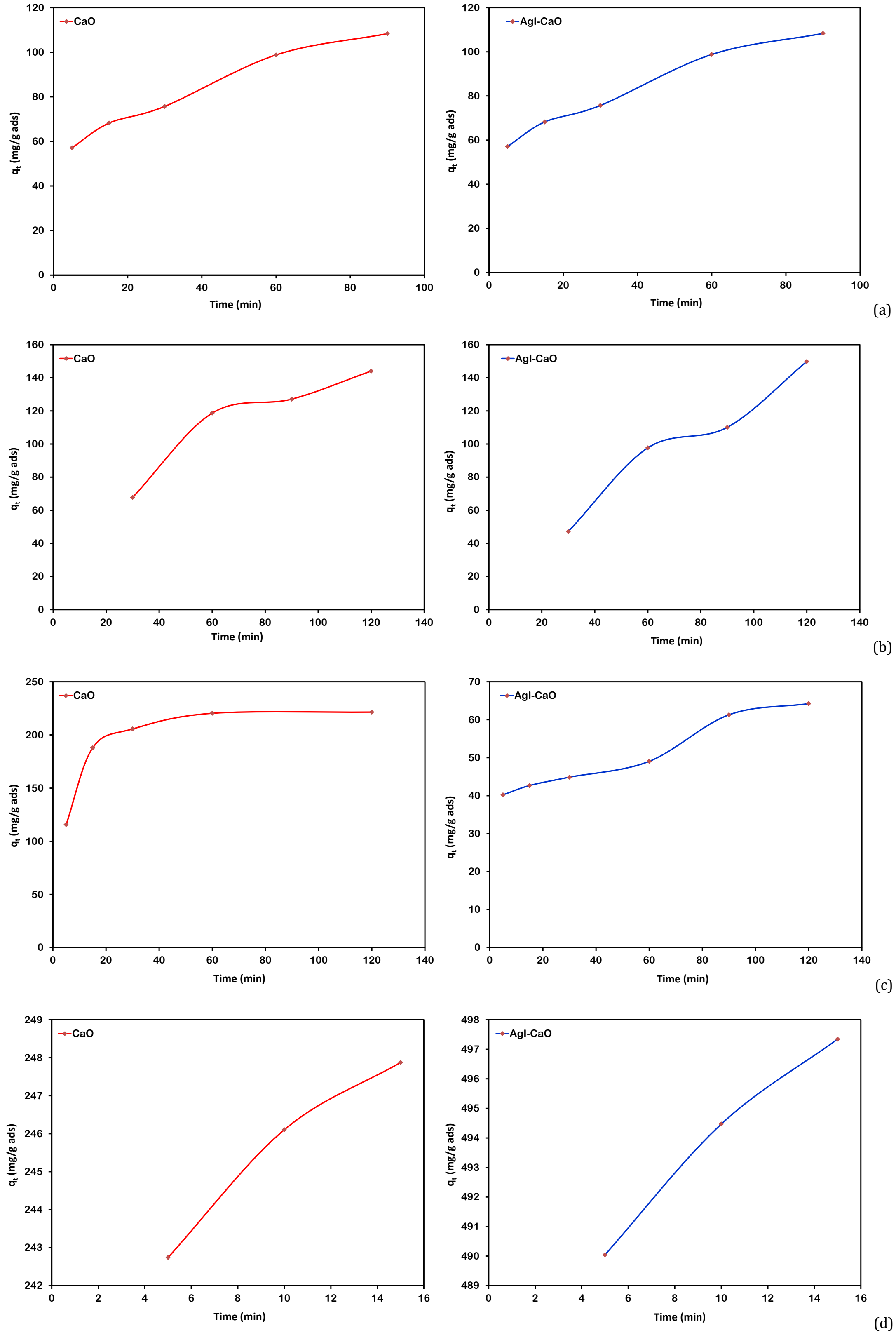


Figure 6. Adsorption kinetic data of dyes onto CaO and AgI/CaO of nigrosine (a), alizarin (b), indigo (c) and acid fuchsin (d).

The photocatalytic decomposition of studied dyes on AgI-modified CaO and removal percentage shown in Figure 7. AgI-modified CaO shows a strong photocatalytic activity toward the adsorption of the acid fuchsin dye. The removal percentage reaches 100% onto 0.01 g of AgI/CaO through only 5 min as shown in Figure 8.

Table 2. The obtained constants of adsorption kinetic models.

