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Preparation and Characterization of Adsorbent Using eggshell and Determination of Removal efficiency of Hexavalent Chromium and Total Organic Carbon

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Abstract: *The study was undertaken to prepare and characterize the adsorbent using eggshell and determination of removal efficiency of Cr6 and Total Organic Carbon (TOC). Unheated adsorbent and heated (at 1500C) adsorbent were prepared. Characterization of adsorbent was performed by Scanning Electron Microscope (SEM). Elemental Analysis (EA) and Fourier transform infrared spectroscopy (FTIR). The Eggshell surface showed porous nature. This study showed that heated eggshells adsorbed more rapidly and efficiently than unheated adsorbents. Heated eggshell removed twice the amount of Cr6 than the Cr6 removed by unheated eggshell. When both heated and unheated eggshells were used to remove TOC, the load of TOC increased. This may be caused by the release of organic carbon from the adsorbent.*

Keywords: *Cr6, TOC, SEM, EA, FTIR*

Introduction

Treatment of industrial wastewater is increasingly necessary concerning international regulations, which mandate the reduction of different compounds in the cleaned water. Various methods are available to remove toxic pollutants from water and wastewater, including reverse osmosis, ion exchange, precipitation, electro-dialysis, adsorption, etc. Among these, adsorption is the most versatile and widely used method for removing pollutants due to its high removal capacity and ease of operation on a large scale. Activated carbon was used metal removal[1]. Commercial activated carbon, available in powdered or granulated form, is commonly used as an adsorbent. However, activated carbon is costlier, and its practical application is limited. Hence, various investigators focused their attention on alternative locally available low-cost adsorbent materials and their technical feasibility by modifying the adsorbent chemically.

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Some low-cost adsorbent materials include fly-ash, bark, peat, sawdust, paper pulp, bagasse and bagasse fly ash, lignite coal, rice husk carbon, blast furnace flue dust, blast furnace slag, bituminous coal, fertilizer waste, human hair, straw, wool, bone char, seaweed, algae, chitosan, eggshell, seed shell, sand and soils, red mud, etc.[2].

Eggshells are used in enormous quantities by food manufacturers, restaurants, and households, and the shells are disposed of as solid waste. Eggshells and eggshell membranes may be adsorbent for iron, cadmium, lead, arsenic, reactive dye, cationic dye, azo dye, malathion, etc., lignosulfonate and humic acid from peat water3. However, no study has been reported in academic literature related to the use of raw and heated powdered eggshells as an adsorbent for the same pollutant. If raw eggshell shows efficiency better than heated eggshell, natural eggshell can be used without any treatment cost. Again, the formation of activated carbon from this waste material can increase the range of eggshell capacity as an adsorbent[4].

The eggshell contains adsorption properties, for example, pore structure that can be developed into an adsorbent[5]. The other researcher already found that calcite from eggshells can be used as an adsorbent to remove heavy metals. For example, dried eggshells (at 700C) can be used to remove iron. Crab's shell also can be used to make a solid Chitosan Membrane to adsorption iron. However, this method is expensive because of the need for PVA (Poly Vinyl Alcohol) and PEG or Poly Ethylene Glycol[6].

The formation of adsorbents from waste eggshells can be done through various processes. The eggshell heated at 1500C can remove Cu and Fe from the aqueous solution[7]. The eggshell was dried in the oven at 400C and crushed into small particle adsorbs Cu (II) efficiently[8]. The natural eggshell powder can be used as an adsorbent to treat peat water. This powder can adsorb pollutants without being treated by heat (Zulfikar et al., 2013). Duck eggshell adsorbent has been activated at 6000C and used to remove Fe(III)[6].

The X-ray diffraction pattern of powdered eggshell proves that it contains CaCO3 mineral[9]. The porous surface area of the eggshell includes various types of pores of different sizes and shapes, which improves its quality as an adsorbent[10]. Scanning Electron Microscopy or SEM image of powdered eggshell heated with various temperatures shows that the sample surface had a packed surface and contained smaller pores as the temperature increased[11].

Eggshell shows a better adsorptive capacity for metal removal. It is found from the experiment that the adsorption of Cu (II) occurred rapidly in the first 15 minutes of the experiment, and almost 100% adsorption efficiency of Cu (II) was attained after 60 minutes 8. 95% Cu and 80% Fe removal were possible with a few amounts of adsorbent from synthetic solution. An increase in the dose of adsorbent shows better performance 7. Eggshell can be used as an adsorbent for the removal of dye concentration too.

