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Investigating the efficiency of humic acid removal from aquatic solutions with eggshell adsorbent

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ABSTRACT

This functional and analytical study aims to determine the efficiency of humic acid removal from aquatic solutions with an organic eggshell absorbent reactor. The studied variables included pH, contact time, dosage of adsorbent and concentration of humic acid. A sample of distilled water with (5–15 mg/L) humic acid was prepared. The eggshell powder was prepared in a laboratory incubator at 105°C for 12 h. The efficiency of removal in different conditions of variables: pH (4–10), contact time (1–80 min), and dosage of adsorbent (4–6 mg/L) was investigated. The average size of eggshell powder diameter was 2 µm. The main component of the eggshell is calcium carbonate ($CaCO_3$). The surface adsorbent apertures are linked and heterogeneous in a regular sequence. At an ideal pH of 4, a contact period of 60 min, and a dose of adsorbent of 5 mg, the maximum effectiveness of humic acid concentration removal of 5 mg/L was attained. The surface adsorbent of humic acid on the eggshell follows a Langmuir equilibrium model ($R^2 > 0.99$). The high contact time increases the removal efficiency and decreases the concentration of absorbent and pH in the removal of acid humic. In total, the findings show that the powdered eggshell could be a suitable, efficient, and low-cost adsorbent for humic acid removal from drinking water purification, in terms of small diameter, hemogeneous surface, and consequently very high reactivity.

Keywords: Aquatic solutions; Eggshell; Humic acid; Isotherm; Water purification; Surface adsorbent

1. Introduction

Regarding the control of surface water during the past few years, dams and reservoirs are considered as the main source of drinking water and have produced high socio-economic advantages and disadvantages such as adverse effects on the eco-environment and society [1]. Based on the importance of humic acid (HA), HA constitutes 60%–90% of natural organic compounds. Humic substances have a negative influence on living organisms which have the ability to transport metals and other pollutants. According to the meaning of humic material (HM), HM is an unformed, acidic, often aromatic, and hydrophilic complex. HA was reported as natural organic material and the main cause of the natural color, increased turbidity, and the potential for the formation of disinfectant products, such as trihalomethanes (THMs) and haloacetic acids (HAAs) [2–4]. Based on the importance of the THMs formation and the health risks of these compounds such as carcinogenicity, teratogenicity and mutagenicity, the researchers suggested the

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most important way for preventing the carcinogenic compounds by removing organic compounds [5]. International Agency for Research on Cancer (IARC) groups chloroform and bromodichloromethane as compounds which are presumably carcinogenic to humans (Group 2B) [6]. Several studies which performed on laboratory animals showed a positive correlation between the risk of colon, bladder, and rectum cancer and THMs-containing water. The effects on reproductive capacity, the property of congenital anomalies, damage to certain organs of the body, such as the liver and kidneys, damage to the nervous system and the appearance of adverse effects in the circulatory system and blood chemistry, are the syndrome of THMs. The guideline level for THMs in drinking water is 100 μg/L, based on European guideline [7,8]. The increase in natural organic matters (NOMS), such as HA levels in ground and surface water have been mainly attributed to anthropogenic (the food, leather, and wood manufacturing) and natural (the microbial degradation of dead plant matter) sources [9]. The concentration of NOMS of Karaj, Jajrood, and Lar Rivers is 11.33, 12.9, and 8.53 mg/L, respectively [10]. Typical THMs removal methods and their precursors (NOMs) include the use of active carbon, membrane processes, advanced coagulation, and advanced oxidation processes [11]. However, these methods have a number of drawbacks, the most significant of which are high operating costs and initial investment, eclipse, high sludge production, water pH lowering, extremely caustic water generation, and the necessity for resuscitation operations [12]. The advantages of adsorption technology were applicable in batch and continuous arrangements, easier accessibility, economical and retain effectiveness at a low fluoride concentration [13]. However, due to expanding economic adsorbents with ample adsorption capacity, these adsorbents have become widely used in removing and isolating pollutants from contaminated water and sewage from industries and factories due to their numerous advantages, such as high efficiency, short-term performance, reuse, and ease of application [14]. Moussavi et al. [15] conducted a study on the efficiency of multi-walled carbon nanotubes (MWCNTs) in adsorbing of HA from aqueous solutions. The results showed that because of small size, high specific surface area, crystalline shape, and unique network order, and resulting in high reactivity and significant performance of multi-walled carbon nanotubes as adsorbents to remove the organic pollutants from water solutions, this adsorbent could be effective in HA removal. The limited solubility of CNTs in aqueous media restricts their uses, as does the inability to investigate the influence of temperature and regeneration efficiency on HA removal, as well as longer contact time. Kashi et al. [13] investigated the efficacy of bone-char in the adsorption of fluoride from drinking water in metropolitan areas. Failures to examine adsorption kinetics, the influence of temperature and regeneration efficiency on fluoride elimination are all flaws in this work. Eustáquio et al. [16] conducted a study on the effectiveness of modification of activated carbon in the adsorption of HA from water. The gaps of this study are failures to check the concentrations of HA, the effect of temperature and regeneration efficiency on HA removal. According to the innovation, eggshell powder as adsorbent is a way of reduction lavish animal waste. According to the Ministry of Jihad Agriculture, about 1.2 million tons of eggs are produced, marketed, and discarded as waste without being recycled annually in Iran country. Dumped eggshell produce an unpleasant odor from biodegradation. The applications of eggshell wastes are at biodiesel production, as an adsorbent, as a fertilizer, as a biomaterial. Therefore, eggshell powder, that is a natural and environment-friend adsorbent, was used to remove HA as a natural organic pollutant. We have designed a batch reactor based on eggshell powder, to increase the adsorption capability of eggshell for HA in an aqueous solution. We aimed to (1) optimize the preparation conditions of eggshell powder; (2) determine the characteristics of eggshell powder using scanning electron microscope-energy-dispersive X-ray spectroscopy (SEM-EDX), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD); (3) investigate the effect of the eggshell powder dose, initial concentration of HA, and initial pH on adsorption performance; (4) evaluate the adsorption properties of eggshell powder through kinetic, and adsorption isotherm models; (5) investigate the mechanism of HA adsorption on eggshell powder.

