Removal of Cd (II) from Aqueous Solution using Eggshell as Low Cost Sorbent

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Abstract

Cd (II) considered one of the pollutants that significantly affect public health, this report aims at investigating the efficiency of Cd (II) removal from water resources using one of the economic, common domestic wastes, the eggshell (ES). Different doses of eggshell powder were applied to serial concentrations of Cd (II) solutions, after being examined to estimate the main influencing parameters (pH, shaking time, and temperature). ES was subject to Scan Electron Microscope (SEM), Infrared (IR), and Energy Dispersive X-ray (EDX) examination before and after it being applied to Cd (II) solutions. Freundlich and Langmuir models were applied. Thermodynamic parameters namely, change in Gibbs free energy change (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were calculated. Nearly 100% of Cd2+ ions were removed successfully. The procedure was also applied successfully for removal Cd^{2+} ions from aqueous and different samples of natural water.

Keywords - *Adsorption isotherms, Eggshell, Natural water; Cadmium (II), Sorption, Thermodynamic parameters.*

I. INTRODUCTION

Some heavy metals are important for living organisms but at low concentration and many of them are harmful at high levels, pollution of water by harmful heavy metals are associated with the appears of various cancers, damage of kidney, harm autoimmunity and loss life in extremely cases[1], [2]. These types of harmful metal ions can be stored through the main food chain even at lower concentration, leading to impairing effects on the aquatic life along with plant life, animal, and man health. The removal of such metals is relevance not only due to their toxicity but also we can reuse it in various industrial applications [3], [4]. Methods of separation which remove the harmful metal ions from industrial streams and polluted water are continually needed. Several methods as solid phase extraction, precipitation, membrane processes, and ion exchange have been used for eliminating the pollution arises from harmful metal ions[5], [6]. The powerful and economic method for elimination of harmful metal ions from wastewater is adsorption [7], [8]. One of the most known adsorbent is activated carbon [9], [10]. Toxic metals as Pb, Hg, Cr, and Cd have high

priorities because they are among most ubiquitous environmental contaminants. These toxic metals are non-biodegradable accumulate easily.

One of the cheap and easily available material having possibilities as a suitable sorbent for heavy metals is eggshell. Due to their high calcium content, eggshells usually have no commercial importance. Disposal of eggshells is also a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs[11], [12].

Numerous investigations have been done on different applications of egg shell, use egg shell as adsorbent for water contaminates is thoughtful venture due to its high ion exchange capacity. Despite such fruitful investigations still there is a need to explore new kind of feasible application.

II. MATERIALS AND METHODS

A. Sorbent material

The eggshell samples (poultry eggshells) used in this study were obtained from a private restaurant (Mering Patisserie) located in Mansoura City, Egypt. After the samples have been collected, washed with water, dried for 3 hrs in the oven at 180°C, they were allowed to cool to room temperature, then crushed, grinded, and sieved. Particles with size (<0.128 cm) were used in the experiments. The samples were then packed into stoppered bottles and stored in desiccators for future use.

The chemical composition (by weight) of by product eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [13], [14]. From IR analysis, eggshell characterized by the observable peaks of 710, 875, 1420, 1807 and 2520 cm^{-1} coincided with those of pure $CaCO_3$.

B. Cd (II) Solution

All the solutions were prepared from certified reagent grade chemicals. Aqueous solutions were prepared in doubly distilled water. The Cadmium stock solution 1000 mg/L was prepared from (BDH Ltd, Poole, England) by dissolving suitable weight of the salt in 50ml doubly distilled water. Further dilutions were prepared daily as required.

C. Apparatus

A VWR model 3500 digital shaker was used for shaking solutions. Infrared spectroscopy was

undertaken via a Mattson 5000 FT-IR spectrophotometer using the KBr disc method. The measurements were carried out using atomic absorption spectrometry AAS240FS (Varian, Australia). Also, the stirring of solutions was performed with a magnetic stirrer, Jenway 1000. The pH values were measured using pH meter (symphony, USA) provided with a glass electrode.

D. Cd (II) adsorption on ES experiments

Serial dilutions of Cd (II) were prepared using Cadmium stock solution 1000 mg/l. Dilutions were prepared by using doubly distilled water. The concentrations of Cd (II) were prepared to be 10, 15, 20, 25, and 30 mg/l. All concentrations were subject to sorption experiment. Different 5 doses of ES (ranges between 0.05 to 0.15 g) were added to 50 ml of each Cd (II) concentration.