Waste eggshells need to become powder to act as an adsorbent. Particle size doesn't show any variation in its adsorptive capacity[3]. This investigation focuses on the development of adsorptive properties in eggshells. As a part of the adsorption process and waste treatment, the development of adsorbent from a waste material has importance in the water treatment process and waste disposal problem reduction. Experiments will be performed on the adsorption of Cr^{6+} and Total Organic Carbon. This waste material may also absorb other pollutants by converting it into activated carbon (4). But the formation of activated carbon from this material needs chemical treatment and temperature treatment before converting into activated carbon. Experiments were performed to remove Cr^{6+} from water solution by pulverized eggshell[12].

The present investigation estimates the number of chromium ions present in its aqueous solutions before and after treatment using heat and unheated eggshell as an adsorbent, and Total Organic Carbon removal efficiency of heated and unheated eggshell an adsorbent from river water is attempted.

Materials and Methods

Adsorbent

Chicken eggshells collected from nearby Dairy and Prantik shops were initially washed with detergent and water. After that, the eggshells were further washed with distilled water and then air-dried for a few days. Afterward, the dried sample was blended to become powder and sieved to get a sample smaller than 1 mm. the sieved sample was divided to get two types of the sample which are heated and unheated waste eggshell samples. The sample was heated for one hour in the oven at 150 ^{0}C temperature 7 for heated eggshells.

Characterization of Adsorbent

Characterization of eggshell powder was performed by using three instruments. First, scanning electron microscopes to investigate particle morphology of powdered eggshells, Fourier transforms infrared spectroscopy within the range 400-4,000 cm-1 to identify the presence of functional groups in the samples, and elemental analysis to determine its elemental composition.

SEM

Elemental analysis (C/H/N/S) of the samples (both heated and raw) was made using an Elemental analyzer and various EL Cube for both unheated and heated eggshell powder. Elemental analysis was used to examine the remaining residues in the preparation of the eggshell adsorbent[14].

FTIR

The IR spectrum (FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER, IR Prestige-21, SHIMADZU CORP, SERIAL NO- A210046, 02158) of eggshell powder was recorded to obtain the information regarding the stretching and bending vibrations of the functional groups which are involved in the adsorption of adsorbate molecules.
For FTIR analysis, a few amounts of powder were pressured with potassium bromide (KBr) to make chips[13].

Adsorption studies

The adsorption experiment is designed based on two objectives. First, as the research target is to grow adsorptive capacity in eggshells, the adsorptive capacity of the prepared adsorbent will be determined to remove heavy metals and TOC from an aqueous solution. On this basis, Cr^{6+} is selected as a representative of heavy metal. Again, river water contains total organic carbon naturally. River water is used for TOC analysis to determine the adsorption efficiency of adsorbents prepared from eggshells.

Adsorption of Cr^{6+}

Potassium dichromate releases Cr^{6+} in an aqueous solution. Adsorption of Hexavalent Chromium using both raw and heated waste eggshell was performed using the potassium dichromate solution. Hexavalent Chromium sample with various concentrations was prepared from stock Potassium Dichromate solution.The 1000 ppm 500 ml Cr^{6+} stock solution was prepared by dissolving accurately weighed 1.414 gm Potassium dichromate in distilled water in a 500 ml Volumetric flask. This stock solution is used for analysis and standard solution preparation.The standard solution was obtained by accurately diluting the stock solution to different initial concentrations. To prepare the standard curve, 100 ml of 50ppm, 100 ppm, 150 ppm, and 200 ppm solutions were prepared. All of these four solutions were diluted 20 times for measurement by AAS. After dilution, all these four samples were used to prepare the calibration curve.

The concentration of Cr^{6+} in the standard solution before adsorption was determined using a Flame Atomic Adsorption Spectrophotometer (Shimadzu, Japan, model AA-6300). Before analysis, the solution was diluted 20 times during this procedure for analysis by AAS [6]. Experiments were performed for unheated and heated waste eggshell adsorbent samples in the same category. The changes in the color of the solution were observed after treatment by the adsorbent. All samples were filtered by Whatman filter paper (Pore size 0.7m) after treatment with eggshell powdered adsorbent. The removal percentage is calculated by the following equation (1) :

$$RE=\sqrt{\left(\frac{ci-c}{ci}\right)x\ 100\%}\ \left(\frac{ci-c}{ci}\right)x\ 100\% \qquad ..(1)$$

Where, ci Initial Concentration
c Concentration after treatment

Adsorbent dose effect

At first, 300 ppm 50 ml Potassium dichromate solution was taken in eight individual conical flasks named FA1, FA2, FA3, and FA4 for heated 0.5,1,1.5 and 2 gm adsorbent, respectively. In contrast, FR1, FR2, FR3, and FR4 for unheated 0.5,1,1.5 and 2 gm of both heated and unheated adsorbent were added into the solution and placed into a shaker at room temperature for 60 minutes. After one hour, all the samples were collected and filtered for AAS analysis[6].