2. Material and methods

In this study, the process of using eggshell powder as a method for removing organic pollutants has been investigated. This research is an experimental study conducted on a pilot scale. The process involves the preparation of an eggshell absorbent, the characterization of eggshell, and the performance of HA removal experiments in the batch absorbent reactor of the powdered eggshell.

2.1. Preparation of eggshell

First, chicken eggshells were collected from local confectioneries of Tehran City. The eggshells were boiling in deionized water for 30 min and washed several times with deionized water, and dried at room temperature. Then eggshells were dried in a hot air oven (Dena, Iran) at 105°C for 12 h. Finally, the adsorbent ground with a laboratory electrical crusher (AIKA, Germany) for 20–30 s and were sieved several times to obtain a homogeny fraction of eggshell in a specific size (60–100 mesh/0.25–0.104 mm), according to ASTM standard [15]. The powdered eggshell was stored in the desiccator after pre-treating with a solution of sodium hypo-chloride (NaOCl) (Merck, Germany), to eliminate the dust particles [17].

2.2. Determination of eggshell characteristics

SEM image (Philips XL30, Holland) was prepared from powdered eggshell. XRD patterns are measured using RINT 2000 (Rigaku Instrument Corp.) with Cu Ka radiation for confirming the structure and mineral composition of powdered eggshells (Philips X'PERT, Holland). An EDX system was used to determine the structural characteristics of the powdered eggshell adsorbent. The eggshell adsorbent components were determined with X-ray distribution device (XRD, Philips USA, 3500 TM). The surface area of powdered eggshell was tested through nitrogen adsorption measurements at 77 K using Micromeritics Gemini 2370 equipment. The zeta potential was tested with a Nano Zetasizer (Philips, Holland).

2.3. Preparation of batch reactor

The batch reactor was a 250 mL glass rectangular container (10 cm × 6 cm × 6 cm). Magnetic stirrer (AIKA, Germany) is used for homogeneous mixing of water samples (120 rpm). For each test, 20 mL of sample water is poured into the reactor. All tests are performed at laboratory temperature (20°C).

2.4. Analytical methods

The experiments were repeated in triplicate. To evaluate the effect of adsorption on the removal process, the samples at pH (4, 7, and 10), contact time (45, 60, and 75 min), HA concentration (5, 10, and 15 mg/L), adsorbent concentrations of powdered eggshell (4, 5, and 6 mg/L) were adsorbed. Therefore, the number of samples was 256 according to the factorial method. Measurement of HA concentration after membrane filtration (0.45 µm) using a spectrophotometer (DR5000, HACH, America) at the maximum wavelength of 254 nm according to the instructions in the standard methods for the examination of water and wastewater. HA was determined by standard method 5510B [18]. pH was measured by pH meter (Hack, America). Chloride acid (HCl) and sodium hydroxide solutions (0.1 N) (Merck, Germany) were used for pH adjustment. The percentage HA removal was calculated according to Eq. (1) [19]:

$$\text{Removal}(\%) = \left(1 - \frac{C_t}{C_{t0}}\right) \times 100 \quad (1)$$

where the percentage of HA removal (R, %) and the HA value before and after treatment (C_{t0} and C_t, mg/L) expressed.

