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Removing of Cadmium Ions and Reactive red Dye from Simulated Wastewater Using Eggshell as an Eco-Friendly Material

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Abstract

The research aims to use eggshells (ES) as civilian residues in the process of removing cadmium ions and reactive red dye according to international standards limits. Synthetic solutions were prepared for cadmium ions and reactive red dye using 0.2 g non-calcined and calcined ES at various temperatures (25, 250, 500, 750, and 1000 ℃) as an adsorbent. The result showed the removal of cadmium ion was (60, 100%) for non-calcined and calcined ES, respectively, with the initial concentration of cd2+ (10 ppm). The removal of reactive red dye was (18.5, 98%) using non-calcined and calcined ES, respectively, at a concentration of red dye (50 ppm). The best removal time was 90 min. XRD and FTIR spectroscopy were performed and the results were identical to the main components of ES and changed with temperature increasing due to dissolution of calcium carbonate ($CaCO_3$).

1. Introduction

It is no doubt that life on earth would not exist without water. Water quality is essential for living beings because it is mainly used for drinking, cleaning, industry, and agriculture. Water pollution has become a serious issue and the major sources of wastewater are industries like textile, paper, rubber, plastic, leather, cosmetics, food mining, metal processing, pesticides, and rubber, plastic, and drug industries[1].

Many organic and inorganic pollutants are responsible for the water pollution discharged from factories. Dyes are organic pollutants harmful and can cause diseases to humans such as derma allergy, irritation to the skin, and cancer[2, 3]. Heavy metals are inorganic pollutants and non-degradable pollutants that their accumulation in the environment can cause harmful influences on human health, animals, and flora life[4]. The most important inorganic pollutants are heavy metals e.g. copper, lead, cadmium, and silver….etc. Cadmium is one of the most hazardous heavy metals because of its toxicity influence on human wellness. Cadmium accumulates in the human body and especially in the kidneys leads to dysfunction of the kidney with impaired re-absorption for instance, proteins, glucose, and amino acids.The International Agency for Research on Cancer (IARC) classifies cadmium in Class 1 as causing agent is carcinogenic to humans like lung, kidney and bones cancer[5]. Several methods are used for removing heavy metals and dyes from water such as chemical coagulation, chemical precipitation, reverse osmosis, electrochemical oxidation, zonation, extraction by solvent, ion exchange, filtration by membranes, and adsorption [3, 6]. Adsorption is one of the most effective methods of removing colors, odors, oils, and organic pollutants from the process or waste effluent. Adsorption was found to be superior to other techniques for water reuse in terms of simplicity of design, initial cost, ease of operation, and insensitivity to toxic substances [7]. Eco-friendly solid wastes like rice husks, eggshells, palm fronds ….etc. are used as an adsorbent to treat water pollution [6]. Eggshell is an emerging abundant solid waste from the sources such as poultry, homes, restaurants, and food manufacturing industries[8]. Throwing ES into the environment without pre-treatment can cause bad effects to the ambient and human health because of the chemical composition of ES which consists of calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%), and organic materials (4%) [9]. ES is used as a beneficial material to produce products such as fertilizer, human supplements, animal nutrition, and as a low-cost adsorbent to treat water and gases from pollutants. The high content of calcium carbonate in ES qualifies it to be a good heavy metals adsorbent [10].

ES was used by many researchers as an adsorbent to recover and remove pollutants, Borhade and Kale used ES as an adsorbent to remove dyes from their aqueous medium [7]. Tsai et al. studied the main physical and chemical characteristics of ES using common isotherm models (Langmuir and Freundlich) depending on the adsorption ability of ES to remove methylene blue from aqueous solution at 25℃[11]. Pramanpol and Nitayapat examined the ability of ES and its membrane under different conditions (temperature, pH, and adsorbent particle size) to adsorb reactive dye (C.I. Reactive Yellow205) [3]. Jai et al. investigated the physical and chemical properties of treated ES, and its applicability to remove heavy metals from synthetic and real wastewater [6]. Kanyal & Bhatt, investigated the efficiency of ES powder as an adsorbent with heavy metals such as copper and lead at a concentration of 5ppm and at different conditions (pH, agitation rpm, and contact time) [12]. Ziad et al evaluated the effectiveness of ES to remove heavy metals (Cu, Cd from aqueous solutions [10]. Rohaizar *et al*. studied different operating conditions (pH, contact time, and agitation speed) on the adsorption efficiency to remove Cu from water using chicken ES and evaluate equilibrium adsorption process using Langmuir and Freundlich isotherm and -pseudo-second-order kinetic models [13]. Zadeh et al. investigated the removal of Cd^{2+} ions from aqueous solutions using ES and studied the influences of different parameters (pH, adsorbent dosage, Cd^{2+} concentration in solution, mixing rate, and contact time) on the adsorption process [5].