Initial Concentration effect

At first, 100 ppm, 200 ppm, 300 ppm, and 400 ppm 50 ml Potassium dichromate solution was taken into four individual conical flasks named FA5, FA6, FA7, and FA8 for 0.5 gm heated adsorbent.
Again, 100 ppm, 200 ppm, 300 ppm, and 400 ppm 50 ml solution were taken into another four individual conical flasks named FA5, FA6, FA7, and FA8 for 0.5 gm unheated adsorbent.

After adding adsorbent to solutions, all solutions were placed into a shaker at room temperature for 60 minutes. Then all of the samples were collected and filtered for AAS analysis[12].

Contact time effect

At first, 100 ppm 50 ml potassium dichromate solution were taken into five individual conical flasks named FA9, FA10, FA11, FA12, and FA13 for heated adsorbent with contact time 15 min, 30min, 45 min, 60 min, and 75 min, respectively. 2 gm of heated adsorbent were added into the solution and placed into shaker at room temperature for 15, 30, 45, 60 and 75 minutes. All the samples were going through AAS analysis after filtration [12].

For analyzing the performance of unheated adsorbent with time variation, 2 gm adsorbent was used for 200 ppm 50 ml solution. 200 ppm and 50 ml solution were taken into four different conical flasks named FA9, FA10, FA11, and FA12 for unheated adsorbent with contact times 15 min, 30min, 45 min, and 60 min, respectively. 2 gm unheated adsorbent was added into the solution and placed into shaker at room temperature for 15,30,45 and 60 minutes. After filtration, all samples were analyzed by AAS[12].

Adsorption of Total Organic Carbon

River water contains a total organic carbon naturally. To determine the adsorbent capacity of waste eggshell (unheated and heated sample) for TOC, river water was used. Water was collected from the nearby Turag River, Aminbazar Ghat. Analysis for TOC was performed by using this river water with various doses of raw and heated eggshell adsorbent.

Adsorbent dose effect

The impact of both unheated and heated waste eggshell samples on Total Organic Carbon in River water is analyzed using a TOC analyzer. Standard curve prepared by Potassium Hydrogen Phthalate.

Sample preparation and analysis

After adding a few drops of nitric acid to the collected river water, 100 ml of river water is taken into eight conical flasks. 0.5,1,1.5 and 2 gm of unheated adsorbent were added into four conical flasks containing R0.5, R1, R1.5, and R2, and heated adsorbents were added into other four conical flasks containing samples named as H0.5, H1, H1.5, and H2. After shaking for 60 minutes, all samples were filtered by Glass Fiber filter paper.Then all the filtered samples were then placed into the TOC analyzer's vial. To determine the initial TOC value of river water, the untreated river water was filtered by Glass Fiber filter paper to remove impurities and taken into the vial to be analyzed[15].

Result and Discussion

Characterization of Adsorbent

The pore structure of adsorbent produced from eggshell

According to the SEM images (Fig. 1 and 2), The eggshell is typically comprised of the irregular shape of particles of various sizes. SEM images also represented many pores of various sizes and shapes. These pores acted to adsorb metal during adsorption. Figure 2 represents the size of pores-1.770 m, 290.3nm,610.2nm, 373.5nm, 457.5 nm, and 539.9nm.