The removal HA adsorption capacity of the regenerated powdered eggshell was calculated according to Eq. (2) [20]:

$$\text{DC}_{\text{FC}} = \left(\frac{S_0 - S_t}{X_{\text{FC}}}\right) \quad (2)$$

where the removal HA capacity of the regenerated powdered eggshell (DC_{FC}, mg/g), the HA concentration before and after treatment (S_0 and S_t, mg/L), and the adsorbent mass of powdered eggshell consumed (g) expressed. To optimize runs and data analysis, based on Taguchi model, was used to study vestiges of the selected variables and minimize the number of experimental runs.

2.5. Adsorption isotherms

We used two isotherms with two parameters, for example Langmuir and Freundlich in order to fitting to explain adsorption processes at the equilibrium point (Table 1).

2.6. Adsorption kinetics

Two kinetic models, including first-order, and second-order, were used for fitting the experimental data and obtain the best results (Table 1).

3. Results

The reduction of HA from urban drinking water was investigated in an adsorption reactor with filler particles made from powdered eggshell in batch mode. Several operational variables were investigated for effects on process reduction capability. The following results were obtained from experiments:

3.1. Characterization of powdered eggshell

Fig. 1 shows the adsorbent SEM images of the powdered eggshell. As can be seen, the average size of the powdered eggshell diameter is 2 µm.

Fig. 2 shows the XRD analysis of powdered eggshell. The XRD measurements accomplished at 2θ of 0° to 60°. In Fig. 2, the powdered eggshell consists of elements like calcium (Ca) and phosphorus (P), which are the main and partial elements, respectively. The spectrum of the analyzed powdered eggshell was adapted to 34.5°–57.8° 2θ.

Fig. 3 shows the EDX analysis of powdered eggshell. As is found in Fig. 3, the analyzed powdered eggshell is composed of elements including calcium (Ca), oxygen (O), magnesium (Mg), carbon (C), and so on. A spectrum of decomposed eggshell powder was matched with 2370

Table 1
Adsorption isotherms and kinetic models

		Equation	Parameters	Equations	References
Isotherm model	Langmuir	$q_e = \frac{bC_eQ_0}{1+bC_e}$	$Q_0 = \frac{1}{\text{intercept}}$ $b = \frac{1}{\text{slop / intercept}}$	3	[21]
	Freundlich	$q_e = K_F C_e^{1/n}$	$n = \frac{1}{\text{slop}}$ $K_F = \exp^{\text{intercept}}$	4	[22]
Kinetic model	First-order	$\ln A = \ln[A]_0 - Kt$	–	5	[23]
	Second-order	$\frac{1}{[A]} = \frac{1}{[A]_0} + Kt$	–	6	[24]

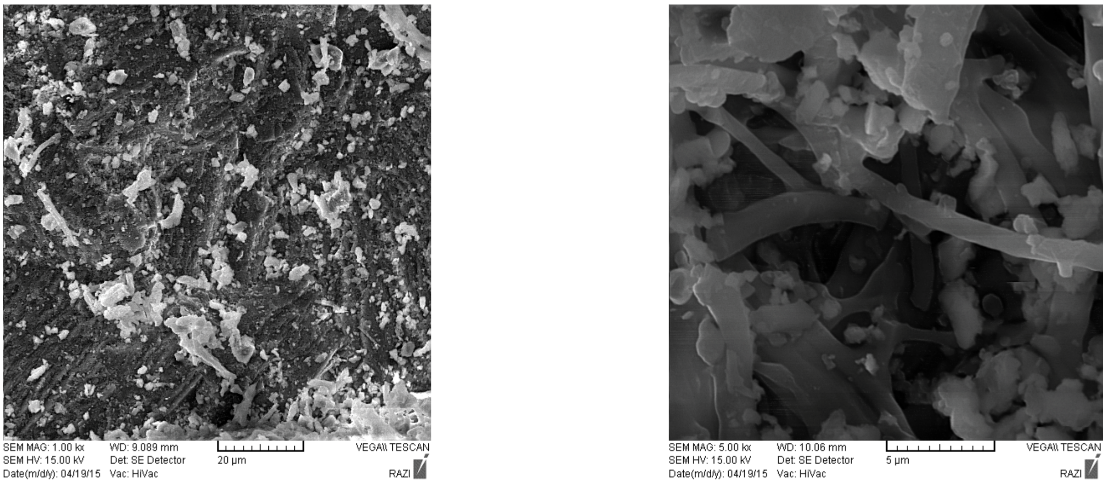

Fig. 1. SEM image of powdered eggshell (a) before and (b) after treatment.

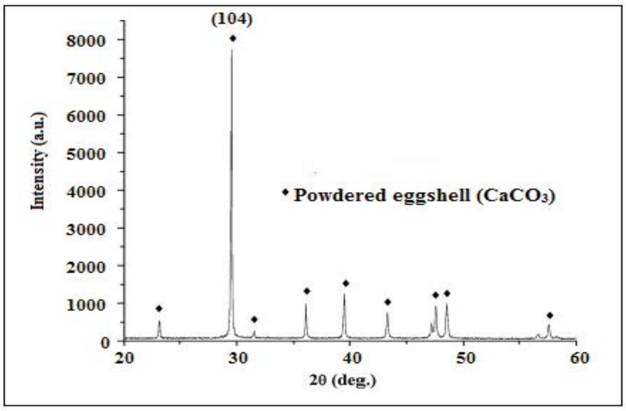

Fig. 2. XRD analysis of powdered eggshell.