All batch sorption experiments were done at room temperature (25 ± 2 °C). The effect of change of pH of the solution was studied at pH = 3, 7 and 9 but most experiments were done at pH = 7. The resulting solutions were then shaken at 200 rpm and samples were taken at fixed time periods (1, 5, 10, 15, 30, 60, and 120 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that 30 min was sufficient for adsorption of Cd (II) ions onto ES. The samples were subsequently filtered off and the residual Cd(II) ions concentration in the filtrate was determined by atomic absorption spectrometry (at a wavelength of 228 nm, lamp current 4 mA, slit width 0.2 nm, acetylene as fuel, air as support and flame stoichiometry is oxidizing). The percentage adsorption of Cd(II) ions from the solution was calculated from the relationship:

$$\% \text{ Adsorption} = (C_i - C_r)/C_i \times 100 \qquad (1)$$

Where C_i corresponds to the initial concentration of Cd(II) ions and C_r is the residual concentration in the filtrate after shaking for a definite time period. The metal uptake, q (mg/g), was calculated as:

$$q = [(C_i - C_r)/m].\, V \qquad (2)$$

Where m is the quantity of sorbent (g) and, V is the volume of the suspension (L). To assess the applicability of the procedure, another series of experiments was conducted on 50 mL of clear and pre-filtered natural water samples with an initial pH adjusted to 7.0. These suspensions contained 20 mg/L of Cd (II) ions, 0.1 g of ES and were shaken for the optimum time (30 min) at 200 rpm.
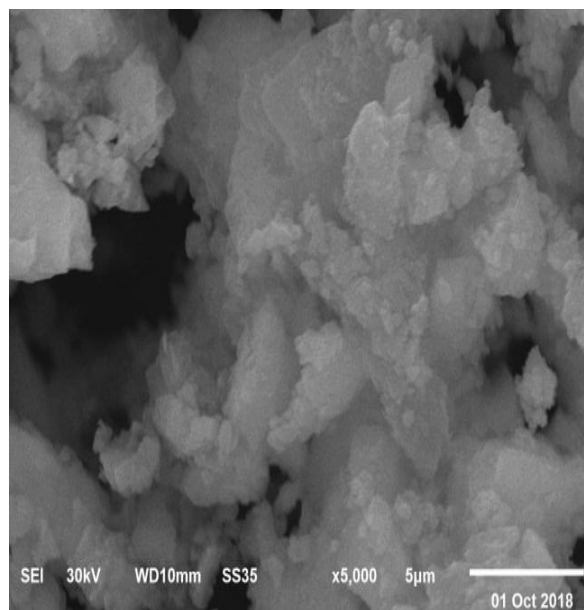
III. RESULTS AND DISCUSSION
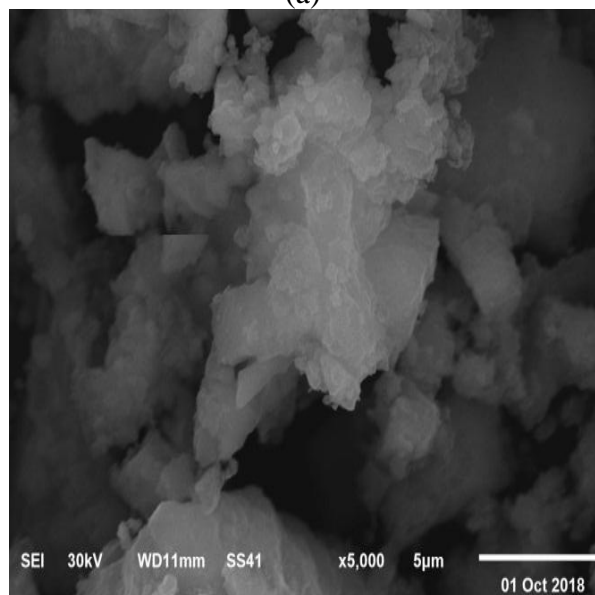
A. Characterization of samples
1) Scanning electron microscope:

In SEM image of ES before and after cadmium adsorption (Fig 1, a and b), corresponding to the morphological changes in the surface of the adsorbents in the coverage of pores of the ES due to the adsorption of Cd (II).

(a)

(b)

Fig 1: SEM photos of (a) ES before treatment, (b) ES after treatment with Cd^{2+} ions

2) Infrared spectra:

Infrared studies help in understanding the changes occurred on the structure of ES sorption. Infrared data (Fig 2) provided clear evidence of modification in the surface morphologies in form of cleavage.
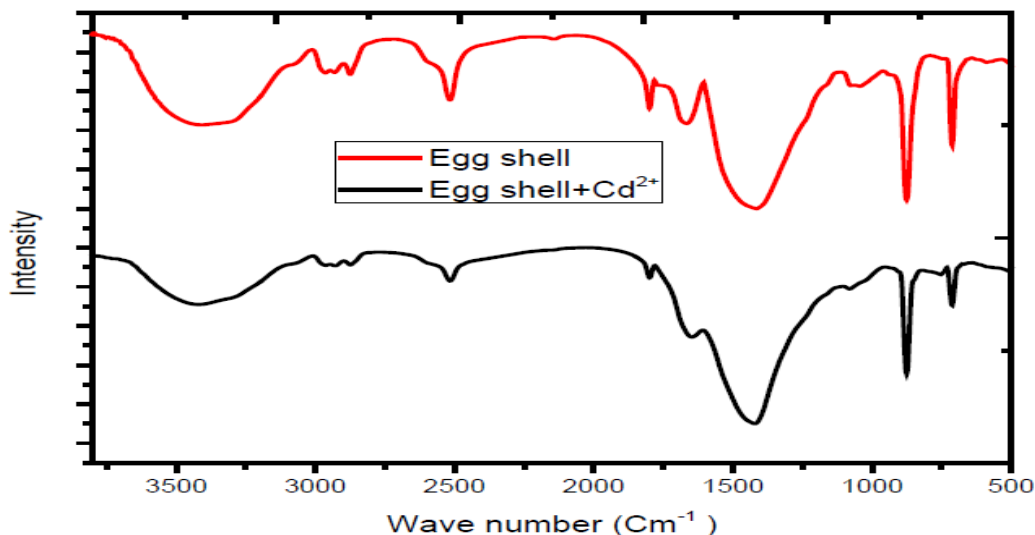
Fig 2: Infrared spectra of ES before treatment and ES after treatment with Cd(II)