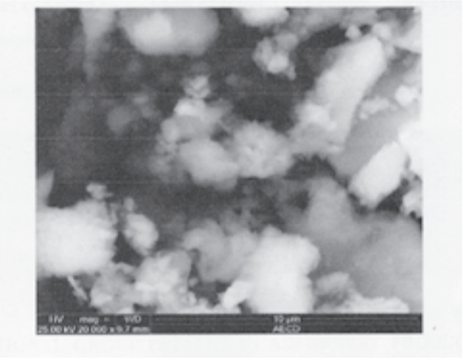

Figure 1: Crystalline structure of eggshell

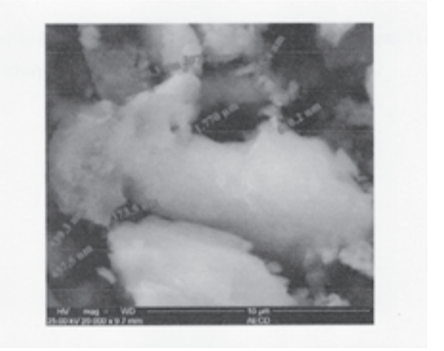

Figure 2: Different sizes of pores on the surface of eggshell

SEM images of heated eggshell powder revealed the porous surface textures, which endorse the adsorbent with increased surface area and high adsorption capacity. The smaller size of the grains could provide higher specific surface areas. The size of the particle should directly respond to the surface area 16. The experiment showed that with the use of heat, the surface morphology of the eggshell becomes rougher and more unstructured, and the total amount of pores is reduced 11. But results showed that heated adsorbent adsorbs are better than raw adsorbents. The SEM image of an untreated sample of eggshell exhibited non-adhesive property. The pores on the surface of the adsorbent were highly heterogeneous, as shown in Figure 2. The heterogeneous pores and cavities provided a larger exposed surface area for the adsorption. The sizes of pores are indicative of the expected adsorption of adsorbate molecules onto the surface of the adsorbent. SEM image also revealed that the eggshells have a crystalline structure, exhibited an angular pattern 10, non-adhesive appearance, and formation of agglomerates. This observation is similar to what other researchers reported[15].

Carbon, Nitrogen, Hydrogen, and Sulfur composition of adsorbent produced from eggshell

Table 1 represents the Carbon, Nitrogen, Hydrogen, and Sulfur composition present in the adsorbent. Both 3A(heated) and 3B(raw or unheated) samples contained Nitrogen and Carbon. The percentage of Nitrogen is 0.426% in heated powder and 0.271% in unheated powder. The percentage of carbon is 13.66% in the heated sample and 13.52% in the unheated sample. The unheated and heated sample contained an almost similar value for Nitrogen and Carbon. However, a different value was observed for Hydrogen and Sulfur.

Results represented that the heated sample contained Hydrogen 0.208% and Sulfur 0.009%, while the unheated or raw powder contained no Hydrogen and Sulfur. Contamination from the oven may be the reason for the Hydrogen and Sulfur percentage in the heated sample. The carbon percentage is high as the eggshell particle should be composed of carbonate minerals, e.g., calcite[14].

Table 1: Carbon, Nitrogen, Hydrogen, and Sulfur analysis

Name of Sample	Nature of Sample	N%	C%	H%	S%
3B	Raw	0.271	13.52	0.000	0.000
3A	Burn	0.426	13.66	0.208	0.009

The functional group present in adsorbent produced from eggshell

Samples used for FTIR analysis were heated (Figure 3), unheated (Figure 4), and heated samples after adsorption (Figure 5). IR spectrum represents the functional group present in the heated adsorbent, unheated adsorbent, and adsorbent sample after the adsorption process (table 2).

Table 2: Abbreviated table of group frequencies for an organic functional group present in eggshell

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity	Observable Peak (3A) (heated)	Observable Peak (3B) (unheated)	Observable Peak (3C) (after adsorpt
O-H	Hydrogen bonded alcohols, phenols	3200-3600	Variable, sometimes broad	3365.78	3315.63	3379.29
C-H	Alkenes	2850-2970	Strong	2873.94	2873.94	2873.94
O-H	Hydrogen-bonded carboxylic acid	2500-2700	Broad	2513.25	2513.25	2513.25
C-H	Alkanes	1340-1470	Strong	1419.61	1419.61	1423.47
C-O	Alcohol, ethers, carboxylic acids, esters	1050-1300	Strong	1082.07	1082.07	1082.07
C-H	Alkenes	675-995	Strong	875.68	875.68	875.68
C-H	Alkenes	675-995	Strong	711.73	711.73	711.73

The peak observed at 3365.78 cm^{-1} may be assigned to the presence of alcohol hydroxyl group (-OH) and N_H groups. The peak observed at 2513.25 cm^{-1} may be assigned to the presence of acidic hydrogen group (-OH) stretching, respectively. The most significant peak of intensity of powdered eggshells was found at 1419.61 cm^{-1} and 1423 cm^{-1}. The intensity peak was almost the same for 3A Figure 3,

3B Figure 4, and 3C Figure 5. It proved that metal adsorption didn't occur due to the formation of new chemical bonds. Instead, adsorption occurred through the pores in adsorbent IR spectra of the powdered eggshells before adsorption. The most significant intensity peak is at 1419.61cm-^{1} and 1432.47cm-^{1}, thereby strongly associated with carbonate minerals within the eggshell's matrix 1^{0,17}. There were also two observable peaks at about 711.73 and 875.68cm-^{1}, which should be associated with the in-plane and out-plane deformation modes, respectively, in the presence of calcium carbonate ^{10,17}. This observation was completely similar to another research work ^{13}.