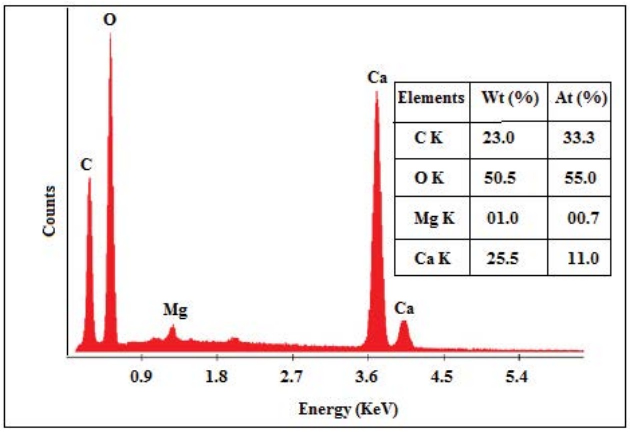

Fig. 3. EDX analysis of powdered eggshell.

standards. Therefore, these maxima confirm that the main part of the eggshell powder is calcium carbonate. The ratio of calcium to carbon to eggshell powder is 2.9.

SEM analysis is another useful tool for analyzing the surface absorption in morphology level. The dense, non-sticky, porous, and irregular structure of adsorption is shown clearly in Fig. 1. Therefore, the apertures on the adsorption surface are regular, sticky, and more homogeneous. As shown in Fig. 1, homogeneous apertures lead to a larger surface level to adsorb HA. The diameter of the aperture is the sign of the predicted adsorption surface of the HA molecule at the adsorption surface. It shows the formation of porous surfaces which by increasing the surface and adsorbing capacity, supports the adsorption surface. SEM analysis shows that the removal of HA affects the direction of eggshell powder. The tested sample shows a regular and sticky appearance that causes more HA adsorption. Characteristics of eggshell powder are shown in Table 2. The specific surface area Brunauer–Emmett–Teller (BET) measurements were performed and the highest BET for powdered eggshell was 7.43 m^2/g. Powdered eggshell functional groups were identified by the FTIR analysis (Fig. 4). The maxima were selected in the range of 710, 875, 1,420, 1,807, and 2,520 cm^{-1} with a maximum $CaCO_3$.

3.2. Effect of solution pH

Experiments on the absorbance level at initial pH of 4–10 range were performed in laboratory conditions such as contact time (60 min), HA concentration (5 mg/L), and powdered eggshell absorption (4 mg). When the pH increased from 4 to 7, the average removal of HA decreased from 72% to 69%. The removal of HA in the adsorption reactor was mainly influenced by the pH of the water. Less absorption in the alkali pH can be created due to the chemical and electrostatic interactions between the surface and the HA ion (Fig. 5).

3.3. Effect of dosage adsorbent

Absorption experiments were conducted at 4 to 6 mg/L spectra in laboratory conditions such as contact time (60 min), HA concentration (5 mg/L), and pH (7). When the amount of absorbent increased from 4 to 5 mg, the average removal of HA increased from 72% to 90%. The increase for adsorbent increased the percentage of HA removal, which is associated with an increase in sportive levels, as active

Table 2
Eggshell absorbent characteristics

Eggshell	Variable
8.2	pH_{ZPC}
1.148	Density (g/cm^3)
7.43	Specific surface area (BET) (m^2/g)
2	Diameter (μm)

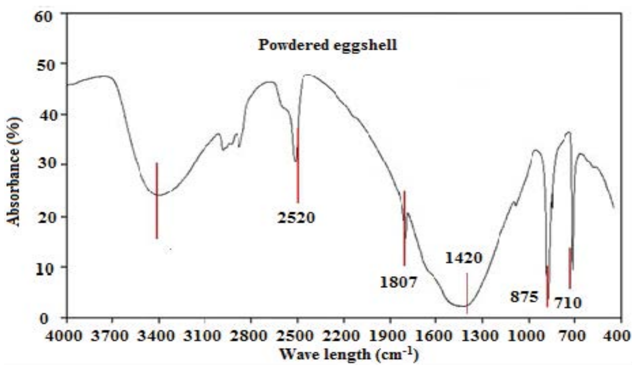

Fig. 4. FTIR analysis of powdered eggshell.