3) Energy dispersive X-ray spectroscopy (EDX):

Energy dispersive X-ray spectroscopy (EDX) affords chemical information about a material. When an incident beam electron strikes an atom, it may knock out an inner shell electron if the beam electron has sufficient energy. As the excited atom returns to its stable state, the excess energy is released as an X-ray photon or Auger electron. The X-rays emitted have energies characteristic for each specific atom, thus they provide chemical information about the sample.

Analysis of the light elements, i.e. C and O are difficult because of their low photon energies. Low photon energy leads to many complications such as:

1- High absorption in the specimen and in the detector
2- The low energy peaks is positioned close to the electronic noise of the detection system (which can be seen at about. keV)
3- with light element this gives a low yield of X-rays

Fig 3 (a, b), indicated the EDX graph of ES sorption before and after treatment with Cd^{2+}. From the obtained results, the newly peaks are shown for the adsorbed metals on the surface of modified ES in addition to the principle peaks for C, O as shown for Fig 3 (a, b).
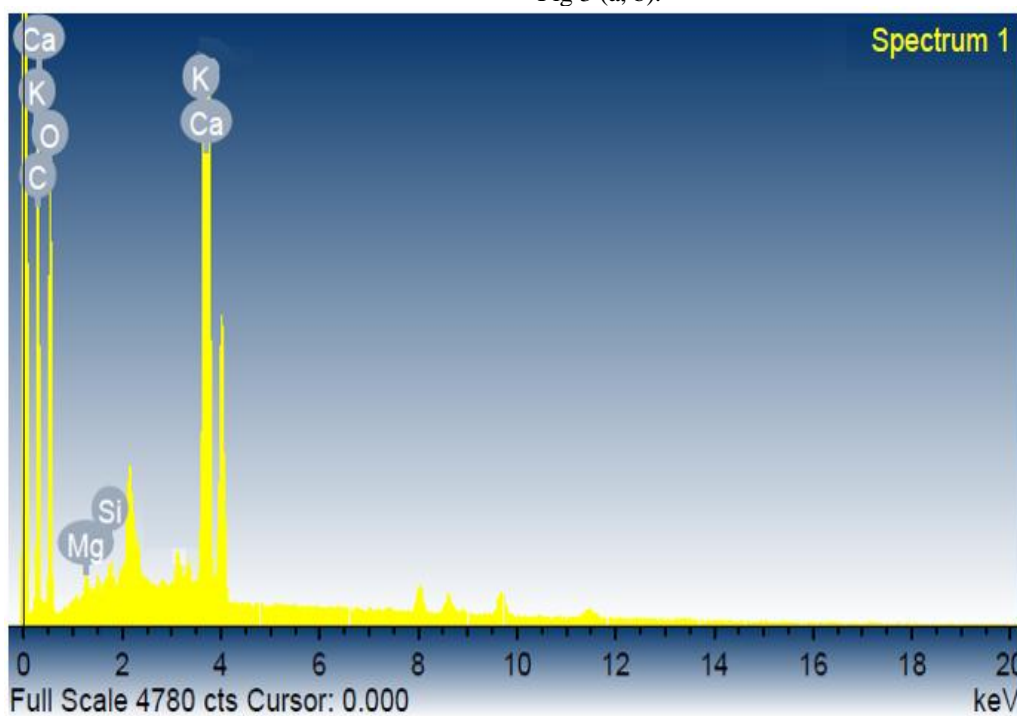