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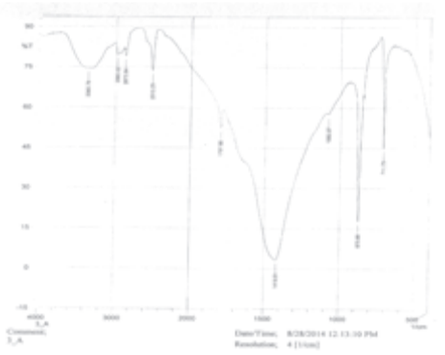

Figure 3: IR Spectrum of eggshell sample (3A)

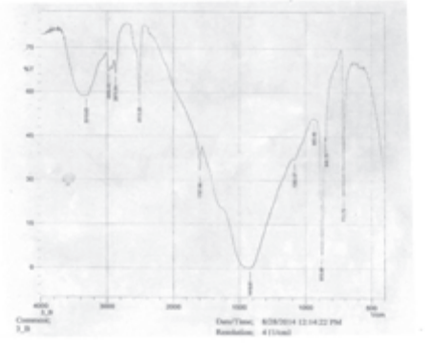

Figure 4: IR Spectrum of eggshell sample(3B)

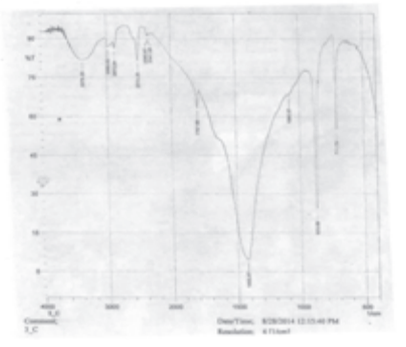

Figure 5: IR Spectrum of eggshell sample (3C)

Adsorption studies

Adsorption of Cr^{6+}

Adsorbent dose effect

Cr6 concentration decreased with the increase of adsorbent doses. For example, 0.5 gm heated and raw adsorbent reduced the concentration from 300 ppm to 97.576 ppm and 133.94 ppm. 1 gm heated and raw adsorbent reduced to 46.06 ppm and 109.696ppm and 2gm heated and raw adsorbent reduced to 36.97 ppm and 76.324 ppm, respectively. This data revealed that the rate of adsorption increased with an increase in the adsorbent dose 18. The heated adsorbent observed better performance. The thermally treated samples displayed a slightly greater uptake capacity than untreated ones ^{14}. So, the

heat increased the capacity of the adsorbent. Table 3 represents the concentration of Cr^{6+} before and after treatment with removal efficiency (RE).

Table 3: Concentration of Cr^{6+} before and after treatment

Sample ID	Dose of Adsorbent, gm	Initial Concentration ci(ppm)	Concentration after treatment c(ppm)	ci-c	RE= $\frac{(\frac{ci-c}{ci}) \times 100\%}{(\frac{ci-c}{ci}) \times 100\%}$	Heated or unheated adsorbent
FA1	0.5	300	97.576	202.424	67.47	Heated
FA2	1	300	64.242	235.758	78.586	
FA3	1.5	300	46.06	253.94	84.6467	
FA4	2	300	36.97	263.03	87.6767	
FR1	0.5	300	133.94	166.06	55.353	Unheated
FR2	1	300	130.91	169.09	56.363	
FR3	1.5	300	109.696	190.304	63.435	
FR4	2	300	76.324	223.676	74.559	

Comparison between RE of heated and unheated adsorbent doses

The rate of removal efficiency for 0.5, 1,11.5, and 2 gm adsorbent (heated and unheated) is shown in Figure 6. Removal efficiency for each adsorbent dose was determined and plotted.

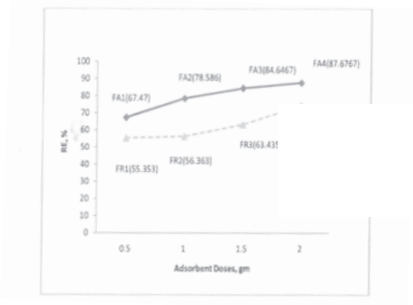

Figure 6: Relationship between adsorbent doses and removal efficiency (RE)(%) of heated and unheated adsorbent for Cr^{6+}

In the Y-axis with a dose of adsorbent on the X-axis. Heated adsorbents showed greater efficiency than unhated adsorbents. FA1 showed 67.4%, FA2 showed 78.586%, FA3 showed 84.6467% FA4 showed87.6767% while FR1 showed 55.353%, FR2 showed 55.363%, FR3 showed 63.435% and FR4 showed 74.559% removal efficiency. Heated adsorbents (FA) gave more efficient performance than unheated (FR) adsorbents, and removal efficiency increased with adsorbent doses.