In nutshell, the main objective of the research is to examine the eggshell characteristics with different temperature exposure and to evaluate eggshell adsorbent performance in adsorption of cadmium ion and reactive red dye in an aqueous solution.

2. Experimental Procedure

2.1. Materials

Eggshell (ES) available from kitchen waste, pastry shops, and restaurants samples were washed in tap water then followed in distilled water to remove all residues. ES samples were dried in the air after that in the oven under (40 ℃) for 5 h to remove moisture. The dried samples were grinded in the ball mill (planetary ball mill PM 400 Retsch) sieved in molecular weight sieve shaker (Retsch Germany)Table 1 shows (50 g) of grinded and sieved eggshell.

Table (1). Range of molecular sieve eggshell

Sieve aperture size (mm)	Weight(g)	Weight %
(2-1.18)	0.567	1.134
(1.18-1.0)	2.143	4.286
(1.0-0.0.25)	11.6	23.2
(0.025-0.18)	22.85	45.7
(0.18-0.075)	12.84	25.68

Sample at range size (0.25- 0.18) mm were selected to laboratory experiments. Reactive red dyes were available in the laboratory as one of the textile dyes used at textile factories in Iraq as shown in Table (2) and Figure (1).

Table (2). Specifications of reactive red dye.

Trade name	Origin	Phase	Wave length (nm)	Solubility g/l	PH	Molecular weight g/mol.
Red 3B	China	Solid/powder	540	100	6.2-6.5	881.5

Dye stock solution prepared by dissolving (0.5) g dye in (1 litter) distilled water to get (500 ppm) dye concentration. Figure (1) shows the chemical structure of the reactive red dye. Cadmium ion stock solution was prepared by dissolving (1.934 g) cadmium chloride ($CdCl_2.H_2O$) from Purm Switzerland Company (97% Cl in 10 ml HCl then diluted to (1000) ml distilled water to get cadmium ion stock solution (1000 ppm) concentration.

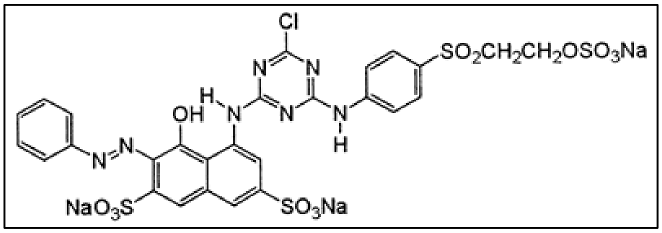

Figure (1). Chemical structure of reactive red dyes

2.2. Experimental Conditions Works

2.2.1. ES Calcination

Eggshell was grinded, dried, sieved and calcinated at different temperatures (250, 500, 750, and 1000) °C then was coded as shown in Table 3. pH and total dissolved solid (TDS) were calculated by adding 0.2 g of non-calcined and calcined ES to 100 ml of distilling water.

Table (3). Explain eggshell samples codes.

Eggshell calcination temperature (°C)	Code
Non-calcined ES 25	A
250	B
500	C
750	D
1000	E

- **Effect of Calcined and Non-calcined Dosage of ES on Cadmium Ion Removal**

Non-Calcined and calcined ES were used to remove cadmium ions from the simulated solution. Five samples of cadmium ion solution (10 ppm, 50 ml) were prepared from cadmium ion stock solution. The amount of non-calcined and calcined ES was (0.2 g) added to the cadmium ion solution samples, all these samples were placed at shaker (GFL 1083 GERMANY) for (4 h) at room temperature, and then filtrated. Cadmium ion concentrations for all filtrate samples were tested using atomic absorption spectrophotometer (BUCK model 210 VGP America).

- **Effect of Cadmium Ions Initial Concentration**

Cadmium ion solutions with (10, 25, 50) ppm as initial concentrations were prepared from cadmium ion stock solution and (0.5) g of non-calcined ES (A) was added for every three samples. After that, the samples wereplaced in the shaker for (4 h) at room temperature then filtrated for cadmium ions testing by atomic absorption spectrophotometer.

- **Effect of Contact Time**

Solution with initial concentrations (10 ppm, 1000 ml) of cadmium ions were prepared as a stock solution for studying contact time effect. Adding 5 g of non-calcined ES and placed on hot plate magnetic stirrer (IKA RH basic 2) at room temperature sampling of 10 ml was taken at an interval time (10, 30, 60, 90,120,180 and 240) min. Each sample was filtrated for cadmium ion testing.

2.2.2. Reactive Red Dye Removal

- **Effect of Non-calcined and Calcined ES Dosage on Removal**

Various samples of non-calcined and calcined ES (A, B, C, and D) were added by weight of (0.2 g) to simulated reactive red dye initial concentration (50 ppm and 50 ml) that obtained from dilution of the origin stock solution as shown in Table 3. The five samples were placed in shaker for (4 h) at room temperature then filtered. The filtrated solutions were tested in the ultraviolet spectrometer (CECIL model CE-2021 England).

