ECOFRIENDLY ADSORBENT FROM FOOD WASTE FOR WATER PURIFICATION

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ABSTRACT

Egg shell, which is a waste material emerging out in large quantities from poultries, homes and restaurants, may be used as a good adsorbent for heavy metals. Different types of eggshells were used in this study for the adsorption of a major pollutant such as iron from surface water. Effect of CaCO3 content in the egg shell, particle size, contact time, temperature and shaking on adsorption were also studied. The adsorption isotherms fitted by the Langmuir model revealed that the adsorption of iron by eggshell samples was monolayer adsorption.

Keywords: Adsorbent, Isotherm, Heavy Metals, Porosity

1. INTRODUCTION

Industrial effluents, greenhouse effect, pharmaceutical products, volatile organic compounds, biological contamination, Radiological elements and many human activities contaminated rivers and lakes making the environmental conservation a difficult task Ghrefat et al. (2014), Cooper and Harrison (2009), Pal et al. (2014), Alireza et al. (2010). There are several methods for the purification of water like ion exchange Alexandratos (2009), Strathmann (2010), membrane treatment Charcosset (2009), reverse osmosis Park and Hu (2010), use of biologically active carbon filtration Branda et al. (2005), magnetic separation Jianxin et al. (2007) and adsorption using chemical adsorbents Jiuhui (2008), Chen et al. (1987), Rahman et al. (2012). All these methods were costly and not environmentally friendly. There were studies using natural adsorbents like clays, mustard oil, neem leaves, mango and eucalyptus leaves etc Karthik et al. (2015), Nargawe et al. (2016), Ibtissem and Malikai (2015) for waste water treatment. Investigations are going on to explore useful applications of natural food waste.

Egg shell is the waste material emerging out in large quantities from poultries, homes, restaurants, bakeries etc. Its disposal is always a challenge to the concerned authorities. Researches revealed that eggshells may be used as a fertilizer and a good adsorbent for heavy metals and organic compounds Chojnacka (2005), Rais and Shaziya (2012), Ziad and Madhloom (2016), Agarwal and Gupta (2014), Nasir et al. (2016), Alok et al. (2016) Egg shell contains carbonates, sulphates and phosphates of calcium and magnesium along with other organic and inorganic matters Tsai et al. (2006), Nakano (2003), Balaz (2014). Surface analysis of egg shell indicates the porous nature and therefore can also be used as effective adsorbent. Thus, use of egg shell as adsorbent is cost effective as well as help in the removal of hazardous chemicals.

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In recent years, chemically modified adsorbents have attracted considerable attention. In this work, different types of eggshells were used for the adsorption of a major pollutant such as iron from surface water. Effect of CaCO3 content in the eggshell, particle size, contact time, temperature and shaking on adsorption were also studied.

2. EXPERIMENTAL METHODS

The reagents used in this study were of analytical grade.

2.1. PREPARATION OF EGGSHELL SAMPLES

Eggs of duck, kaada hen, local hen, and broiler hen were bought from the markets of Pulluvila and Kanjiramkulam areas of Thiruvananthapuram district. Collected eggshells were cleaned with distilled water and dried for three hours in sunlight. These eggshells were powdered using a pestle and mortar. The eggshell powder was sieved to collect different particle sizes of area 0.1377 cm², 0.174 cm² and 0.1974 cm².

2.2. DETERMINATION OF CACO3 CONTENT IN EGG SHELL

The Major component of eggshell is calcium carbonate (CaCO3), which was estimated volumetrically. 0.50 grams of each type of eggshell powder was weighed into a 250 ml conical flask and five drops of ethanol was added to the flask to activate dissolution of eggshell. 10 ml of 1M HCl was added to into each flask. Conical flasks were kept for about 24 hours for the complete dissolution of the eggshells. 2-3 drops of phenolphthalein were added. Each one was titrated against 0.5M NaOH solution. The titre value gives the amount of unreacted HCl. From this value, percent of CaCO3 was determined.

2.3. PREPARATION OF IRON CONTAMINATED WATER

10 mg of A.R ferric alum was dissolved in one litre distilled water to prepare 1 ppm of iron solution. 300ml of this iron solution was diluted to 1000 ml to prepare iron contaminated water which contains iron above 0.3 ppm which is the acceptable limit of iron in potable water.