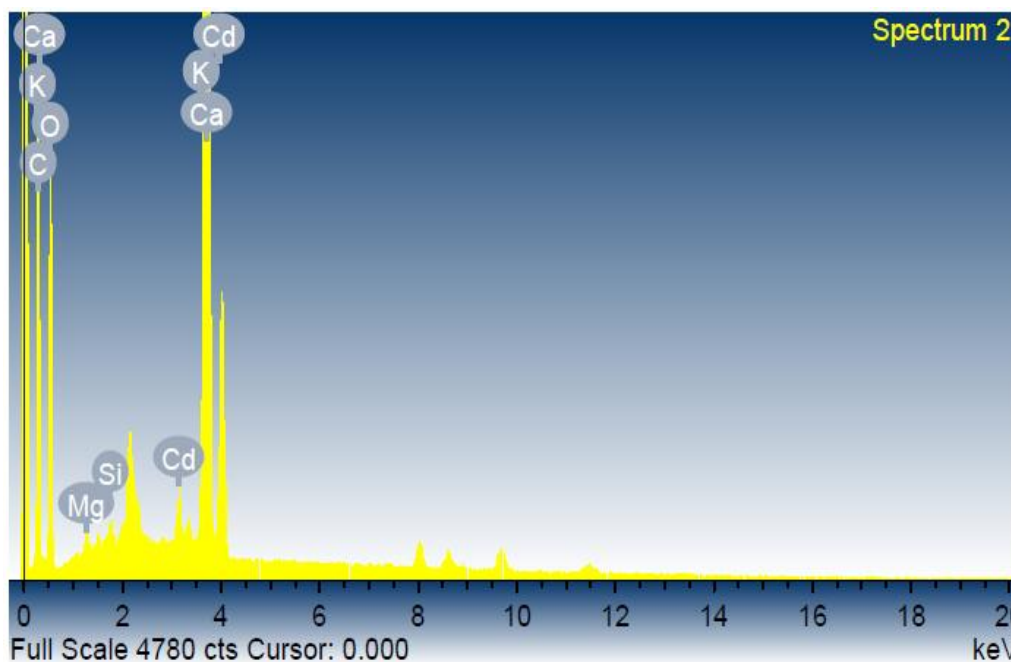**Fig 3 (a): EDX of ES before treatment with Cd(II)**

Fig 3 (b): EDX of ES after treatment with Cd(II)

B. Influence of pH

Initial pH has a great effects on the chemical adsorption of harmful metal ions from aqueous metal ion solutions as previously reported [15]. So as to study the effect of pH of the medium on Cd(II) adsorption by ES, some experiments were carried out at different pH values, pH 3, 7 and 9. As shown in Fig4, the adsorption of Cd(II) was highly pH-dependent at pH value below 2.0 (data not included), the removal of Cd(II) reached zero because of high solubility of the sorbent ($CaCO_3$ and $MgCO_3$), thereby hindering the sorption process. At low pH values, H^+ ions compete with Cd (II) for the surface of the adsorbent which would hinder the Cd (II) ions from reaching the binding sites of the adsorbent. As the pH value increase, the removal efficiency begins to increase, reaching a maximum value about of 100% at pH 9. which may be attributed to a possibility of Cd(II) precipitation on the surface of the adsorbent as $CdCO_3$ by ion-exchange mechanism between Cd (II) and calcium containing ES in a similar manner to that reported [16], and/or $Cd(OH)^+$ forming successive layers on the sorbent surface. The pH was selected to be 7.0 for further experiments.
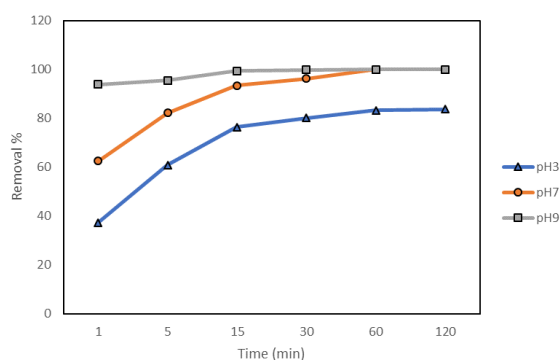

Fig 4: Influence of pH on the removal of Cd (II) (50 ml of 20 mg l^{-1}) by ES (0.1 g)

C. Influence of initial concentrations of Cd (II) and sorbent dose

The effect of initial Cd (II) concentration (10 - 30 mg l^{-1}) on its uptake by 0.1 g ES after shaking from 1 to 120 min was illustrated in Fig 5. It was found that by increasing the concentration of Cd^{2+}, the uptake increased. The effect of changing the amounts of ES (in the range 0.05- 0.15 g), on the % adsorption of 20 mg l^{-1} Cd (II) from aqueous solutions at pH 7 was depicted in Fig 6. It was found that, the adsorption efficiency increased as the amount of ES increased. This may be attributed to an increase in the amount of the sorbent and hence the number of binding sites available to the metal ions.
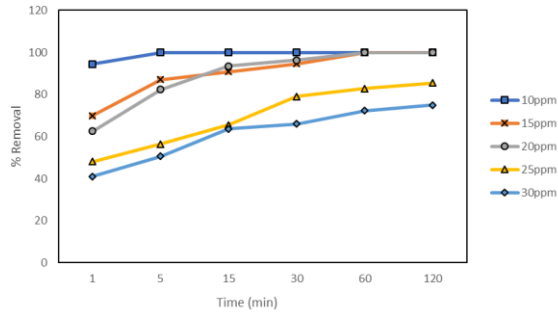
Fig 5: Effect of different Cd (II) concentrations on its % removal using 0.1g ES
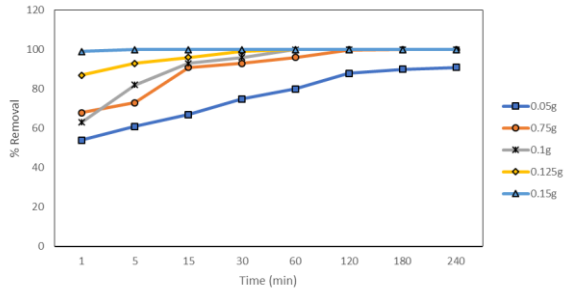