- **Effect of Reactive Red Dye Initial Concentration.**

Three Samples of (50 ml) volume and different concentrations (25, 50, 100) ppm of reactive dye that diluted from the origin stock solution were prepared by adding (0.2 g) of non-calcined ES (A) to all three samples. They were shacked for (4 h) and filtrated to be ready for testing by Ultraviolet spectrometer (CECIL model CE-2021 England). The percentage of removal cadmium ion and dye was calculated from equation (1) [11]

$$Removal\ \% = \frac{C_i - C_e}{C_i} X100 \quad (1)$$

$$q_e = \frac{C_i - C_e}{m} X\ V \quad (2)$$

where Ci & Ce (ppm) are liquid-phase concentrations of cadmium ion and dye at initial and equilibrium respectively [13].

2.3. Dye Standard Curve

Ultraviolet analysis method was adopted for analyzing reactive red dyes standard curve, four samples of reactive red dyes solution were prepared (5,10, 25, 50) ppm concentration then tested at wavelength (540nm) [14]. A linear relationship between dye solutions concentrations and absorbance with square regression is shown in the Figure below:

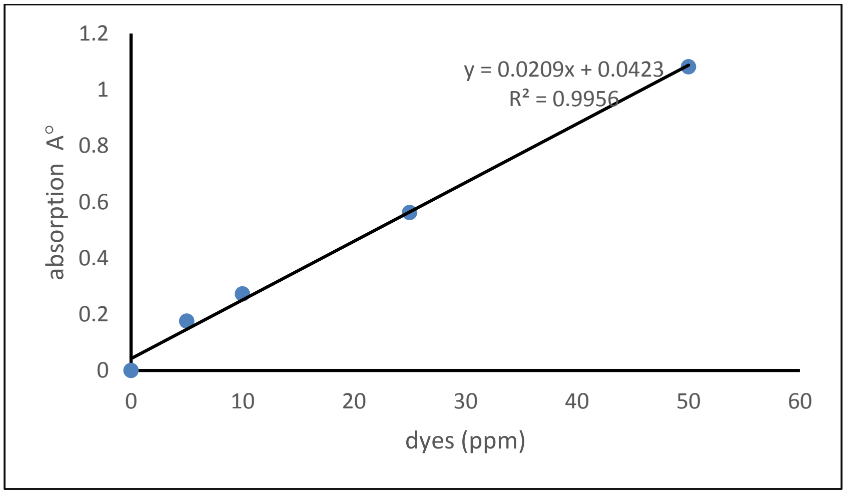

Figure (2). Reactive red dye standard curve.

3. Results and Discussion

3.1. Effect of Calcination on pH and TDS

Figure (3) shows increasing pH and TDS with increasing temperature. The pH and TDS were increased to 12, 1985, respectively when the material was heated to 1000 °C because of decomposing of calcite ($CaCO_3$) as a main component of ES to CaO. Dissolving of CaO in water generate $Ca(OH)_2$ in solution which led to a raised pH value. These results are in agreement with Awal et al. (2017) which asserted the calcination processes of calcite led to converting the eggshell to calcium oxide [8].

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad \text{....(3)}$$

The color of was changed as seen at all the procedures of calcination until reached (1000 ℃) which became white color as shown clearly in Figure (4) which refers to decomposing all $CaCO_3$ to CaO due to the calcination.

