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Research Article

**Comparision studies on Adsorbants for removal of
Hardness from Water by using newly Prepared Zeolite**

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ABSTRACT

Most of the water resources should be treated for purification before consumption. In some countries, ground water is the main safe drinking water resource. About 97% of earth's water is saline and is contained in oceans. Reaming 3% is water. About 68.7% of fresh water is trapped in the ice caps and glaciers, while 30.1 % of fresh water exists in the form of groundwater, 0.3 %in surface water and 0.9% in other form. Adsorbent dose is 6g/L, contact time is 60 minutes by LPZ; Adsorbent dose is 12g/L, contact time is 30 minutes by Commercial Zeolite; Adsorbent dose is 4g/L, contact time is 150 minutes by Activated Carbon; Adsorbent dose is 6g/L, contact time is 90 minutes by Silica gel is the best adsorbents for removal of the hardness ions from stock solution.

Keywords: Environmental pollution, adsorbent, hardness, water and zeolite.

INTRODUCTION

Water hardness problem is reported to exist in various places around the world⁵. Among several known forms of pollution, water pollution is great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms. Various technologies for water pollution control are available; 'adsorption' process is considered better as compared to other methods because of convenience, easy operation and simplicity of design. This process can minimize/remove different type of pollutants and it has a wider applicability in water pollution control¹. Hard water minerals such as calcium, magnesium, iron and manganese result in scaling problems and serious failures in pipelines of boilers and heat-transfer equipment. In addition, these divalent ions can react with soap anions decreasing the cleaning efficiency and hence, high consumption of detergents occurred as a result. However, calcium and magnesium are the most common sources of water hardness⁴.

The main objective of this research was to removal of hardness of water by using as a adsorbent of a new low cost effective product which possess properties

similar to Zeolite and it could be used in water processing at industrial scale level.

MATERIALS AND METHODS

Chemicals and adsorbents:

All the chemicals were used in this experiment were purchased from the Qualigens Fine Chemicals, Mumbai by the Department of Chemical Engineering, Andhra University, Visakhapatnam.

Preparation of the Adsorbents:

Synthetic hard water was prepared by 1g of CaCO₃ dissolved in a litre deionized water to make a water with hardness of 1000 mg/L as CaCO₃ equivalent used as a stock solution.

Fly Ash samples were collected from NTPC power plant, Visakhapatnam was washed thoroughly and dried to obtain constant weight. Thus prepared sample is used in preparation of Zeolite by high temperature heat treatment.

Experimental Procedure:

Fly Ash and Alkali (Na₂CO₃) was used in ratios 5:95, 10:90, 15:85, 20:80, 30:70 and kept in the furnace at

temperatures 300°C, 400 °C, 500 °C, 600 °C, 700°C for 2 h.

Once the activation time was reached, the content was cooled. The Zeolite material was then washed with distilled water until residual Alkali was fully removed. Thus the sample is filtered & dried in an oven at 100°C for 2hrs and its CEC is determined to check the Zeolite content.

The treated Fly Ash is made into pellets by agglomeration with Lime, Sodium Silicate and Sodium Alignate.

Testing of LPZ(Laboratory Prepared Zeolite) for CEC(Cation Exchange Capacity):

3g of Zeolite was added in 25 mL of raw water shaken thoroughly for 5 minutes in Flask shaker. The treated Zeolite was filtered and washed several times with DM water.

Determination of total hardness

Two millilitres of Ammonia buffer solution was added in twenty millilitres of hard water sample (pH 9-10) with EBT indicator appears wine red colour was used in titrate against EDTA.

Total hardness was identified by using the following formula:

$$\text{Total hardness} = (V_1 * N * 50 * 1000) / (V_2) \text{ mg/L}$$

Here, V_1 - volume of EDTA, V_2 - volume of sample, N - Normality of EDTA and 50 - Equivalent weight of CaCO_3

Optimization of batch experiments:

Optimization of adsorbent mass (2-16 g/L), initial ion concentrations (100-1200 mg/L) and contact time (1-240 minutes) experiments were carried out. Optimized adsorption times for Commercial Zeolite, LPZ, Activated Carbon and Silica gel adsorbents were first examined by varying the contact time at room temperature.