Fig 6: Effect of different ES doses on the removal of 20 mg. l⁻¹ Cd (II) ions

D. Adsorption kinetics models

Kinetics determination has important rule for scheming the sorption system and better understanding the mechanism of sorption, on addition to recognizing the adsorption rate degerming step. It was found previously from Fig 5 illustrated the variation of the Cd (II) uptake by 0.1g ES with shaking time. It was found that the adsorption of Cd (II) ions was quite rapid at the first stage, which may suggest that the adsorption occurred at the surface of the solid sorbent and to some extent by the internal macro-pores, transitional pores and micro-pores. The uptake increases with increasing the initial Cd (II) concentration, which may be attributed to higher collision between the Cd (II) and the sorbent. The 60min of shaking was found to be suitable for maximum adsorption and was used in all subsequent measurements.

Plotting the amount of Cd^{2+} ions adsorbed q_t in (mg/g) on the ES against the square root of shaking time (t) in min, as Morris-Weber equation was illustrated in Fig 7. the non-linearity correlation obtained mean that there are other surface phenomena are involved

$$q = K_d (t)^{1/2} \qquad (3)$$

This may indicates that an intra-pore diffusion mechanism was involved in adsorption of Cd(II) by ES. From Fig 7, there is two distinct regions: an initial linear portion due to the boundary layer effect [17] and a second portion due to the intra-particle diffusion effect [18]. Apart from outer surface adsorption, there is also the possibility of intraparticle

diffusion, outer the surface into pores of material. The adsorption mechanism of sorbate onto adsorbent follows three steps vis. Film diffusion, pore diffusion and intraparticle transport. The value of the initial rate constant of Intraparticle diffusion (K_d) was evaluated as 0.0460 mg g⁻¹ min⁻⁰·⁵, which gives indication about the mobility of the Cd(II) towards the ES surface.
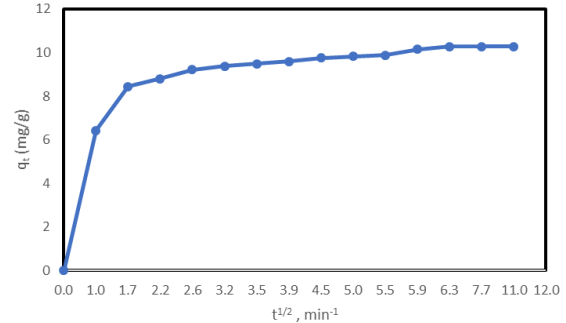

Fig 7: Amount of Cd(II) adsorbed onto 0.1 g ES vs. square root of time, pH 7, shaking rate 200 rpm, at 25°C

In order to investigate the kinetics models of Cd (II) ions adsorption onto eggshell, the linear pseudo first order and pseudo-second order kinetics models were tested to fit the experimental data.

The pseudo first-order model can be expressed as Lagergren equation [19].

$$\text{Log } (q_e – q) – \log q_e = K_{ads}\ t/2.303 \qquad (4)$$

Where q_e (mg g⁻¹) is the amount of Cd (II) adsorbed per unit mass of the adsorbent at equilibrium, q (mg g⁻¹) is the amount of Cd (II) absorbed per unit mass of the adsorbent at current time t (min), and k_{ads} (min⁻¹) is the equilibrium rate constant of pseudo-first-order model.

The linear plot of log (q_e − q) versus time (t) (Fig 8) showed of pseudo-first order rate of reaction involved. The value of the pseudo-first order reaction rate constant (K_{ads}) was calculated to be 0.052 g mg⁻¹min⁻¹.
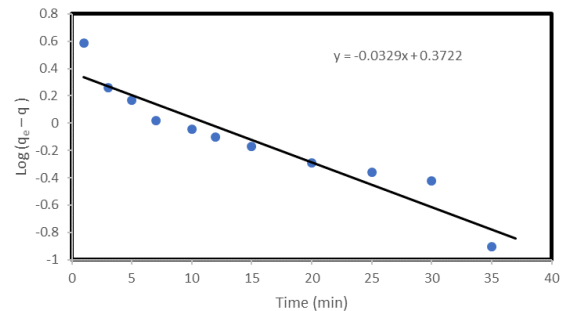