Dye	Adsorbent	q_e (exp.) (mg/g)	Pseudo first order			Pseudo second order		
			q_e (Cal.) (mg/g)	K_1 (min^{-1})	r^2	q_e (Cal.) (mg/g)	K_2 (min^{-1})	r^2
Nigrosine	CaO	108.333	65.484	0.0305	0.9602	117.647	83.142×10^{-5}	0.9851
	AgI/CaO	28.0357	16.542	0.0144	0.7388	30.0300	216.580×10^{-5}	0.9427
Alizarin	CaO	144.068	144.142	0.0251	0.9339	217.391	7.587×10^{-5}	0.9663
	AgI/CaO	149.834	154.208	0.0158	0.9427	434.783	0.975×10^{-5}	0.7116
Indigo	CaO	221.474	143.610	0.0801	0.9899	227.273	118.773×10^{-5}	0.9996
	AgI/CaO	64.242	36.503	0.0394	0.9403	67.114	140.959×10^{-5}	0.9710
Acid Fuchsin	CaO	247.880	14.890	0.2129	1.0000	250.000	2285.714×10^{-5}	1.0000
	AgI/CaO	497.345	18.534	0.1863	1.0000	500.000	2000.000×10^{-5}	1.0000

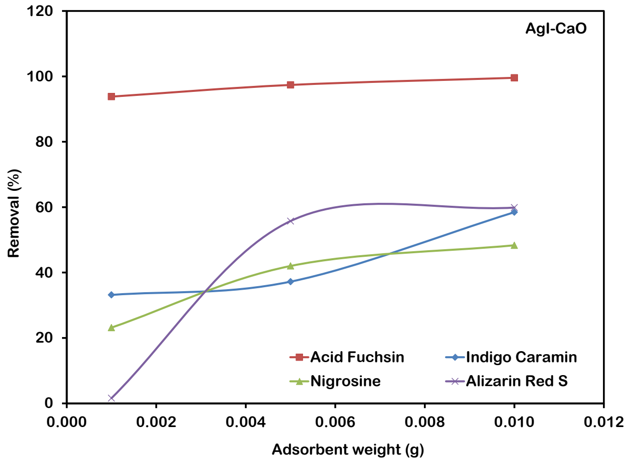


Figure 7. Removal percentage of dyes onto AgI/CaO after exposed to sunlight.

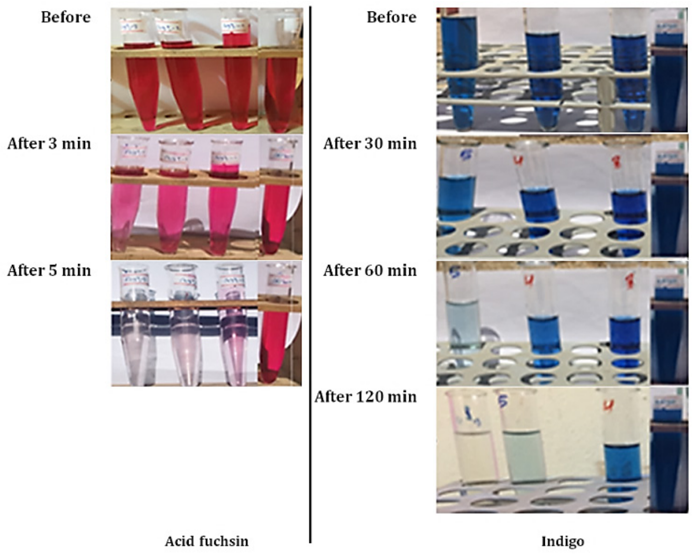


Figure 8. Color changes of acid fuchsin (A) and indigo (B) onto AgI/CaO before and after they exposed to sunlight at different times.

4. Conclusions

The results show that CaO modified AgI is efficient adsorbent for removal of acid fuchsin and alizarin dyes from aqueous solutions, and due to the higher capacity, it can be used in wastewater treatment. The presence of three anionic groups of SO_3^-, as well as the different structure of acid fuchsin compared to other dyes which represent three phenyl groups connected with a central carbon helps it to rotate in consequently increases the chance of the dye adsorption on the positive, high surface area of the modified adsorbent. The equilibrium obeys the Sips isotherm. Therefore, it can be concluded that both CaO and AgI/CaO provide a heterogeneous surface for adsorption of dyes. The results show that the modified adsorbent is a strong solar photocatalyst.

Supporting information

Electronic supplementary information (ESI) available: The online version of this article contains supplementary material, which is available to authorized users. Langmuir, Freundlich and Sips isotherms onto CaO and AgI/CaO of nigrosine (A), alizarin (B), indigo (C) and acid fuchsin (D). Pseudo-first order and Pseudo-second order kinetics onto CaO and AgI/CaO of nigrosine (A), alizarin (B), indigo (C) and acid fuchsin (D).