Removal efficiencies (RE) were identified at various initial ion concentration (100mg/L, 200 mg/L, 300 mg/L, 450 mg/L, 600 mg/L, 800 mg/L, 1000 mg/L, 1200 mg/L) as follows:

$$\text{Removal efficiency (\%)} = (C_i - C_e) / C_i * 100$$

The quantity of adsorbed hardness on the adsorbate; i.e. uptake was calculated by the difference of initial and final (or) equilibrium concentrations with the equation

$$q_e = (C_i - C_e) * V / m$$

here C_i - initial ion concentration, C_e - final ion concentration, q_e - quantity of hardness adsorbed on the adsorbate, m - amount of adsorbate and V - volume of the solution

RESULTS AND DISCUSSION

Effect of contact time on hardness removal:

A) Commercial Zeolite:

Hardness removal percentage approached equilibrium at 60 minutes (Fig 1). Further increase in contact time does not show significant change in hardness. This might be due to fact that, large number of vacant surface sites is available for the adsorption during the initial stage and with the passage of time.

B). LPZ

The percentage of hardness removal approached equilibrium within 30 minutes. Further increase in contact time does not show significant change in hardness. This might be due to fact that, large number of vacant surface sites is available for the adsorption during the initial stage and with the passage of time. After some times, repulsive forces between solute molecules on solid phase and liquid phase create difficultness for the solute molecules to occupy remaining vacant surface sites.

C). Activated Carbon:

The percentage hardness removal approached equilibrium within 150 minutes. Further increase in contact time does not show significant change in hardness. This might be due to fact that, large number of vacant surface sites is available for the adsorption during the initial stage and with the passage of time. After some times, repulsive forces between solute molecules on solid phase and liquid phase create difficultness for the solute molecules to occupy remaining vacant surface sites.

D). Silica gel:

The percentage hardness removal approached equilibrium within 90 minutes. Further increase in contact time does not show significant change in hardness. This might be due to fact that, large number of vacant surface sites is available for the adsorption during the initial stage and with the passage of time. After some times, repulsive forces between solute molecules on solid phase and liquid phase create difficultness for the solute molecules to occupy remaining vacant surface sites.

4.2. Effect of Adsorbent dose on hardness removal

A). Commercial Zeolite:

Adsorbent dose was varied between 2 - 12 g/L and it was indicated that the removal efficiency of hardness improved by increasing the adsorbent dose up to 6 g/L (Fig 5). Further increasing dose, yields were negligible adsorption. Greater availability of exchangeable sites at higher concentration of

adsorbent was the reason for the increase in hardness removal with the increase in adsorbent dose.

B). LPZ:

Adsorbent dose was varied between 2-16 g/L and it was indicated that the removal efficiency of hardness improved by increasing the adsorbent dose up to 12 g/L (Fig 6) Further increase in dose, yields negligible adsorption. Greater availability of exchangeable sites at higher concentration of adsorbent is the reason for the increase in hardness removal with the increase in adsorbent dose.

C). Activated Carbon:

The effect of the adsorbent dose on hardness removal is shown in Fig 4.7 Adsorbent dose was varied between 2-10 g/L and it was indicated that the removal efficiency of hardness improved by increasing the adsorbent dose up to 4 g/L where further dose increase yields negligible adsorption. Greater availability of exchangeable sites at higher concentration of adsorbent is the reason for the increase in hardness removal with the increase in adsorbent dose. After a certain dose of adsorbent, the maximum adsorption is attained and hence the amount of ions remains constant even with further addition of adsorbent. That's why beyond 4 g/L, the adsorption found to be constant².

D). Silica gel:

The effect of adsorbent dose was varied between 2-12 g/L and it was indicated that the removal efficiency of hardness improved by increasing the adsorbent dose up to 6 g/L where further dose increase yields negligible adsorption. Greater availability of exchangeable sites at higher concentration of adsorbent is the reason for the increase in hardness removal with the increase in adsorbent dose. After a certain dose of adsorbent, the maximum adsorption is attained and hence the amount of ions remains constant even with further addition of adsorbent. That's why beyond 6 g/L, the adsorption found to be constant².