Fig 8: Plot of log (qe-q) vs. stirring time (t) for the adsorption of 20 mg l-1 Cd(II) by 0.1 g ES, pH 7, shaking rate 200 rpm, at 25°C

The pseudo-second-order rate is given by equation [4]:

$$t/q_t = 1/(k_2\ q_e^2) + (1/ q_e)t \qquad (5)$$

Where $k_2 q_e$ is regarded as the initial adsorption rate (mg g^{-1} min^{-1}), k_2 is the rate constant of pseudo second order adsorption (g mg^{-1} min^{-1}) and q_t is the metal uptake at time (t). The straight line obtained as illustrated in Fig 9, illustrated that, the pseudo-second-order kinetics can applicable for the adsorption of metal ions onto ES at the experimental condition of 0.1 g ES at pH = 7 .
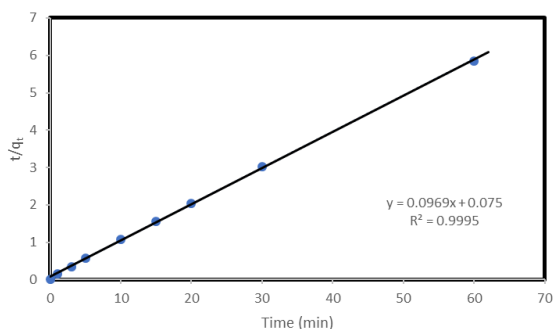

Fig 9: Plot of t/qt vs. stirring time (t) for the adsorption of Cd (II) by 0.1 g ES, pH 7, shaking rate 200 rpm, at 25ᵒC

E. Adsorption isotherms

The Langmuir isotherm model assumes a monolayer adsorption with uniform distribution of adsorption heat and affinities over the homogeneous surfaces, i.e. the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption. The linearized Langmuir equation is given by equation:

$$1/q_e = 1/q_{max} + (1/ q_{max} k_L) 1/ C_e \qquad (6)$$

Where q_e is the amount of Cd (II) (mg g^{-1}) adsorbed at equilibrium, C_e is the final equilibrium concentration (mg L^{-1}), k_L is the Langmuir equilibrium constant (Lmg^{-1}) and q_{max} is the maximum adsorption capacity (mg g^{-1}). FIG. 10 showed that, the plot of $(1/q_e)$ vs. $(1/C_e)$ gave a straight line suggesting the applicability of the Langmuir model.

The values of q $_{max}$, K_L and the correlation coefficient (R^2) were 11.098 mg.g^{-1}, 1.13 L mg^{-1} and 0.9802, respectively. The high values of q $_{max}$ and K_L indicated good adsorption of Cd^{2+} ions on the surface of ES.
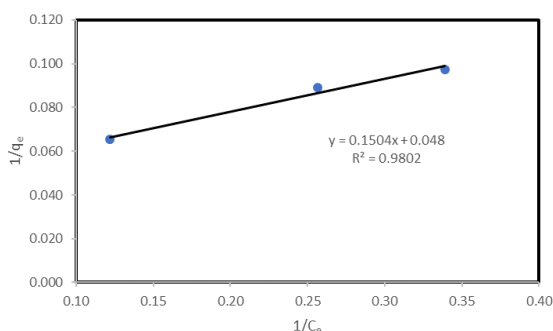

Fig 10: Langmuir plot for Cd (II) adsorption onto 0.1 g ES

Data were also analyzed with the Freundlich isotherm, which can be given in its logarithmic form as following:

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (7)$$

Where k_f is a Freundlich constant that shows adsorption capacity of adsorbent, n is a constant which shows greatness of relationship between adsorbate and adsorbent.

In Freundlich adsorption isotherms, the model assumes a heterogeneous surface with a no uniform distribution of heat of adsorption over the surface [20]. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero, respectively. FIG 11 shows the applicability of this equation on the adsorption of Cd (II) on the ES. The K_F and n for Cd (II) adsorption onto ES were calculated from intercept and the slope of the figure giving the values 2.417 mg g^{-1} and 0.1005, respectively with a correlation coefficient $R^2 = 0.653$. It was known that favourable adsorption occurs when n >1 [4].

From the correlation coefficient values, we can conclude that, Langmuir model is more appropriate for the adsorption equilibrium experimental data.
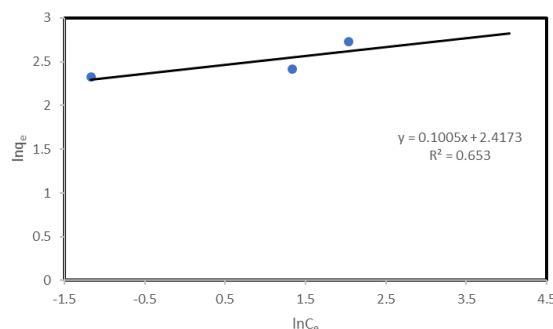