Initial concentration effect

Initial concentration didn't show any effect on the adsorption process. The heated adsorbent performed better than the raw adsorbent. 0.5 gm heated adsorbent reduced the concentration from 100 ppm to 9.696 ppm, 200 ppm to 21.818 ppm, 300 ppm to 32.91 ppm, and 400 ppm to 49.09 ppm. 0.5 gm raw adsorbent reduced the concentration from 100 ppm to 52.122, 200 ppm to 94.546 ppm and 300 ppm to 124.848 ppm, and 400 ppm to 146.06 ppm. Initial concentration didn't affect the adsorption process. The experiment showed that when the solution contains one more metal ion, the percentage of adsorption decreases 7. But in the solution containing a single metal ion, the initial concentration doesn't affect the adsorption rate. Various metals may influence the adsorption rate in a single solution. But for. For a single metal, the initial concentration doesn't affect it significantly. Table 4 represents the concentration of Cr6 before and after treatment with removal efficiency (RE).

Table 4: Concentration of Cr^{6+} before and after treatment

Sample ID	Dose of Adsorbent, gm	Initial Concentration ci(ppm)	Concentration after treatment c(ppm)	ci-c	RE= $\frac{(\frac{ci-c}{ci}) \times 100\%}{(\frac{ci-c}{ci}) \times 100\%}$	Heated or unheated adsorbent
FA5	0.5	100	9.696	90.304	90.304	Heated
FA6	0.5	200	21.818	178.182	89.091	
FA7	0.5	300	32.91	267.09	89.03	
FA8	0.5	400	49.09	350.91	87.7275	
FR5	0.5	100	52.122	47.878	47.878	Unheated
FR6	0.5	200	94.546	105.454	52.727	
FR7	0.5	300	124.848	175.152	58.384	
FR8	0.5	400	146.06	253.94	63.485	

Comparison between RE of heated and unheated adsorbent based on initial concentration Cr^{6+}

Figure 7 represents the RE of heated and unheated adsorbent for 100, 200, 300, and 400 ppm solution. Removal efficiency for each initial concentration was determined and plotted on the Y-axis with an initial concentration on the X-axis. Around 90% RE was found for heated adsorbent while the initial concentration was 100 ppm. RE for 200, 300, and 400 ppm were around 89%, 89%, and 87% for heated 0.5 gm adsorbent.

Raw adsorbent also improved removal efficiency, around 47%, 52%, 58%, and 63% for 100, 200, 300, and 400 ppm initial concentration, respectively. Initial concentration didn't affect the adsorption process.

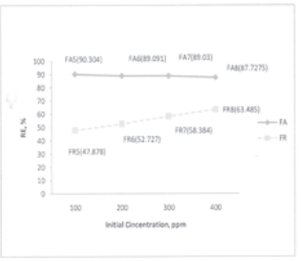

Figure 7: Relationship between initial concentration and removal efficiency (RE) (%) of heated and unheated adsorbent for Cr^{6+}

Contact time effect

Contact time positively impacted the adsorption rate. 2 gm heated adsorbent adsorbed 9 ppm, 32.728 ppm, 60 ppm, 75.152 ppm from 100 ppm Cr6 solution after 15 min, 30min, 45min, 60 min, and 75 min, respectively. On the other hand, 2 gm unheated adsorbent adsorbed 14.546 ppm, 32.728ppm, 50.91ppm, and 74.364ppm Cr6 from 200 ppm solution after15,30,45 and 60 min, respectively. The result showed that the adsorption rate was higher within a short period for heated adsorbents than for raw adsorbents. Table 5 shows the concentration of Cr6 before and after treatment with removal efficiency (RE).

Table 5: Concentration of Cr^{6+} before and after treatment

Sample ID	Dose of Adsorbent, gm	Contact time, minutes	Initial Concentration ci (ppm)	Concentration after treatment, c(ppm)	ci-c	RE= $\frac{(\frac{ci-c}{ci}) \times 100\%}{(\frac{ci-c}{ci}) \times 100\%}$	Heated or unheated adsorbent
FA9	2	15	100	91.576	9	9	Heated
FA10	2	30	100	67.272	32.728	32.728	
FA11	2	45	100	40	60	60	
FA812	2	60	100	24.848	75.152	75.152	
FA13	2	75	100	18.788	81.212	81.212	
FR9	2	15	200	185.454	14.546	7.273	Unheated
FR10	2	30	200	167.272	32.728	32.728	
FR11	2	45	200	149.09	50.91	50.91	
FR12	2	60	200	125.636	74.364	74.364	

Comparison between RE of heated and unheated adsorbent based on contact time

Figure 8 represents the removal efficiency for heated and unheated adsorbents based on contact time. Removal efficiency for each initial concentration was determined and plotted on the Y-axis with contact time on the X-axis. Removal efficiency of heated adsorbent was found 9%,32.728%,60%,75.152% and 81.212% after 15,30,45,60 and 75 min of shaking, respectively. Removal efficiency of unheated adsorbent was 7.273%,16.364%,25.455% and 37.182% after 15,30,45 and 60 min, respectively. Removal efficiency for both heated and unheated adsorbents increased with time. But the heated adsorbent adsorbed faster and more efficiently than the unheated sample.