2.4. PREPARATION OF STANDARD SOLUTIONS OF IRON

0.864g of A.R. ferric alum was weighed accurately into 100ml standard flask and dissolved in distilled water. The solution was acidified with 10ml of conc. HCl and then made up to 100ml.10ml of this solution was pipetted out into another standard flask and made up to 100ml. This solution contains 100ppm iron.

0.1ppm, 0.2ppm, 0.3ppm, 0.5ppm, 1ppm, 2ppm of iron solutions were prepared by transferring 10ml,20ml,30ml,50ml,1ml,2ml of 100ppm iron solution into different 100ml standard flasks. To these standard flasks, 5ml 4N HCl and 10ml 20% ammonium thiocyanate solutions were added and then made up to 100ml. A blank solution was prepared using only the reagents 5ml of 4N HCl and 10ml 20% ammonium thiocyanate in 100ml distilled water. The absorbance values of prepared samples were measured using Systronics Double Beam Spectrophotometer 2203 with a filter of 490 nm.
2.5. **EFFECT OF PARTICLE SIZE OF EGG SHELL POWDER ON ADSORPTION OF IRON FROM WATER**

10ml of iron contaminated water was taken in each of twelve 50 ml beaker. To this 0.5g each of different types of eggshells (Kaada hen, Local hen, Broiler hen, Duck) having particle sizes 0.1377 cm², 0.174 cm² and 0.1974 cm² were added. Iron solutions with egg shells were kept at room temperature at about 28°C for 24 hours. Absorbance values of the filtered samples were measured to estimate the amount of iron removed by the adsorbent.

2.6. **EFFECT OF CONTACT TIME**

0.5g of eggshell samples each of broiler hen and local hen of particle size 0.174 cm² were taken in two 50ml beakers with 10ml of iron contaminated water. Absorbance value of each solution was determined at 15, 30, 45, 60, 75, 90, 105, 120, 135, 150 minutes.

2.7. **EFFECT OF TEMPERATURE ON ADSORPTION OF IRON**

0.5g each of broiler hen eggshell powder having particle size of 0.174 cm² were taken in four 50ml beakers. 10ml of iron contaminated water was added to each beaker. Adsorption studies were conducted at 30o, 40o, 50o and 90oC respectively using a water bath. Absorbance values were measured after conducting the experiment.

2.8. **EFFECT OF SHAKING ON ADSORPTION OF IRON**

0.5g eggshell powder of broiler hen and local hen with particle sizes 0.174 cm² were taken in two 100ml conical flasks and to these 10ml of iron contaminated water were added. The samples were shaken for one hour at 150rpm and 300rpm speed in an electric shaker Rivotek and then kept 5 minutes at rest to attain stability. The absorbance values of the filtered samples were measured.

3. **RESULT AND DISCUSSION**

**Calcium Carbonate Determination**

0.5g each of eggshell samples dipped in 10ml 1M HCl for 24 hours. The unreacted HCl is titrated against 0.5M NaOH. From the titre values, the weight of CaCO₃ and its percentage in each eggshell were calculated and given in [Figure 1](#).

**PERCENTAGE OF CaCO₃**

![Diagramatic representation of percentage of CaCO₃](#)
This diagram showed that the percentage of CaCO3 decreases in the order, Duck > Kaada hen > Local hen > Broiler hen

**Determination of Iron Content**

The absorbance values of the standard iron solutions were measured and are given in Table 1.

| Iron Conc. (ppm) | Absorbance |
|-----------------|------------|
| 0.1             | 0.045      |
| 0.2             | 0.074      |
| 0.3             | 0.099      |
| 0.5             | 0.157      |
| 1.0             | 0.332      |

**Adsorption of Iron by Eggshells**

Eggshells of particle size 0.1377cm², 0.174cm² and 0.1974cm² were prepared and dipped in iron contaminated water for 24Hrs. The absorbance values of samples after adsorption study were noted and are given in Table 2.

| Eggshell Samples | Particle Size | Absorbance |
|------------------|--------------|------------|
|                  | 0.1377(cm²)  | 0.174(cm²) | 0.1974(cm²) |
| Duck             | 0.074        | 0.055      | 0.075       |
| Kaada Hen        | 0.036        | 0.030      | 0.034       |
| Local Hen        | 0.032        | 0.025      | 0.036       |
| Broiler hen      | 0.036        | 0.022      | 0.030       |