Fig 11: Freundlich plot for Cd (II) adsorption onto 0.1g ES

F. Influence of temperature and thermodynamic parameters

The temperature has two main effects on the sorption process. Increasing the temperature is known to raise the rate of the sorbate diffusion; changing the temperature will change the equilibrium capacity of the sorbent for a particular sorbate. In this research, a series of experiments were conducted on the adsorption of 20 mg L^{-1} Cd (II) onto 0.1 g of ES at 278, 283, 298, 313 and 333 K, to investigate the effect of temperature on the sorption dynamics at various stirring times. Fig 12 illustrated that the sorption increased as the temperature increased confirming that the process is endothermic in nature. Such results may either be attributed to the creation of some new active sites on the sorbent or to the acceleration of some originally slow adsorption steps. Additionally, the enhancement of mobility of Cd (II) from the bulk of solution towards the adsorbent surface should also be taken into consideration. Also, there was a decrease in the equilibration time to reach

to a maximum Cd^{2+} adsorption. Such results could suggest that the adsorption of Cd (II) included chemical bond formation and ion exchange. Accordingly, chelate formation may take place between Cd (II) and oxygen atoms on the ES surface together with ion exchange to form $CdCO_3$. This adsorption process may find an application in the industrial wastewater treatment for the removal of Cd (II).
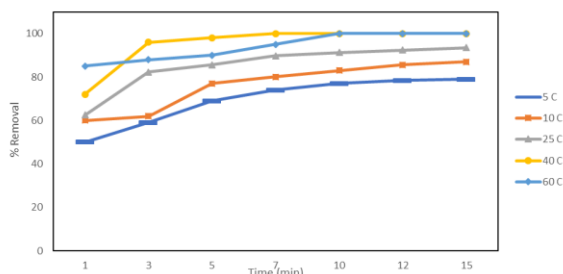

Fig 12: Influence of temperature on the % removal of Cd(II) using ES at different shaking times

In order to study the thermodynamic parameters for the adsorption of Cd^{2+} by ES, the distribution coefficient K_d $(L.g^{-1})$ was calculated at 278, 283, 313, 333 K according to the following equation [21], [22].

$$K_d = q_e / C_e \qquad (10)$$

The K_d values were 1.86, 2.97, 7.02, and 20.11 $L.g^{-1}$ at 287, 382, 283, 313 and 333 K, respectively. The results show that the K_d increased with the increasing of temperature and indicating that the sorption process of Cd (II) may be endothermic. The enthalpy change (ΔH^o) and the entropy change (ΔS^o) were calculated from the slope and intercept of the plot of ln K_d against 1/T (Fig 12) according to the following equation [21, 23, 24]:

$$\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \qquad (11)$$

The Gibbs free energy change (ΔG^o) was calculated from the relation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (12)$$

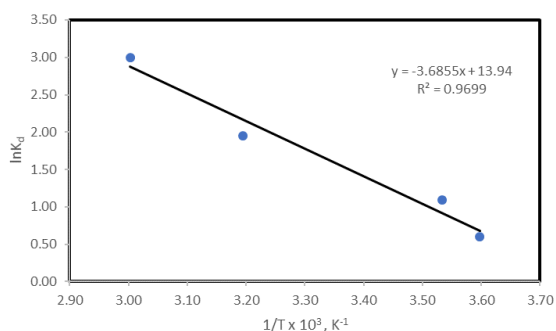**Fig 12: Thermodynamic distribution coefficient (Kd) calculated for the adsorption of Cd (II) onto ES as a function of temperature**

The ΔH^o value was solved to be equal (30.64 J mol^{-1}). The positive value of ΔH^o proved that the sorption process is endothermic. The ΔS^o value was (115.89 $Jmol^{-1}k^{-1}$).

From the results of the present investigation, it was suggested that Cd(II) in bulk phase (aqueous solution) was in a much chaotic distribution compared with the relatively ordered state of solid phase (sorbent surface). Furthermore, the ΔG^o is -13.85, -5.64, -50.72, and -83.09 kJ mol^{-1} at 278, 283, 313 and 333 K, respectively. The value of ΔG^o indicated that the process of Cd^{2+} adsorption onto the surface of ES was increased by increasing the temperature; which proved that the adsorption process was endothermic.

G. Applications

To study the applicability of the suggested procedure, a number of experiments were carried out to recover 20 mg L^{-1} of Cd (II) added to aqueous and some natural water samples. The experiments of adsorption were performed using 50 ml sample solutions with their natural pH values. The results are shown in Table 1.