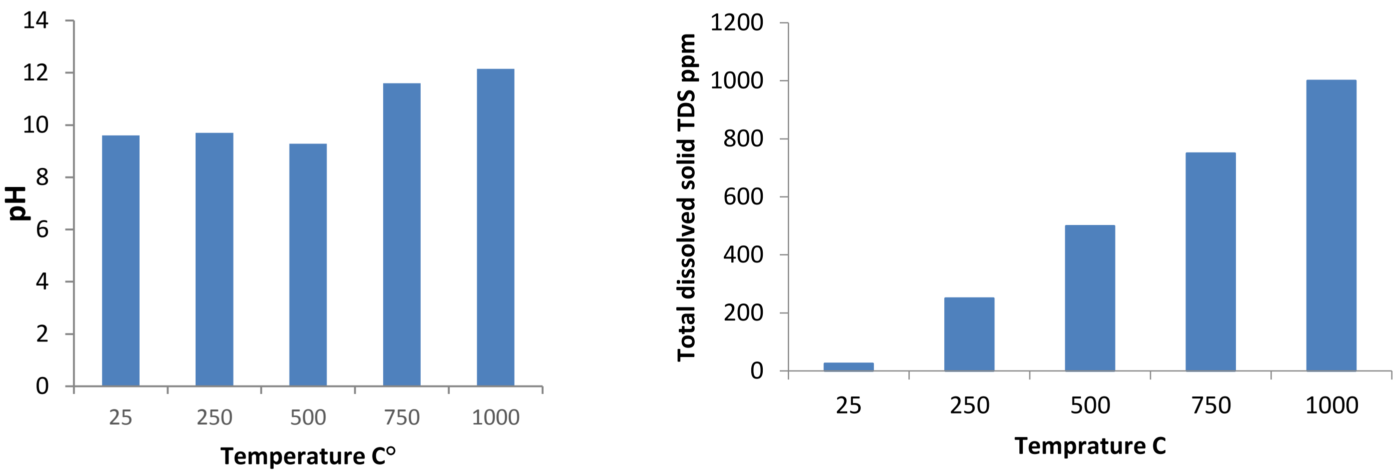

Figure (3). Effect of the calcination temperature of ES on pH and TDS.

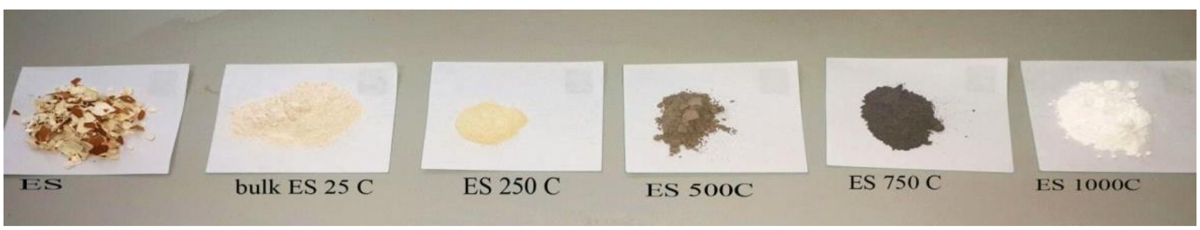

Figure (4). Effect of the calcination temperature of ES on ES color.

3.2. XRD and FTIR Analysis

XRD patterns of eggshell powder are presented in Figure (5). The mineral phase was identified as calcite ($CaCO_3$) no other crystalline species was detected. The structure of the XRD pattern of eggshell powder was not changed with increasing temperature up to 750 °C. Whereas it observed different structures at 1000 °C. The calcite phase was decreasing and the intensity of new reflection peaks were increasing which belongs to calcium oxide. At this temperature, the sample becomes fragile, porous, and very white in color. It is concluded from the apparent that the calcite ($CaCO_3$) decomposes in the heating . This observation confirms earlier findings [15].

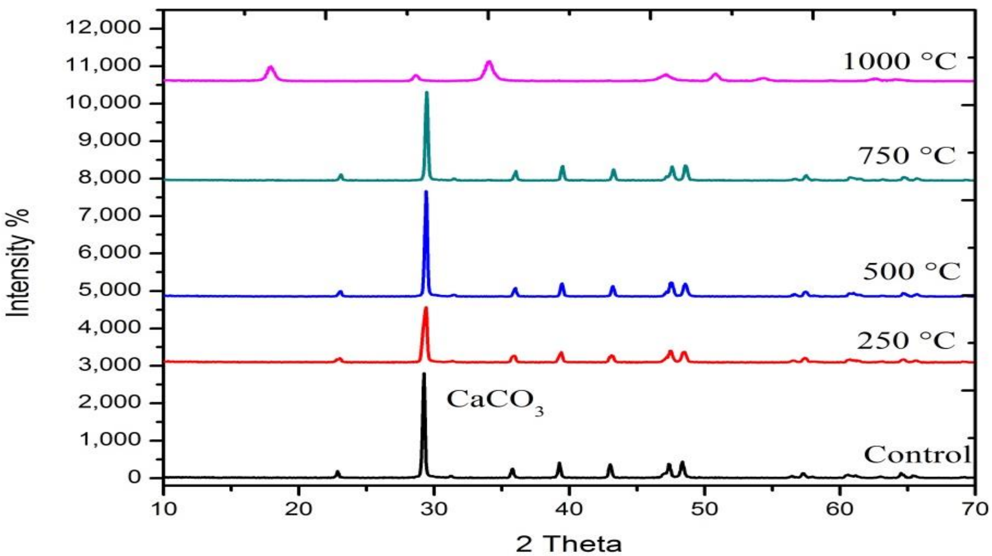

Figure (5). XRD Pattern for calcined ES at different temperatures.

The infrared spectra of ES powder are shown in Figure (6). The absorption bands of CO_3^{-2} are observed at wavenumbers of 872 cm^{-1}, and (1403-1417) cm^{-1} which are the common feature of the CO_3^{-2} ions in $CaCO_3$. The relative intensity of CO_3^{-2} band decreases at 1000 °C because of the loss of carbonate. The existence of a small vibration band of CO_3^{-2} molecule at 1000 °C indicates that the transformation of calcite to CaO is not completed. In addition, there is an absorption band observed at about 3639 cm^{-1} which is attributed to OH stretching mode [7, 16].