From Table 2, it was observed that, among all these eggshell samples, maximum adsorption was shown in the particle size (0.174 cm²). Broiler hen eggshells showed greater iron adsorption than all other samples. Least adsorption was shown by eggshell of duck in all particle sizes. Adsorption efficiency of eggshell samples decrease in the order, Broiler Hen > Local Hen > Kaada Hen > Duck

**Effect of Contact Time**

0.5g of eggshell samples each of broiler hen and local hen of particle size of 0.174cm² which showed maximum adsorption capacity were taken in two 50ml beakers with 10ml of iron contaminated solution. Adsorption study was conducted determined by varying contact time from 15 to150min. Absorbance values after adsorption is given in Table 3.
Table 3 shows that adsorption of iron increased with contact time up to 105 minutes for broiler eggshell and 90 min for local hen eggshell. Further increase in contact time did not enhance the iron adsorption process. The adsorption process attained equilibrium at 105 and 90 minutes on the surface of broiler and local hen eggshell samples respectively. The fast adsorption rate at the initial stage may be explained by the increase in availability of the number of active binding sites on the adsorbent surface. After the saturation point, there is no further increase in the rate of adsorption.

### Effect of Temperature on Adsorption

0.5g each of broiler hen eggshell having particle size 0.174cm²(best adsorbent obtained) were taken in four 50ml beakers containing 10ml iron contaminated solution. Adsorption study was conducted at different temperatures (30, 40, 50 and 90°C) using a water bath for one hour. The resultant absorbance values obtained are given in Table 4.

| Temperature(°C) | Absorbance |
|-----------------|------------|
| 28 (room temperature) | 0.022 |
| 30               | 0.011 |
| 40               | 0.057 |
| 50               | 0.034 |
| 90               | 0.044 |
From Table 4, it is observed that, the adsorption rate decreases when the temperature increases above 30°C. This can be explained due to the increase in pore size of the adsorbent and increase in the kinetic energy of the adsorbate molecule with rise in temperature. After 30°C, pore size of adsorbent increase above the size of adsorbate molecule and as a result the adsorbate will move out of the surface of adsorbent.

**Effect of Shaking**

0.5g of eggshell samples of broiler hen and local hen of particle size 0.174cm² were taken in two 100ml conical flasks along with 10ml of iron contaminated solution. Absorbance was determined after shaking the samples at 150 rpm and 300 rpm speed for about 1 hours and attaining steady state is given in Table 5.

| Sample       | Absorbance | Shaking Speed |
|--------------|------------|---------------|
|              |            | 150rpm | 300rpm |
| Broiler Hen  | 0.017      | 0.010   |
| Local Hen    | 0.022      | 0.021   |

Table 5 showed that iron adsorption increases with agitation at 150 rpm speed. The reason for the increase in adsorption is that, better contact between the adsorbent and adsorbate takes place at higher speed. But after a particular limit ie; at 300 rpm, there is a probability of removal of adsorbate from the adsorbent surface.

**Isothermal Studies**

**Freundlich isothermal studies**

The Freundlich isothermal studies were conducted using the absorbance value of Table 2. The Freundlich isothermal equation is given by, \( \log \frac{x}{m} = \log k + \frac{1}{n} \log c \) where \( x \) is mass of adsorbate adsorbed, \( m \) is mass of adsorbent, \( k \) & \( n \) are Freundlich constants and \( C \) is the equilibrium concentration of adsorbate. Freundlich parameters were calculated and are given in Table 6.

| Samples       | x     | m     | x/m   | log(x/m) | C    | logC |
|---------------|-------|-------|-------|----------|------|------|
| Kaada Hen     | 0.1377cm² | 0.05  | 0.50  | 0.1      | -0.8538 | 0.25 | -0.6382 |
|               | 0.174cm² | 0.13  | 0.50  | 0.26     | -0.5850 | 0.17 | -0.7695 |
|               | 0.1974cm² | 0.07  | 0.50  | 0.14     | -0.8538 | 0.23 | -0.6382 |
| Local Hen     | 0.1377cm² | 0.20  | 0.50  | 0.4      | -0.3979 | 0.10 | -1    |
|               | 0.174cm² | 0.23  | 0.50  | 0.46     | -0.3372 | 0.07 | -1.1549 |
|               | 0.1974cm² | 0.18  | 0.50  | 0.36     | -0.4436 | 0.12 | -0.9208 |
From Table 6, using calculated values of \(\frac{x}{m}\) on Y-axis and C on X-axis, Freundlich adsorption isotherms were drawn for the adsorption of iron by each eggshell samples and are shown in Figure 2.