TABLE 1
Recovery of Cd (II) added to some natural water samples using 0.1 g of ES sorbent

Sample (location)	Added (mg L^{-1})	Adsorbed (mg L^{-1})	Removal %
Distilled water	20	19.8	99%
Tap water (Mansoura City)	20	19.5	97.5%
Nile water (Mansoura City)	20	19.4	97%
Underground water (Mansoura City)	20	18.8	94%

IV. CONCLUSIONS

This research reveals that the powdered eggshell (ES) could be used as a cheap and effective inorganic sorbent for the removal of Cd (II) ions from aqueous solutions, which included some natural water samples. Adsorption is a pH-dependent process; there was a rise in cadmium ions removal by increasing the pH up to 9. The adsorption process occurred mainly at the surface of the solid EG and slightly in the internal pores. The data of adsorption are perfectly described by the models of Freundlich and Langmuir on the concentration range has been studied. Adsorption is chemical and endothermic process in its nature. However, the values of negative $\Delta G\circ$ showed that the adsorption of Cd (II) ions on ES is spontaneous, feasible and thermodynamic. Importantly, the cadmium ions were detained by ES sorbent and would not be leached out using acids due to the solubility of the sorbent. Accordingly, the waste of the metal-loaded solid could be solidified to

an eco-friendly form; that achieve the double-fold aim of water treatment and solid waste disposal.

REFERENCES

[1] Zendehdel, M., A. Barati, and H. Alikhani, Removal of heavy metals from aqueous solution by poly (acrylamide-co-acrylic acid) modified with porous materials. Polymer bulletin, 2011. 67(2): p. 343-360.

[2] Hokkanen, S., E. Repo, and M. Sillanpää, Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulose. Chemical engineering journal, 2013. 223: p. 40-47.

[3] Sen, T.K., S. Mahajan, and K.C. Khilar, Adsorption of Cu^{2+} and Ni^{2+} on iron oxide and kaolin and its importance on Ni2+ transport in porous media. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2002. 211(1): p. 91-102.

[4] Murugesan, A., et al., Removal of Pb (II), Cu (II) and Cd (II) ions from aqueous solution using polyazomethineamides: equilibrium and kinetic approach. Desalination, 2011. 271(1-3): p. 199-208.

[5] Ning, R.Y., Arsenic removal by reverse osmosis. Desalination, 2002. 143(3): p. 237-241.

[6] Bailey, S.E., et al., A review of potentially low-cost sorbents for heavy metals. Water research, 1999. 33(11): p. 2469-2479.

[7] Reddad, Z., et al., Cadmium and lead adsorption by a natural polysaccharide in MF membrane reactor: experimental analysis and modelling. Water Research, 2003. 37(16): p. 3983-3991.

[8] Ciesielski, W., et al., Interactions of starch with salts of metals from the transition groups. Carbohydrate polymers, 2003. 51(1): p. 47-56.

[9] Hu, Z., et al., Chromium adsorption on high-performance activated carbons from aqueous solution. Separation and Purification Technology, 2003. 31(1): p. 13-18.

[10] Rahman, M.M., et al., Removal of heavy metal ions with acid activated carbons derived from oil palm and coconut shells. Materials, 2014. 7(5): p. 3634-3650.

[11] Özcan, A.S., B. Erdem, and A. Özcan, Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2005. 266(1-3): p. 73-81.

[12] EL SAYED, G.S., A.A.H. EL ASMY, and A.M. EL NOKRASHY, Batch removal of nickel by eggshell as a low cost sorbent. 2011.

[13] Tsai, W.-T., et al., Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution. Bioresource technology, 2008. 99(6): p. 1623-1629.

[14] Stadelman, W., Encyclopedia of food science and technology. 2000.

[15] Monier, M. and D. Abdel-Latif, Synthesis and characterization of ion-imprinted chelating fibers based on PET for selective removal of Hg2+. Chemical engineering journal, 2013. 221: p. 452-460.

[16] Ghazy, S., A. El-Asmy, and A. El-Nokrashy, Separation of chromium (III) and chromium (VI) from environmental water samples using eggshell sorbent. Indian Journal of Science and Technology, 2008. 1(6): p. 1-7.

[17] Giddings, J.C., Dynamics of chromatography: principles and theory. 2011: CRC Press.

[18] Mckay, G., M. Otterburn, and A. Sweeney, The removal of colour from effluent using various adsorbents—III. Silica: rate processes. Water Research, 1980. 14(1): p. 15-20.

[19] Gupta, G. and S. Shukla, An inexpensive adsorption technique for the treatment of carpet effluents by low cost materials. Adsorption science & technology, 1996. 13(1): p. 15-26.

[20] Foo, K.Y. and B.H.J.C.e.j. Hameed, Insights into the modeling of adsorption isotherm systems. 2010. 156(1): p. 2-10.

[21] Sarı, A., M. Tuzen, and M. Soylak, Adsorption of Pb (II) and Cr (III) from aqueous solution on Celtek clay. Journal of Hazardous Materials, 2007. 144(1-2): p. 41-46.

[22] Mane, V.S., I.D. Mall, and V.C. Srivastava, Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. Journal of Environmental Management, 2007. 84(4): p. 390-400.

[23] Donat, R., et al., Thermodynamics of Pb2+ and Ni2+ adsorption onto natural bentonite from aqueous solutions. Journal of colloid and interface science, 2005. 286(1): p. 43-52.

[24] Gupta, S.S. and K.G. Bhattacharyya, Interaction of metal ions with clays: I. A case study with Pb (II). Applied clay science, 2005. 30(3-4): p. 199-208.