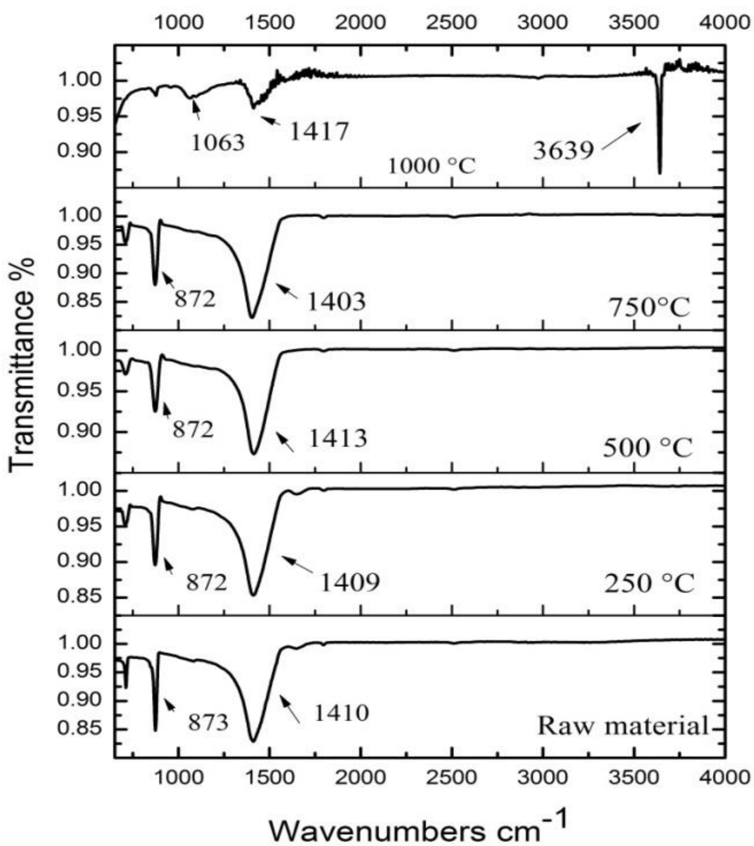

Figure (6). FTIR functional group of calcined ES structure at different temperatures.

3.3. Effect of Non-calcined and Calcined ES on Cadmium Ions and Dye Removal

Figure (7) shows the effect of ES calcination temperature on the removal of cadmium ions and reactive red dye. The removal of cadmium ions and reactive red dye at 0.2 g of non-calcined ES, was (60, 18.5%), respectively. It is observed that at 1000 °C, the best removal was (100, 98%) for cadmium and reactive dye, respectively. This is due to the formation of $Ca(OH)_2$ which plays a role in chemical precipitation because of heavy metals (cadmium) and dye (reactive red dye) precipitate as insoluble materials [16,17].

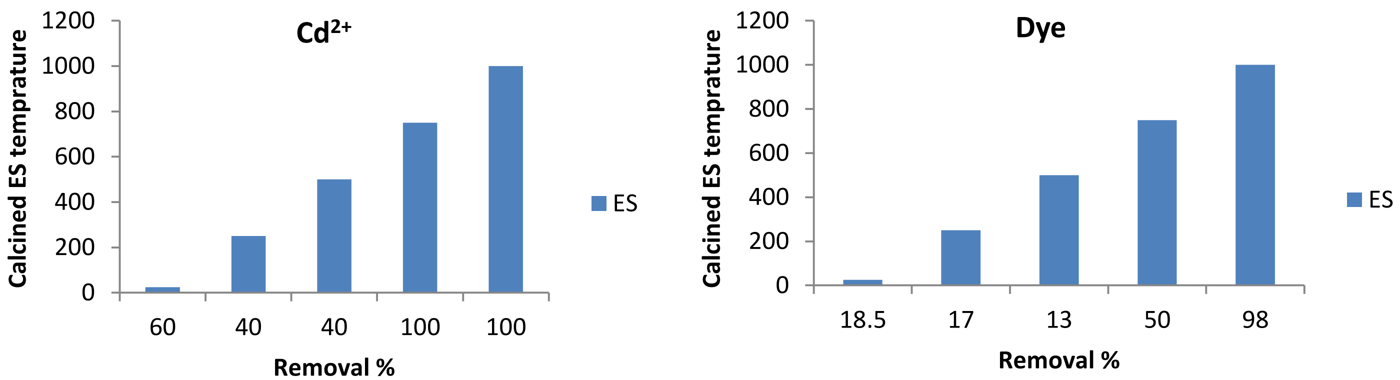

Figure (7). Effect of ES calcination temperature on removal % of cadmium ions and dye.