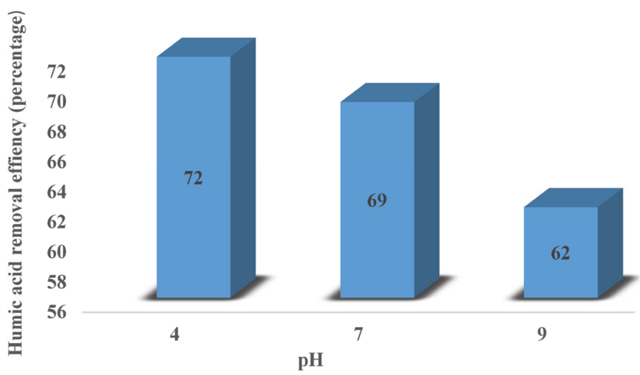

Fig. 5. Effect of water pH on the HA removal in absorption batch reactor (T = 20°C; HA dosage = 5 mg/L; contact time = 60 min; powdered eggshell dose = 5 mg).

adsorption sites and porosity coefficients became more available. The optimum amount of powdered eggshell absorption is 5 mg/L. It can be seen that 5 mg/L has a better absorption rate than 4 mg/L (Fig. 6).

3.4. Effect of contact time

The absorption level experiments were conducted as a function of the time levels in the range of 45–75 min in laboratory conditions such as the amount of powdered eggshell absorption (5 mg/L), HA concentration (5 mg/L), and pH value (7). When the contact time increased, the ability to HA removal increased. When the contact time increased from 45 to 60 min, the average HA removal increased from 89% to 92%. When the contact time was high, at first the ability to

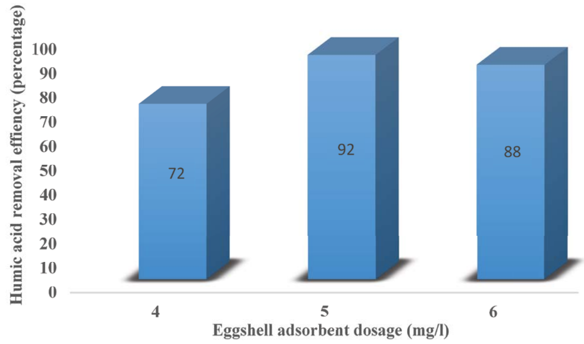

Fig. 6. Effect of powdered eggshell adsorbent dosage on HA removal in the batch absorption reactor (T = 20°C; HA dosage = 5 mg/L; contact time = 60 min; pH = 7).

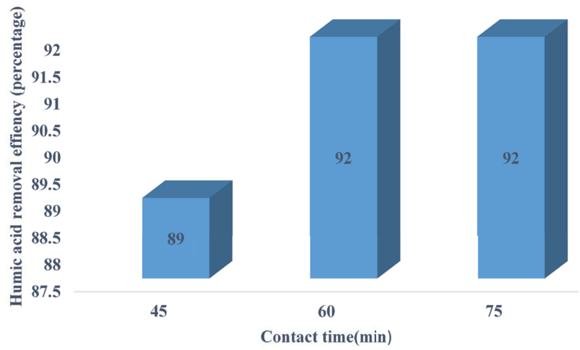

Fig. 7. Effect of contact time on the HA removal in the batch adsorption reactor (T = 20°C; HA dosage = 5 mg/L; pH = 7; powdered eggshell dose = 5 mg).

HA removal increased, but then gradually increased to a less or more stable amount while achieving equilibrium. Since there was no increase in the ability to remove HA between 60 and 75 min, the time interval of 60 min for the absorption levels of eggshell was selected. During this period, the remaining HA changed from a maximum of 1.07 mg/L for 20 min of contact time to a minimum of 0.0 mg/L for a 60 min contact time. The highest removal rate of powdered eggshell (5 mg/L) was obtained for 60 min (Fig. 7).

3.5. Effect of concentration of HA

Experiments on the adsorption level at the initial concentrations of HA in the range of 5–15 mg/L were performed in laboratory conditions such as contact time, amount of powdered eggshell adsorption surface and pH value (7). When the initial concentration of HA was increased from 5 to 15 mg/L for 60 min, the average HA removal decreased from 97% to 87% (Fig. 8).

3.6. Effect of temperature

Adsorption experiments were carried out with the water temperature in the range of 288 to 318 K in the experimental conditions such as contact time (60 min), adsorbent amount of powdered eggshell (5 mg/L), HA concentration (5 mg/L), and pH value (7). The adsorption of HA protonated on powdered eggshell was studied at various temperatures, 288–318 K. The mean HA protonated removal decreased from 100% to 64% when the initial temperature decreased from 293 to 318 K for the duration of 60 min (Fig. 9).