4.3. Effect of Initial ion concentration on hardness removal

A). Commercial Zeolite:

The initial ion concentration was varied between 100-1200 mg/L and it was indicated that the removal efficiency decreases by increasing the initial ion concentration (Fig 9).

B). LPZ

The initial ion concentration was varied between 100-1200 mg/L and it was indicated that the removal

efficiency decreases by increasing the initial ion concentration (Fig 10).

C). Activated Carbon:

The initial ion concentration was varied between 100-1200 mg/L and it was indicated that the removal efficiency decreases by increasing the initial ion concentration (Fig 11).

D). Silica gel:

The initial ion concentration was varied between 100-1200 mg/L and it was indicated that the removal efficiency decreases by increasing the initial ion concentration (Fig 12).

4.4. Comparison of four adsorbents by their equilibrium time and dose:

The contact time observed from 1-240 minutes, dosages are observed from 2-16 g/L (Fig 13).

4.5. The minimum percentages of removal efficiencies of four adsorbents:

The adsorbents are treated for contact time, dosage, initial ion concentration, the minimum removal efficiency (RE) percentages (Fig 14).

4.6. The maximum percentages of removal efficiencies of four adsorbents:

4.7. Isotherm study:

Langmuir isotherm:

The linear form of Langmuir isotherm

$$C_e/q_e = 1/(q_m * K_L) + C_e/q_m \quad (1)$$

here, q_e - the ion concentration on adsorbent at equilibrium (mg/g),

q_m - (mg/g) and K_L (g/L) - Langmuir constants related to the maximum adsorption capacity and adsorption energy (equilibrium adsorption constant).

q_e is calculated by:

$$q_e = (C_i - C_e) * V/m \quad (2)$$

C_i - ion concentration (mg/L),

C_e - equilibrium (or) final ion concentration (mg/L), Q_e - quantity of hardness adsorbed on the adsorbate (mg/g), m - amount of adsorbate (g) and V - volume of the solution (L).

The dimensionless constant separation factor R_L can be used to define essential features of Langmuir isotherm model. R_L is expressed by the following equation:

$$R_L = 1 / (1 + K_L * C_i) \quad (3)$$

here, C_i - initial hardness (mg/L) and

K_L - Langmuir constant (g/L).

The separation factor R_L indicates the isotherm's shape and the nature of the adsorption process, that is, unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$). If the condition is

favourable, it indicating that the adsorption process is favourable for the removal of hardness ions³.

Isotherm kinetics:

4.7.1. Langmuir adsorption isotherm:

A). Commercial Zeolite:

The values of R_L was found to be 0.0010, indicating that the adsorption process is favourable for the removal of hardness ions. The observed values of R^2 , q_m and K_L from the following plot that are 0.966, 250 and 0.957 respectively. The values are satisfactory for the adsorption on to Commercial Zeolite (Table 2).

B). LPZ:

The values of R_L was found to be 0.0014, indicating that the adsorption process is favourable for the removal of hardness ions. The observed values of R^2 , q_m and K_L from the following plot that are 0.984, 200 and 0.711 respectively.

C). Activated Carbon:

The values of R_L was found to be 0.0005, indicating that the adsorption process is favourable for the removal of hardness ions. The observed values of R^2 , q_m and K_L from the following plot that are 0.984, 333 and 1.608 respectively.

D). Silica gel:

The values of R_L was found to be 0.0007, indicating that the adsorption process is favourable for the removal of hardness ions. The observed values of R^2 , q_m and K_L from the following plot that are 0.988, 333 and 1.188 respectively.