3.4. Effect of Non-calcined Eggshell Dosage on Cadmium Ion and Dye Removal.

The results, as shown in Figures (8 & 9) indicate the removal of cadmium better than the removal of reactive red dye. The result may be explained by the existence of (CO_3^{-2}) on the surface of a non-calcined eggshell which attracts the positive charge of cadmium ions more than the negative charge of reactive red dye. Sulayman and Abood approved that increase in the removal of yellow active dye depending on the charge and the pH of the surface of the adsorbent when they used activated carbon for the removal of yellow active dye in simulated wastewater [18].

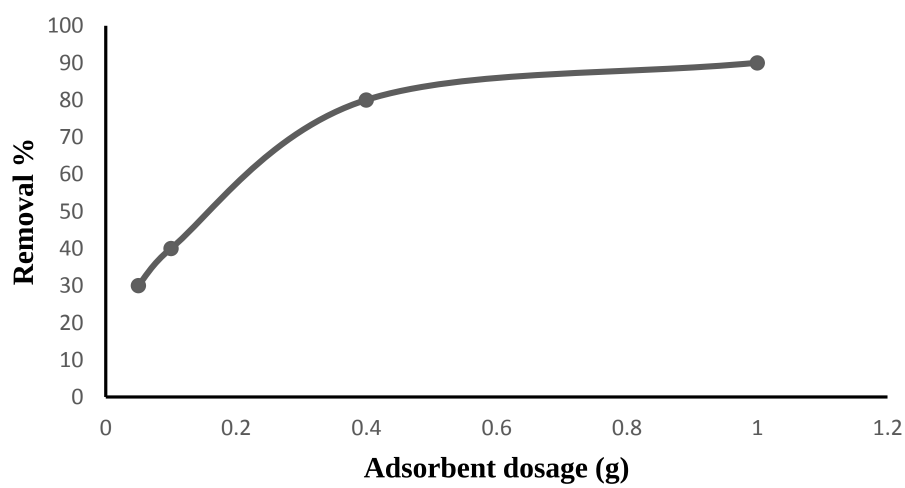

Figure (8). Removal% of cadmium ion at the different dosage of non-calcined ES.

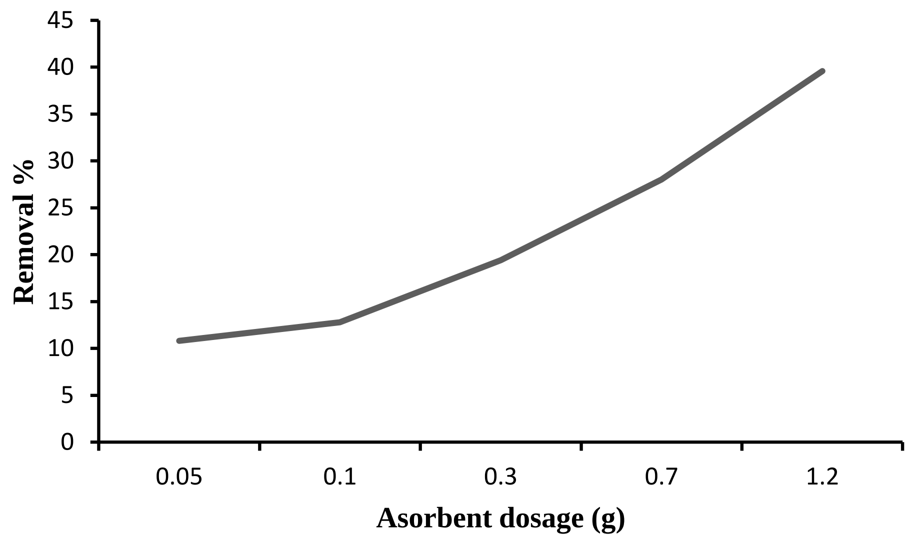

Figure (9). Removal% of dye at the different dosage of non-calcined ES.

3.5. Effect of Cadmium Ions and Reactive Red Dye Concentration.

Figure (10) and Figure (11) show different effects of increasing the initial concentration of cadmium ion and reactive red dye on the removal. The removal of cadmium ion at the concentration of (10, 25, 50) ppm was (70, 50, 68) %.While the removal of dye at the concentration of (25, 50, 100) ppm were (52.7, 24.2, 13.9) %. This is due to the repulsive charge of ES and dye and attractive charge of ES and Cd ion which may lead to increased removal of Cd ion more than dye without the effect of concentration as the driving force in the adsorption process.