3.7. Effect of regeneration efficiency

The effect of adsorbent reusability on HA removal was carried out with the tenth repetition in the experimental conditions such as contact time (60 min), adsorbent amount of powdered eggshell (5 mg/L), HA concentration (5 mg/L), and pH value (7). The mean HA protonated removal decreased from 100% to 60% after 10 times reuse due to decreasing active sites on the adsorbent surface. The regeneration efficiency decreased after each desorption cycle. Up to 4 times reuse, there was no significant reduction in HA removal efficiency. In view of economic the application of powdered eggshell adsorbent for at least 4 times is cost-effective due to its ability to reuse adsorption with high removal efficiency (Fig. 10).

4. Discussion

4.1. SEM and XRD analysis

SEM analysis was used to evaluate the morphology and surface characteristics of eggshell membranes. The results of this analysis in Fig. 4 shows the irregular structure with the porous surface of the powdered eggshell. This porous structure plays a special role in absorption capability and leads to an increase in the absorption of HA material into the absorbent in terms of the increased contact surface. The chemical composition of the eggshell was measured by using an XRD and the results indicate that the main component is calcium that it can be replaced with the pollutant during the ion exchange reaction. Zulfikar et al. [25] discovered the crystallinity of powdered eggshell and the presence of holes in the structure. The BET of powdered eggshell was 22.4 m^2/g, according to Nathan [26]. Calcium carbonate (51%) was the predominate component of powdered eggshell, according to Gajjar and Zala [27]. According to XRD analysis, CaO, $CaCO_3$ and $Ca(OH)_2$ were found in powdered eggshell samples, according to Mohadi et al. [28]. Bhaumik et al. [29] reported that the particle size of the eggshell powder is 150–350 μm. The highest BET for eggshell powder was 7.43 m^2/g. Agarwal and Gupta [30] reported that the highest composition of powdered eggshell is calcium carbonate. The spectrum of the analyzed powdered eggshell was adapted to 34.5° (main peak), 42.2°, 46°, 50.9°, 56°, and 57.8° 2θ and confirmed the presence of calcite ($CaCO_3$) in the eggshell texture. This result is agreed to Daraei et al. [31]. The spectrum of the analyzed powdered eggshell included about 710 cm^{-1} (P–O stretching), 875 cm^{-1} (S=O stretching), 1,420 cm^{-1} (C=O stretching), 1,807 cm^{-1} (CO_3 stretching), 2,520 cm^{-1} (O–H stretching) shows $CaCO_3$. Ahmed et al. reported that the main composition of the eggshell powder is calcite [32].

4.2. pH effect

pH is the main variable in the removal efficiency of pollutant by absorption method in terms of effect on pollutant ionization and absorption surface load. Based on the results, the removal rate at pH 7 is the highest and less than 7, but in more than that amount, that is, in the alkaline condition, this percentage has decreased. Daraei et al. [31] in the removal of phenol also pH rises to about 3.44 for phenol. Afterward, with the gradual increase of pH to 10, the efficiency begins to decrease. These results suggest that pH has an impact on both the absorbent surface load and the quantity of HA ionization in water. The absorbent is

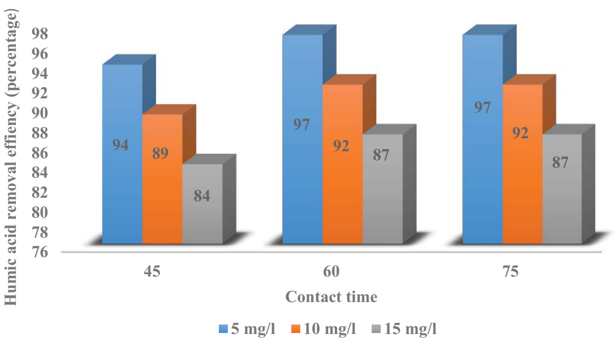

Fig. 8. Effect of initial HA concentration on the HA removal in the batch adsorption reactor (T = 20°C; pH = 7; contact time = 60 min; powdered eggshell dose = 5 mg).

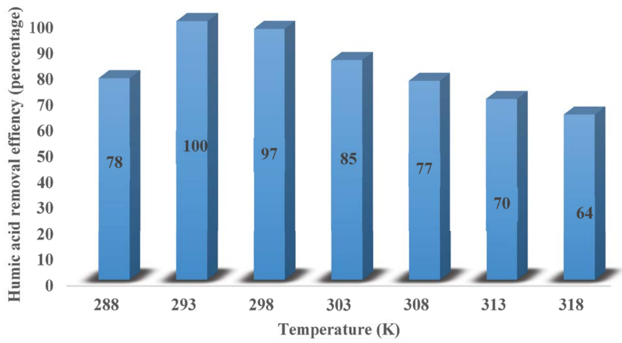

Fig. 9. Effect of temperature on HA removal in the batch adsorption reactor (HA dosage = 5 mg/L; contact time = 60 min; pH = 7; powdered eggshell dose = 5 mg).