Freundlich isotherm:

Freundlich isotherm (Freundlich, 1932) is another isotherm model; it considers adsorption on heterogeneous surfaces. The linear form of Freundlich model can be written as:

$$\log q_e = \log K_f + (1/n)\log C_f \quad (3)$$

Here q_e is calculated by using the formula given below:

$$q_e = (C_i - C_e) * V / m \quad (4)$$

In the above equations:

C_i - initial ion concentration (mg/L),

C_e - equilibrium (or) final ion concentration (mg/L),

Q_e - quantity of hardness adsorbed on the adsorbate (mg/g), m - amount of adsorbate (g), V - volume of the solution (L).

Isotherm kinetics:

4.7.2. Freundlich adsorption isotherm:

A). Commercial Zeolite:

The observed values of R^2 , n and K_f from the following plot that are 0.926, 1.669 and 0.612 respectively (Table 3).

B). LPZ:

The observed values of R^2 , n and K_f from the following plot that are 0.912, 2.141 and 0.891 respectively.

C). Activated Carbon:

The observed values of R^2 , n and K_f from the following plot that are 0.993, 1.46 and 0.342 respectively.

D). Silica gel:

The observed values of R^2 , n and K_f from the following plot that are 0.970, 1.567 and 0.505 respectively.

CONCLUSION

1. The affinity of the four adsorbents for removing the hardness was in the order of 100 > 200 > 300 > 450 > 600 > 800 > 1000 > 1200 mg/L, the order was as a result of a combination of different factors, but maximum removal efficiencies of four adsorbents obtained at initial ion concentration 100mg/L.
2. The key factors found to control the adsorption efficiency of the adsorbents were: adsorbent contact time, adsorbent dose, initial ion concentration.
3. The following conditions were found to be the best for the removal of the hardness ions from stock solution by the four adsorbents:
 - Adsorbent dose is 6g/L, contact time is 60 minutes by LPZ,
 - Adsorbent dose is 12g/L, contact time is 30 minutes by Commercial Zeolite,
 - Adsorbent dose is 4g/L, contact time is 150 minutes by Activated Carbon,
 - Adsorbent dose is 6g/L, contact time is 90 minutes by Silica gel.

4. LPZ has a low maximum adsorption capacity (200 mg/g) compared with commercial adsorbents.

LPZ is essential to improvise the capacity for more washes, hence save economy and time. In order to reduce the cost of the adsorbent, use the natural substances having similar properties as chemicals instead of chemicals used in the preparation in the present study.