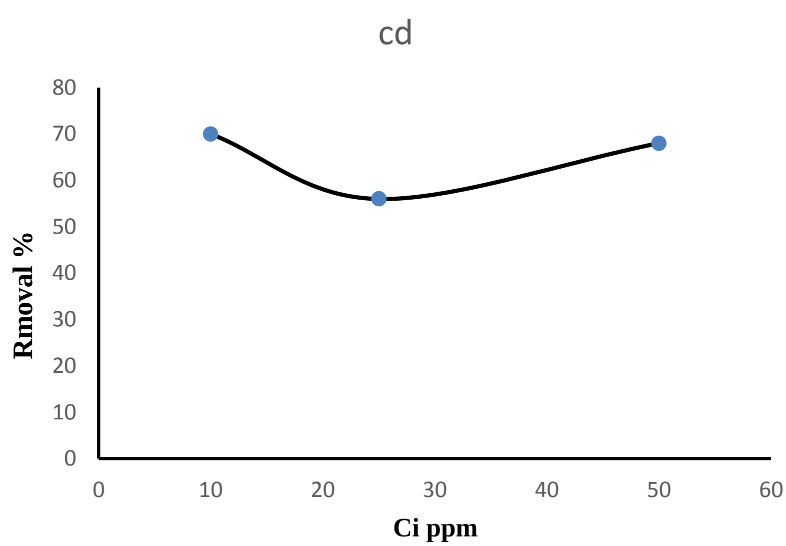

Figure (10). Effect of increasing initial concentration of cadmium ion on the removal (%).

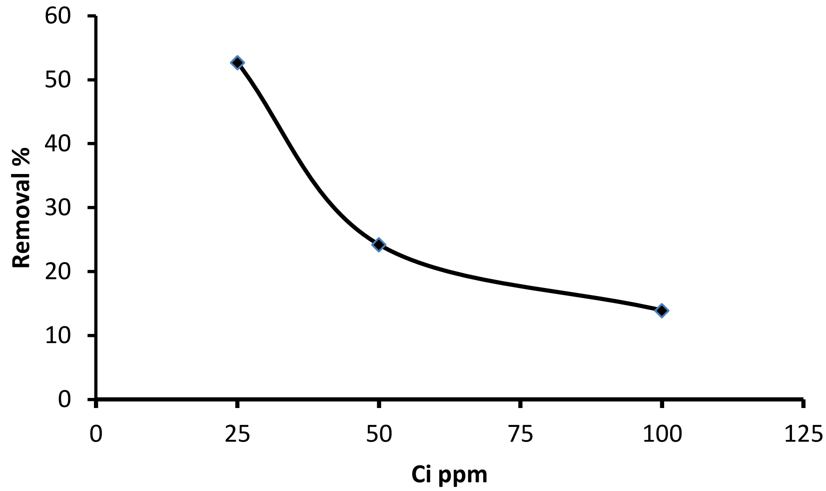

Figure (11). Effect of increasing initial concentration of dye on the removal (%).

3.6. Effect of Contact Time

Figure (12) shows the effect of contact time for removing cadmium ions, The obtained results of Cd^{+2}removal with time at initial concentration 10 ppm and sample volume. 1000 ml with (5g) calcined ES at 1000 °C. The process showed a rapid reduction of Cd^{+2} in solution with removal (100%) at (90 min) [5].

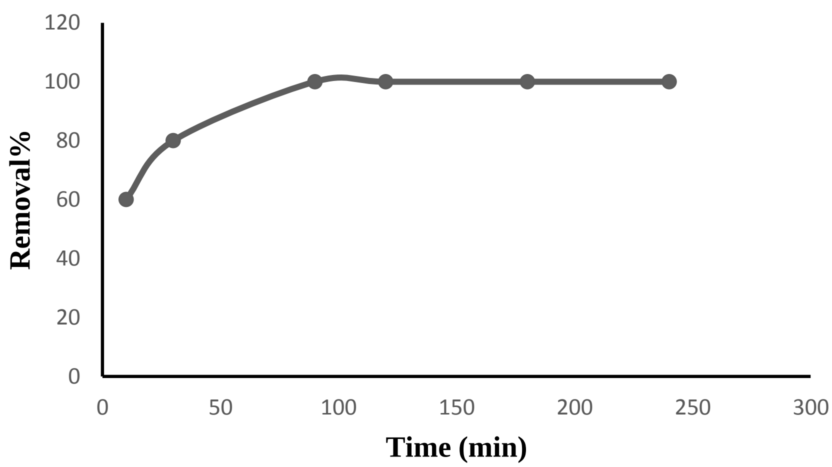

Figure (12). Effect of contact time on cadmium removal.

4. Conclusions

The present study shows the calcined ES can be effectively used as an adsorbent to remove heavy metals and reactive red dye. X-ray diffraction identified one crystalline phase which is calcite and it disappeared after calcination at 1000°C. FTIR confirms the transformation of calcite to CaO at 1000 °C. Total Dissolved Solids (TDS) and pH in solution were increased. In addition, the result shows cadmium removal better than dye due to attraction between cadmium ion and ES surface, and the contact time effect shows rapid removal of cadmium ion at (90) min with adsorption capacity (2 mg/g).