In Freundlich adsorption isotherm nonlinear plot was obtained, which reveal the non-applicability of this isotherm. This showed that adsorption of the iron by these eggshell samples was not multilayer adsorption. This indicates that there is no stacking of adsorbed molecules. Pores on the surface of eggshell adsorb iron only on single layer and do not allow the adsorption on the second layer.

**Langmuir isothermal studies**

The Langmuir isothermal studies were conducted using the absorbance value of Table 2. The Langmuir isothermal equation is given by, 
\[
\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}
\]
where, \(C_e\) is equilibrium concentration of adsorbate, \(q_e\) amount of adsorption at equilibrium, \(Q_m\) is monolayer adsorption capacity and \(K_L\) is Freundlich constant. The Langmuir parameters were calculated and are given in Table 7.
Table 7 Langmuir isothermal studies

| Samples     | Ce | qe   | Ce/qe   |
|-------------|----|------|---------|
| Kaada Hen   | 0.1377 cm² | 0.25 | 0.001   | 250 |
|             | 0.174 cm² | 0.17 | 0.0026  | 65.38 |
|             | 0.1974 cm² | 0.23 | 0.0014  | 164.28 |
| Local Hen   | 0.1377 cm² | 0.10 | 0.004   | 25  |
|             | 0.174 cm² | 0.07 | 0.0046  | 15.21 |
|             | 0.1974 cm² | 0.12 | 0.0036  | 33.33 |
| Broiler Hen | 0.1377 cm² | 0.12 | 0.0036  | 33.33 |
|             | 0.174 cm² | 0.05 | 0.005   | 10  |
|             | 0.1974 cm² | 0.09 | 0.0042  | 21.43 |
| Duck        | 0.1377 cm² | 0.11 | 0.0038  | 28.94 |
|             | 0.174 cm² | 0.09 | 0.0042  | 21.43 |
|             | 0.1974 cm² | 0.10 | 0.004   | 25  |

From Table 7, using calculated values of Ce/qe on Y-axis and Ce on X-axis, Langmuir adsorption isotherms were drawn for the adsorption of iron by each eggshell samples and are shown in Figure 3.
A linear plot was obtained for Langmuir adsorption isotherms of all the eggshells samples which showed its applicability. In this study, monolayer adsorption of iron by eggshell samples was taken place.

The removal of iron from the polluted water by the application of powdered eggshell samples took place by physisorption. There is no multilayer adsorption happening due to the absence of chemical bonding between the adsorbent and adsorbate molecules. This process is found to be very good eco-friendly method for water treatment.

The simplest and still the most useful isotherm, for both physical and chemical adsorption, is the Langmuir isotherm. This model assumes that adsorption is limited to a monolayer. Only a single layer of molecule on the eggshell surface was adsorbed due to the homogeneous nature of eggshell surface. The energy of adsorption is uniform for all sites. Similar to the reported studies Reyhaneh et al. (2015), there is no interaction between iron molecules adsorbed on neighboring sites. As a result, the tendency to form multilayer adsorption is less.

4. CONCLUSION

Efficient removal of heavy metal ions from wastewater is of extreme important due to the occurrence of large number of toxic organic and inorganic pollutants water bodies. Low cost, high efficiency and biodegradable nature of the adsorbents made adsorption an eco-friendly and clean technology. It helps in the removal of heavy metals present in low concentration. Eggshell powder is a cheap, natural adsorbent material used for removal of different heavy metals from water by adsorption which becomes a solution for the increasing eggshell waste now a day. The parameters used in this study gave certain information about their effects on adsorption of iron from water. This work reveals that eggshell containing least amount of calcium carbonate showed greater adsorption capacity. Eggshell samples having particle size 0.174cm² showed higher adsorption rate than the other two particle sizes used in this work. Adsorption process has inverse relation with temperature and direct relation with contact time. Shaking process is a good method for increasing the adsorption rate. This work confirmed that eggshell is an excellent substitute to commercial and nonrenewable adsorbents to remove toxic heavy metal like iron in water resource efficiently. The adsorption isotherms fitted by the Langmuir model revealed that the adsorption of iron by eggshell samples was monolayer adsorption and only physisorption occurs on the surface of eggshell.

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