Eggshell naturally contains some pores on its surface. When heated, more pores may be created on its surface, leading to the increased capacity to hold the metal. So, the temperature increase for eggshell adsorbent may lead to greater uptake of metal and can be used for salinity

removal in drinking water.

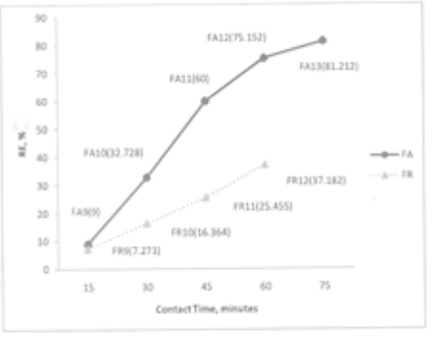

Figure 8: Relationship between contact time and removal efficiency (RE) (%) of heated

Adsorption of total organic Carbon

Adsorption doses affect TOC

The initial Total Organic Carbon value of river water was 3.311 ppm. The amount of total organic carbon was increased after shaking. As a result, TOC value increased from 3.311 ppm to 30.03 ppm, 17.70 ppm, 37.32 ppm, and 32.05 ppm for 0.5 gm, 1gm, 1.5gm, and 2 gm unheated adsorbent, respectively. For the use of heated 0.5 gm, 1gm, 1.5gm, and 2gm adsorbent, TOC values increased from 3.311 ppm to 22.44 ppm, 15.71ppm, 34.72 ppm, and 47 ppm, respectively. TOC value before and after treatment using various adsorbent doses is represented by the following Table 6.

Table 6: Concentration of TOC before and after treatment

Sample ID	Dose of Adsorbent, gm	Initial Concentration ci(ppm)	Concentration after treatment, c(ppm)	Heated or unheated adsorbent
R 0.5	0.5	3.311	30.03	Heated
R 1	1	3.311	17.70	
R 1.5	1.5	3.311	37.32	
R 2	2	3.311	32.05	
H 0.5	0.5	3.311	22.44	Unheated
H 1	1	3.311	15.71	
H 1.5	1.5	3.311	34.72	
H 2	2	3.311	47	

The amount of total organic carbon was increased after treatment with eggshells. It was due to the organic carbon released in the eggshell powder. Both unheated and heated adsorbents showed increased TOC levels in sample water.

1.5 gm unheated adsorbent releases the highest organic carbon into sample water during treatment. On the other side, a heated 2 gm sample releases the highest organic carbon in sample water. In water, calcium salts undergo a displacement reaction (Oka et al., 2008), resulting in a basic solution13. Therefore, an increase in TOC level in sample solution may result from this displacement reaction.

It is well known that eggshells contain CaCO3 as the major component (up to 95%). This CaCO3 may act as the carbon source in the solution to increase the TOC value. In water, calcium salts undergo a displacement reaction (Oka et al., 2008). CaCO3 produced from eggshells may release Ca2+, CO32-, HCO3-, and OH- ions 19,20. These ions may be adsorbed onto the surface of the eggshell particles and form a negative charge. This negative charge may attract Cr6+ to the porous eggshell surface. This displacement reaction may release carbon into water. This may be the reason for the increment of TOC in river water.

Conclusions and Recommendation

Eggshells generated as a by-product of food industries occupy a significant portion of the total mass of eggs, representing a significant waste from the egg-derived product's processor because it was traditionally useless and commonly disposed of in landfills without any pretreatment. Due to its intrinsic pore structure and the amount in abundance, it is thus feasible to grind the eggshell waste in the preparation of fine powders, which might have the way for available materials such as porous adsorbents. Furthermore,

chicken eggshells can be used to adsorb heavy metals in wastewater due to their calcium carbonate content responsible for metal adsorption. This alternative method will not produce chemical sludge; hence no secondary pollution, and it is more efficient and easier to operate than other methods. The adsorption behavior of heated (1500 C) and unheated powdered eggshell is clarified by this study. The study indicates that both heated and unheated eggshells adsorb metal, but they show negative results for organic carbon adsorption. In the future, the experiment should be performed based on the pH of the solution. A better result may be found in the eggshell that can convert to activated carbon. That activated carbon may adsorb various types of metal and organic load in the wastewater.