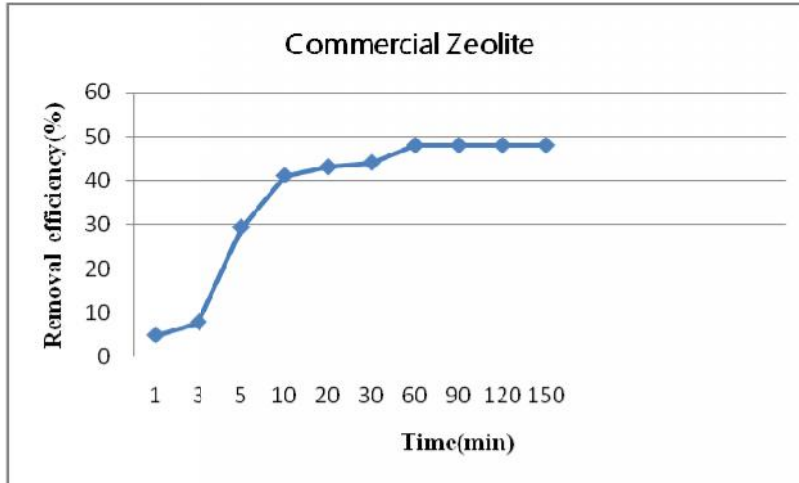


Fig 1
Effect of contact time on hardness removal by Commercial Zeolite

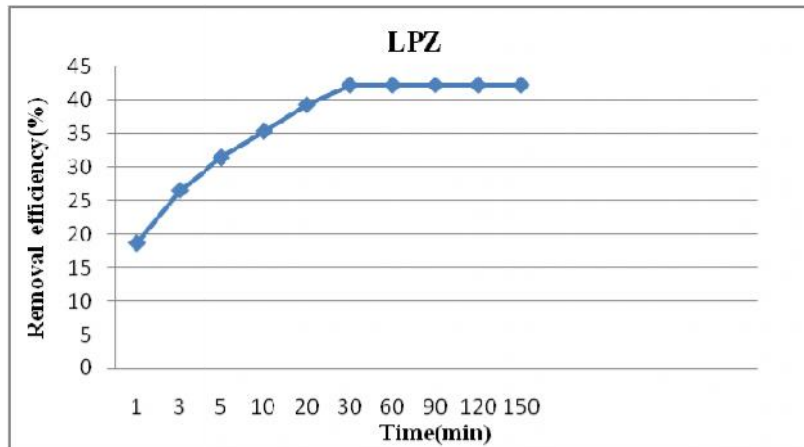


Fig 2
Effect of contact time on hardness removal by Commercial LPZ

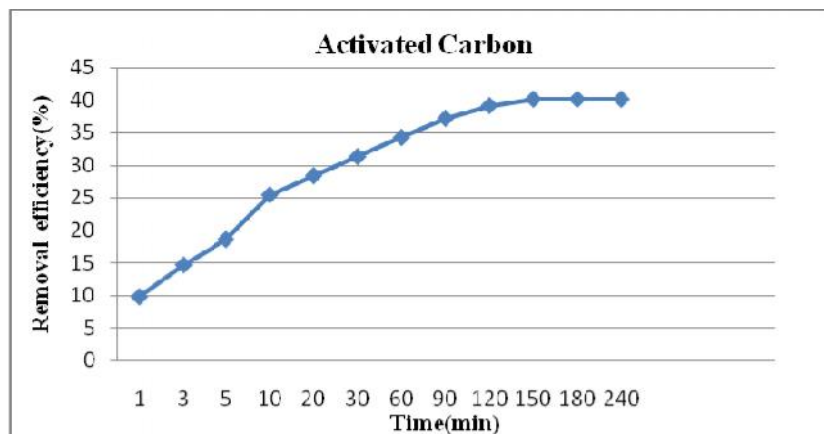


Fig 3
Effect of contact time on hardness removal by Activated Carbon

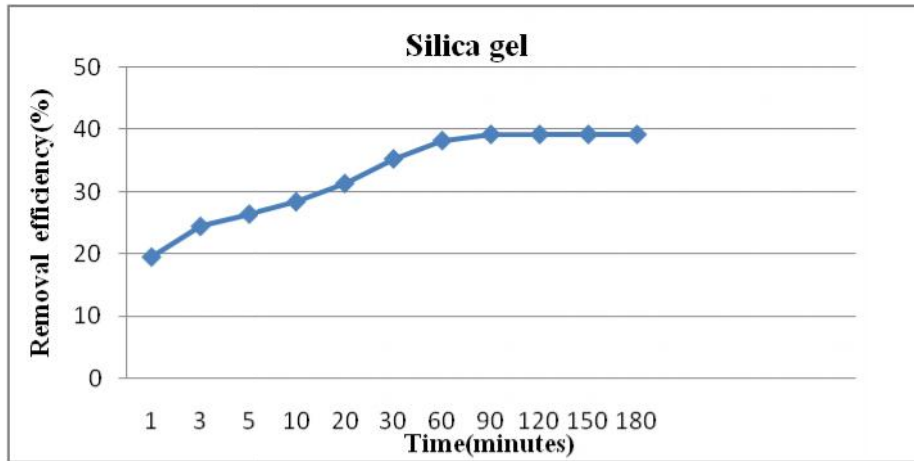


Fig 4