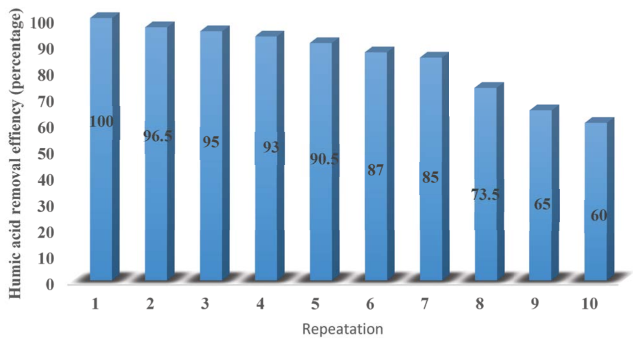

Fig. 10. Effect of repetition on HA removal in the batch adsorption reactor (T = 20°C; HA dosage = 5 mg/L; contact time = 60 min; pH = 7; powdered eggshell dose = 5 mg).

surrounded by a positive charge at pH levels less than 4, and the pollutant ions experience a strong pull. Furthermore, the opacity of the samples increases as the pH rises. This increase in opacity can be in terms of the dissolution of some membrane compounds such as water fat, which may be one of the reasons for reducing the system efficiency by increasing pH. Thus, low HA removal at higher pH may be attributed to decreasing in protonation. This is in agreement with Bhatti and Amin [33], who reported that the fastest removal rate occurred at a pH equal to 6.5. This phenomenon can be in terms of the exposures of active adsorption sites that allow HA ions to allow direct contact with the eggshell powder, thus increasing the absorption capacity. Increasing the amount of absorption also led to a decrease in the range between the absorption of eggshell and absorbed material in terms of the formation of the masses. Increasing the amount of absorption level leads to an increase in pH. Zulfikar et al. [34] reported that the fastest removal rate of HA occurred at a pH equal to 4.01 with eggshell powder.

4.3. Effect of dosage adsorbent

The quantity of absorption has risen with increasing adsorbent content, according to the conclusions of this investigation, while more precise study results suggest that the percentage of absorption has decreased with increasing adsorbent mass. The case of this phenomenon is a lack of saturation of active sites in the absorption of pollutants, with means that increasing adsorbent mass does not fully utilize the total capacity of active sites present in the adsorbent surface, resulting in a decrease in adsorption per unit mass of adsorbent. The results show that the amount of powdered eggshell up to 5 mg/L has increased the rate of absorption of HA from water, but up to 6 mg/L absorption has decreased somewhat. Besides, in the removal of anionic dyes with rice milling waste absorption, Bhatti and Safa [35] showed similar results that the adsorption of pollutants has increased with increasing adsorbent content. Suneetha et al. [36] reported that the optimum amount of activated carbon of plant skins, Vitex negundo, was 4.0 g/L. Oulego Blanco et al. [37] reported that the best results were obtained with copper (15% wt.) supported on calcined eggshell, achieving a HA as chemical oxygen demand removal of 74.1% after 3 h of wet oxidation.

4.4. Effect of contact time

The results show that by increasing the contact time to 60 min, the removal efficiency is increased and then, with increasing contact time to 75 min, the removal efficiency remains almost constant. HA absorption at high time period can be attributed to the superficial bond among active compounds in the absorbent surface and the ion of pollutants. The contact time of 60 min for the removal of cadmium with eggshell powder by Ozcan et al. [38]. These alternations might be the result of the fact that adsorption levels were unoccupied and active at start, as well as the gradient dissolved concentration and the possibility of a large absorbent reactor. The rate of HA absorption in the eggshell absorber's surface then reduced dramatically in the absorbent solution. This experiment showed a single layer of HA ions on the outer surface and powdered eggshell apertures and the distribution of aperture on the inner surface of the powdered eggshell throughout the shell during the experiments. The contact time of 40 min for the removal of anionic dye acid red nylon 57 with titanium dioxide-calcined eggshell powder by El-Kemary et al. [39].

4.5. Effect of concentration of HA

The findings of this experiment revealed that when the pollutant concentration increased, the absorption efficiency declined. Furthermore, at a concentration of 5 mg/L, this quantity had the largest percentage decrease of 97%. This decrease in efficiency with rising concentrations might be related to lower activity levels on the absorbent surface, since the active bands become less accessible to the pollutants at higher concentrations, reducing the rate of mass transfer. The adsorption capacity increases from 56.27 to 70.25 mg/g with increase in initial dye concentration from 20 to 100 mg/L by Chowdhury et al. [40]. At HA concentrations of 2, 5, and 10 mg/L, the adsorption capacities were 4.39, 17.37, and 29.73 mg/L, respectively, as the contact time reached 10 min by Naghizadeh et al. [41]. It is concluded that powdered eggshell adsorbent has a limited number of binding sites, which become saturated at a certain concentration. On the other hand, increasing the concentration of HA leads to lower pH_{ZPC} and lower electrostatic absorption between adsorption levels and HA anions.