References

1. *Agarwal, A. and Gupta, P.K. (2014). Removal of Cu & Fe from aqueous solution by using eggshell powder as low-cost adsorbent. Adv Appl Sci Res, 5(2), pp.75–79.*
2. *Arunlertaree, C., Kaewsomboon, W., Kumsopa, A., Pokethitiyook, P. and Panyawathanakit, P. (2007). Removal of lead from battery manufacturing wastewater by egg shell.*
3. *Bhaumik, R., Mondal, N., Das, B., Roy, P., Pal, K., Das, C. and Baneerjee, A. (2012). Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: equilibrium, kinetic and thermodynamic studies. EJournal of Chemistry, 9(3),pp.1457–1480.*
4. *Buasri, A., Chaiyut, N., Loryuenyong, V., Wongweang, C. and Khamsrisuk, S. (2013). Application of eggshell wastes as a heterogeneous catalyst for biodiesel production. Sustainable Energy, 1(2), pp.7–13.*
5. *Carvalho, J., Ribeiro, A., Graça, J., Araújo, J., Vilarinho, C. and Castro, F. (2011). Adsorption process onto innovative eggshellderived lowcost adsorbent in simulated effluent and real industrial effluents.*
6. *Elwakeel, Khalid Z and Yousif, A.M. (2010). Adsorption of malathion on thermally treated egg shell material. Water Science and Technology, 61(4), pp.1035–1041.*
7. *Iriany, K. (2013). Adsorption of Heavy Metal Iron Fe (III) using Activated Powdered Duck Eggshell Adsorbent. [online] www.semanticscholar.org. Available at: https://www.semanticscholar.org/paper/Adsorption-of-Heavy-Metal-Iron-Fe-(-III-)-using-Iriany/ecce5 cae98c599941761e4d9986362b16e655e96 [Accessed 30 Jul. 2022].*
8. *Murakami, F.S., Rodrigues, P.O., Teixeira, M. and Marcos, S. (2007). Physicochemical study of CaCO3 from egg shells. Food Science and Technology, 27, pp.658–662.*
9. *Nadar, A., Balasubramanian, N., Venkatachalam, T. and Prabakaran, T. (1992). Pollution load of Cauvery River water. Journal. of Natcon, 42, pp.91–104.*
10. *Ngadi, N. and Nur, W. (2013). Removal of etyhl orange dye using waste eggshell. Jurnal Teknologi, 64(1).*
11. *Nurlaela, A. (2009). Penumbuhan Kristal Apatit Dari Cangkang Telur Ayam Dan Bebek Pada Kitosan Dengan Metode Presipitasi.*
12. *Ogunlaja, Adeniyi Sunday, Alade, O.S. and Oladipo, F.Y. (2010). Preparation of CoMo catalyst using activated carbon produced from egg shell and SiO2 as support–A hydrogenation study. Orbital: The Electronic Journal of Chemistry, 2(2), pp.140–150.*
13. *Pramanpol, N. and Nitayapat, N. (2006). Adsorption of reactive dye by eggshell and its mem brane. Agriculture and Natural Resources, 40(6 (Suppl.)), pp.192–197.*
14. *Rajendran, A. and Mansiya, C. (2011). Extraction of chromium from tannery effluents waste egg shell material as an adsorbent. British journal of environment and climate change, 1(2), p.44.*
15. *Rohaizar, Nurul Aimi Binti, Hadi, A. and Sien, W.C. (2013). Removal of Cu (II) from water by adsorption on chicken eggshell.*
16. *Singh, A. (2012). The Deadly Metals: Some Removal Technologies From Drinking Water. Everyman's Science, P.285.*
17. *Sivamani, S. (2008). Batch adsorption studies for chromium removal. Journal of environmental science & engineering, 50(1), pp.11–16.*
18. *Tsai, W., Yang, J., Lai, C., Cheng, Y., Lin, C. and Yeh, C. (2006). Characterization and adsorption properties of eggshells and eggshell membrane. Bioresource technology, 97(3), pp.488–493.*
19. *Zulfikar, Muhammad Ali and Setiyanto, H. (2013). Adsorption of congo red from aqueous solution using powdered eggshell. International Journal of ChemTech Research, 5(4), pp.1532–1540.*
20. *Zulfikar, M., Novita, E., Hertadi, R. and Djajanti, S. (2013). Removal of humic acid from peat water using untreated powdered eggshell as a low-cost adsorbent. International Journal of Environmental Science and Technology, 10(6), pp.1357–1366.*