Effect of contact time on hardness removal by Activated Carbon

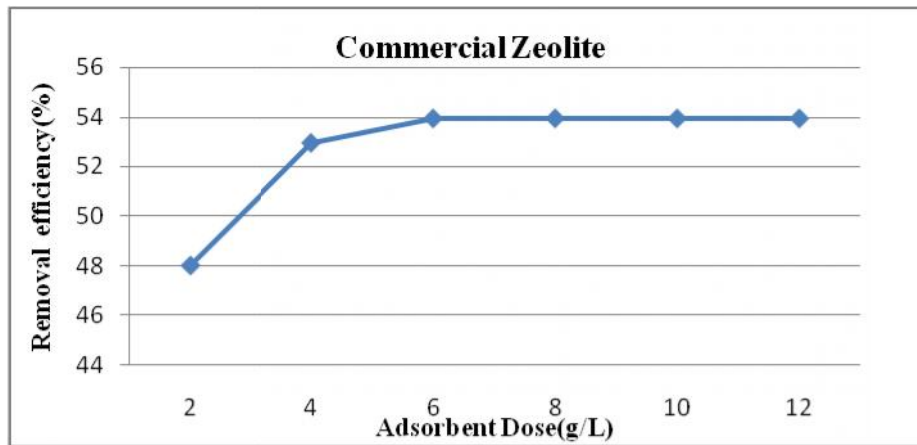


Fig 5
Effect of contact time on hardness removal by Commercial Zeolite

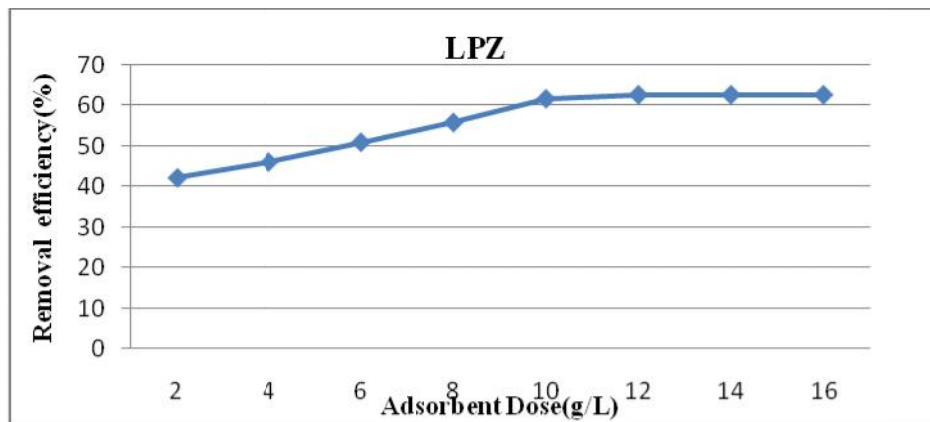


Fig 6
Effect of contact time on hardness removal by LPZ

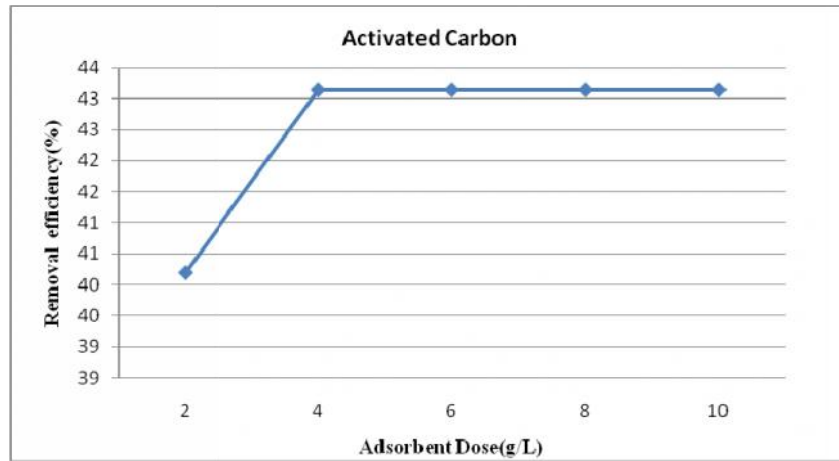


Fig 4.7

Effect of contact time on hardness removal by LPZ : (Hardness 510mg/L, Contact time (150 min).