4.6. Effect of temperature

Pretests show that when the temperature was increased from 293 to 303 K for 60 min, the average HA removal decreased from 100% to 85% due to occurring exothermic reaction. Temperature was increased from 105°C to 510°C, the average HA removal decreased to occurring transformation of calcium hydroxide to calcium oxide by Kim and Olek [42]. By increasing the temperature, the *solubility* HA increased and adsorption of HA by eggshell s powder kinetically decreased in terms of increasing repulsive force and depressing bond Ca-HA. If the HA ions were larger than the absorption site, the absorption level was reduced due to the saturation of the adsorption site at constant concentrations.

4.7. Mechanism, adsorption isotherms, and reaction kinetic

The proposed mechanism of HA uptake rate onto the powdered eggshell surface included the replacement (ion exchange adsorption), chelation, intra-particle diffusion, and electrostatic attraction. The CO_3 stretching could act as adsorption sites for HA protonated. The removal of HA protonated occurred by chemisorption in monolayer fashion on the surfaces of powdered eggshell in terms of the availability of higher binding sites and due to less aggregation of powdered eggshell. The most common desorbing agents were used, such as 0.1 M chloric acid (HCl) and nitric acid solutions, and HCl was used to renew the powdered eggshell adsorbent. The Langmuir isotherm model and second-order kinetic are used to reduce HA (Tables 3 and 4).

Regarding the increase of concentration gradient, it increased the balanced adsorption until adsorption

Table 3
Parameters of isotherm models of powdered eggshell

Isotherm model	Parameters
Langmuir	q_{max} = 101 (mg/g) K_L = 1.16 (L/mg) R_L = 0.016 R^2 = 0.996
Freundlich	n = 3.04 K_F = 43.51 (mg/g)(L/mg)$^{1/n}$ R^2 = 0.927

Table 4
Parameters of kinetic reactions of powdered eggshell

Kinetic reactions	Parameters
First-order	q_e = 20.05 (mg/g) K_1 = 0.28 (/min) R^2 = 0.926
Second-order	q_e = 48.7 (mg/g) K_2 = 0.01 (g/mg min) R^2 = 0.998

saturation was obtained. When the initial concentration of HA increased, the ability to HA removal was reduced. On the other hand, increasing the concentration of HA leads to lower pH_{ZPC} and lower electrostatic absorption among the absorption levels and HA anions. It is concluded that desorption with the 0.1 M HCl was by ion exchange process. The highest regeneration was reported with 0.1 M HCl solution by Ahmad et al. [32]. The Langmuir model explains the data with the highest adsorption capacity (q_{max}) of 101 mg/g (R^2 = 0.996). The Langmuir model (q_{max} of 107.66 mg/g and R^2 = 0.996) was selected for predicting ciprofloxacin removal using magnetization of functionalized multi-walled carbon nanotubes (FMWCNTs-Fe_3O_4) by Yousefi et al. [43]. The reduction of HA follows the second-order kinetic (q_e of 48.7 mg/g and R^2 = 0.998). Yousefi et al. [44] reported that reduction of HA on granular ferric hydroxide (GFH) followed the pseudo-second-order (q_e of 1.08 mg/g and R^2 = 0.997). Soleimani et al. [3] reported that reduction of HA on modified pumice stone followed the D-R isotherm and the HA adsorption process was physical on all the adsorbents. Karami et al. [45] reported that malachite green reduction on manganese-modified pumice adsorbent followed the pseudo-second-order.

5. Conclusions

Powdered eggshell is a waste material that is obtained by the food industry. The results showed the role of the powdered eggshell as an effective adsorbent for removing HA from water solutions. Powdered eggshell had small diameter and heterogeneous surface. The maximum removal efficiency was obtained in acidic pH. The effect of dosage adsorbent had been tested and found 5 mg/L for the highest adsorption efficiency. The results showed that as contact time increased, HA adsorption rate increased too and equilibrium time was obtained 60 min. The critical concentration for higher adsorption efficiency were 5 mg/L. The temperature of samples affected the removal efficiency to remove HA. Up to 4 times reuse, there was no significant reduction in HA removal efficiency. Finally, it can be concluded that the powdered eggshell can be used as an inexpensive and effective adsorbent for the removal of organic pollutants. Also, laboratory results showed that the batch powdered eggshell reactor is a hopeful way for HA contaminated water. The reactor was able to remove HA in pH (4) with a reaction time of 60 min. It is suggested that the performance of process is studied the other materials. Therefore, a powdered eggshell in adsorption reactor at batch mode is an efficient and feasible process for dealing with a high amount of humic acid reduction from drinking water and as a hopeful technology for drinking water contaminated with humic acid in developing countries. This tested water with eggshell powder presented remaining and permitted humic acid that recommended by the WHO and the national standards of Iran.

Conflict of interests

The authors of this article declare that they have no conflict of interests.

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