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

ORCID

Ibtighaa Kadhim Radhi
http://orcid.org/0000-0002-1424-8811
Mouayed Abdulaali Hussein
http://orcid.org/0000-0001-7465-1939
Zaki Naser Kadhim
http://orcid.org/0000-0002-7475-269X

References

[1]. Angyu, C.; Yasuhiro, O.; Fumihide, S. *Chem. Eng. J.* **2010**, *156*, 98-105.
[2]. Hu, J.; Song, Z.; Chen, L.; Yang, H.; Li, J.; Richards, R. *J. Chem. Eng. Data* **2010**, *55*, 3742-3748.
[3]. Hejazifar, M.; Azizian, S.; Sarikhan, H.; Li, Q.; Zhao, D. *J. Anal. Appl Pyrolysis* **2011**, *92*, 258-266.
[4]. Belessi, V.; Romanos, G.; Boukos, N.; Lambropoulou, D.; Trapalis, C. *J. Hazard. Mater.* **2009**, *170*, 836-844.
[5]. Tan, X.; Liu, Y.; Zeng, G.; Wang, X.; Hu, X.; Gu, Y.; Yang, Z. *Chemosphere* **2015**, *125*, 70-85.
[6]. Ahmad, M.; Lee, S. S.; Dou, X.; Mohan, D.; Sung, J. K.; Yang, J. E.; Ok, Y. S. *Bioresour. Technol.* **2012**, *118*, 536-544.
[7]. Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. *Bioresour. Technol.* **2001**, *77*, 247-255.
[8]. Muruganandham, M.; Amutha, R.; Lee, G. J.; Hsieh, S. H.; Wu, J. J.; Sillanpaa, M. *J. Phys. Chem. C* **2012**, *116*, 12906-12015.
[9]. Pimpaporn, S.; Sumpun, W. *J. Sol-Gel Sci. Technol.* **2014**, *71*, 86-95.
[10]. Bhatnagar, A.; Sillanpaa, M. *Chem. Eng. J.* **2010**, *157*, 277-296.
[11]. Isık, M.; Sponza, D. T. *Chemosphere* **2004**, *55*, 119-128.
[12]. Beak, M. H.; Ijagbemi, C. O.; Kim, D. O. *J. Environ. Sci. Heal. A* **2009**, *44*, 623-629.
[13]. Lau, Y. Y.; Wong, Y. S.; Teng, T. T.; Morad, N.; Rafatullah, M.; Ong, S. A. *Chem. Eng. J.* **2014**, *246*, 383-390.
[14]. Venkata Mohan, S.; Karthikeyan, J. *Clean Technol. Envir. J.* **2004**, *6*, 196-212.
[15]. Nguyen-Phan, T. D.; Song, M. B.; Yun, H.; Kim, E. J.; Oh, E. S.; Shin, E. W. *Appl. Surf. Sci*. **2011**, *27*, 2024-2031.
[16]. Han, R.; Wang, Y.; Han, P.; Shi, J.; Yang, J.; Lu, Y. *J. Hazard. Mater*. **2006**, 137, 550-554.
[17]. Vadivelan, V.; Vasanth Kumar, K. *J. Colloid Interface Sci*. **2005**, *286*, 90-100.
[18]. Otero, M.; Rozada, F.; Calvo, L. F.; Garcia, A. I.; Moran, A. *Biochem. Eng. J*. **2003**, *15*, 59-68.
[19]. Jafari, S.; Tryba, B.; Nejman, E.; Kozar, J.; Morawski, A. W.; Sillanpaa, M. *J. Mol. Liq*. **2016**, *220*, 504-512.
[20]. Janus, M.; Kusiak, E.; Choina, J.; Ziebro, J.; Morawski, A. W. *Desalination* **2009**, *249*, 359-363.
[21]. Aksu, Z. *Process Biochem*. **2005**, *40*, 997-1026.
[22]. Jafari, S.; Feiping Z.; Dongbo Z.; Manu L.; Amit B.; Mika S. *J. Mol. Liq*. **2015**, *207*, 90-98.
[23]. Cheng, X.; Yu, X.; Xing, Z. *Appl. Surf. Sci*. **2012**, *258*, 3244-3248.
[24]. Koumanova, B.; Peeva, P.; Allen, S. J.; Gallagher, K. A.; Healy, M. G. *J. Chem. Technol. Biotechnol.* **2002**, *77*, 539-545.
[25]. Tsai, W. T.; Yang, J. M.; Lai, C. W.; Cheng, Y. H.; Lin, C. C.; Yeh, C. W. *Bioresour. Technol.* **2006**, *97*, 488-493.
[26]. Saxen, B. *Memoranda Soc. Fauna Flora Fennica* **2011**, *87*, 29-40.
[27]. Aksu, Z. *Sep. Purif. Technol.* **2001**, *21*, 285-294.
[28]. Bulut, Y.; Baysal, Z. *J. Environ. Manage.* **2006**, *78*, 107-113.
[29]. Rauf, M. A.; Bukallah, S. B.; Hamour, F. A.; Nasir, A. S. *Chem. Eng. J.* **2008**, *137*, 238-243.
[30]. Banerjee, S.; Sharma, G. C.; Chattopadhyaya, M. C.; Sharma, Y. C. *J. Environ. Chem. Eng.* **2014**, *2*, 1870-1880.