References

[1] D. Mohan, A. Sarswat, Y. Sik, and C. U. Pittman, “Bioresource Technology Organic and inorganic contaminants removal from water with biochar , a renewable , low cost and sustainable adsorbent – A critical review,” *Bioresour. Technol.*, vol. 160, pp. 191–202, 2014.

[2] G. Oros, E. Forgacs, and T. Cserha, “Removal of synthetic dyes from wastewaters : a review,” *Environ. Int.*, vol. 30, pp. 953–971, 2004.

[3] N. Pramonpol and N. Nitayapat, “Adsorption of reactive dye by eggshell and its membrane Adsorption of Reactive Dye by Eggshell and Its Membrane,” *kasetsart J.*, vol. 40, pp. 192–197, 2006.

[4] C. Arunlertaree and W. Kaewsomboon, “Removal of lead from battery manufacturing wastewater by egg shell,” *Songklanakarin J. Sci. Technol*, vol. 29, no. 3, pp. 858–867, 2007.

[5] B. S. Zadeh, H. Esmaeili, and R. Foroutan, “Cadmium(II) removal from aqueous solution using microporous eggshell: Kinetic and equilibrium studies,” *Indones. J. Chem.*, vol. 18, no. 2, pp. 265–271, 2018.

[6] P. H. Jai, J. S. Wook, Y. J. Kyu, K. I. M. B. Gil, and L. E. E. S. Mok, “Removal of heavy metals using waste eggshell,” *J. Environ. Sci.*, vol. 19, no. 12, pp. 1436–1441, 2007.

[7] A. V. Borhade and A. S. Kale, “Calcined eggshell as a cost effective material for removal of dyes from aqueous solution,” *Appl. Water Sci.*, vol. 7, no. 8, pp. 4255–4268, 2017.

[8] K. Awal, P. Sulfur, D. Menggunakan, and K. Telur, “Preliminary study of silfur dioxide removal using calcined egg shell,” *Malaysian J. Anal. Sci.*, vol. 21, no. 3, pp. 719–725, 2017.

[9] M. Alexandra, “Eggshell valorisation by composting process for environmental applications,” University of Coimbra, 2015.

[10] Z. Tark, A. Ali, and M. A. Ibrahim, “Eggshell Powder as An Adsorbent for Removal of Cu (II) and Cd (II) from Aqueous Solution : Equilibrium , Kinetic and Thermodynamic Studies,” *Al-Nahrain J. Eng. Sci.*, vol. 91, no. 2, pp. 186–193, 2016.

[11] W. T. Tsai, J. M. Yang, C. W. Lai, and Y. H. Cheng, “Characterization and adsorption properties of eggshells and eggshell membrane,” *Bioresour. Technol.*, vol. 97, pp. 488–493, 2006.

[12] M. Kanyal and A. A. Bhatt, “Removal of Heavy Metals from Water (Cu and Pb) Using Household Waste as an Adsorbent Bior emediation & Biodegradation,” *J. Bioemediation Biodegration*, vol. 6, no. 1, pp. 1–6, 2015.

[13] N. Rohaizar, N. Abd. Hadi, and W. C. Sien, “Removal of Cu (II) from Water by Adsorption on Chicken Eggshell,” *Int. J. Eng. Technol.*, vol. 13, no. 1, pp. 40–45, 2013.

[14] A. H. Sulaymon and W. M. Abood, “Equilibrium and kinetic study of the adsorption of reactive blue , red , and yellow dyes onto activated carbon and barley husk,” *Desalin. Water Treat.*, vol. 52, pp. 5485–5493, 2014.

[15] T. Zaman and C. Engineering, “Evolution and characterization of eggshell as a potential candidate of raw material,” *Cerâmica*, vol. 64, no. 370, pp. 236–241, 2018.

[16] A. a Jazie, H. Pramanik, and a S. K. Sinha, “Egg Shell Waste-Catalyzed Transesterification of Mustard Oil : Optimization Using Response Surface Methodology (RSM),” in *2nd International Conference on Power and Energy Systems*, 2012, vol. 56, no. 10, pp. 52–57.

[17] M. M. Barbooti, A. Altameemi, M. N. Al-terehi, and N. Al-shuwaiki, “Removal of Heavy Metals Using Chemicals Precipitation,” *Eng. Tech. J.*, vol. 29, no. 3, pp. 595–612, 2011.

[18] A. H. Sulaymon and W. M. Abood, “Removal of reactive yellow dye by adsorption onto activated carbon using simulated wastewater,” *Desalin. Water Treat.*, vol. 52, pp. 37–41, 2014.