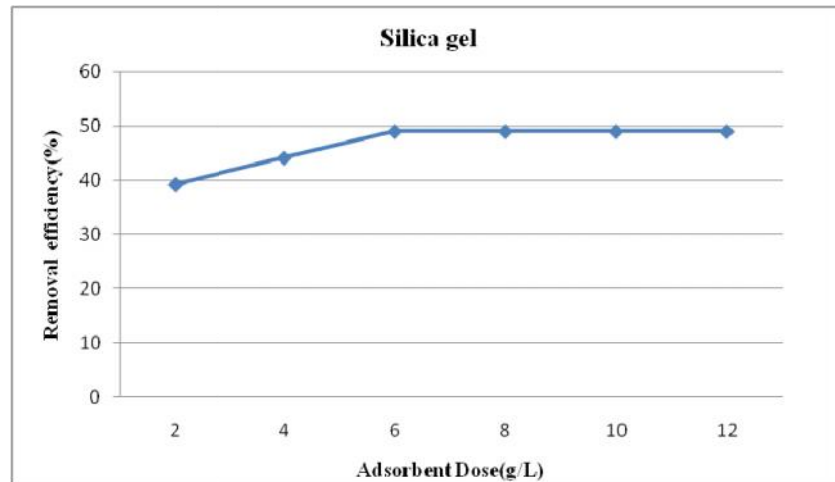


Fig 8

Effect of contact time on hardness removal by Silica gel: (Hardness 510mg/L, Contact time(90 min).

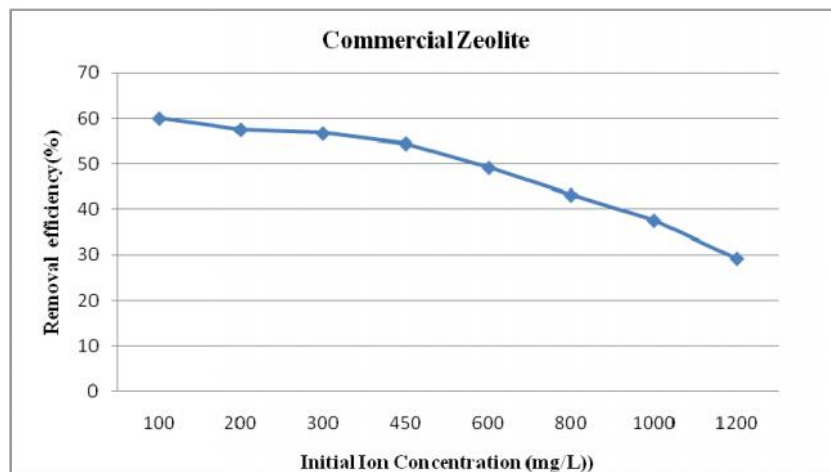


Fig 9

Effect of initial ion concentration on hardness removal by Commercial Zeolite: (Contact time 60 min, Dosage 6g/L).

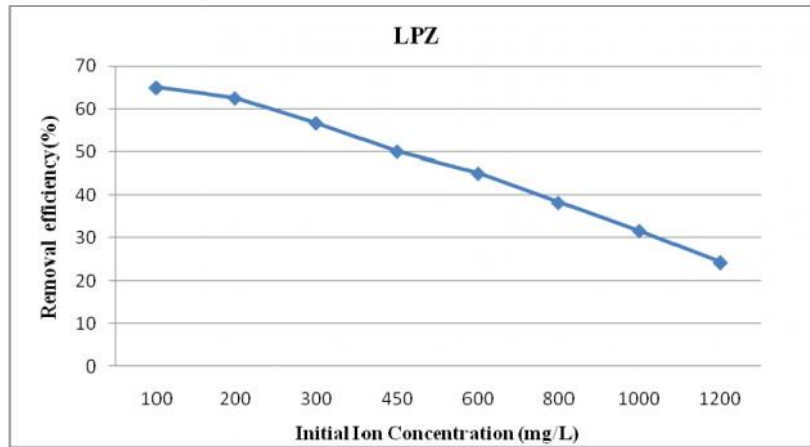


Fig 10

Effect of initial ion concentration on hardness removal by LPZ: (Contact time 30 min, Dosage 12g/L).

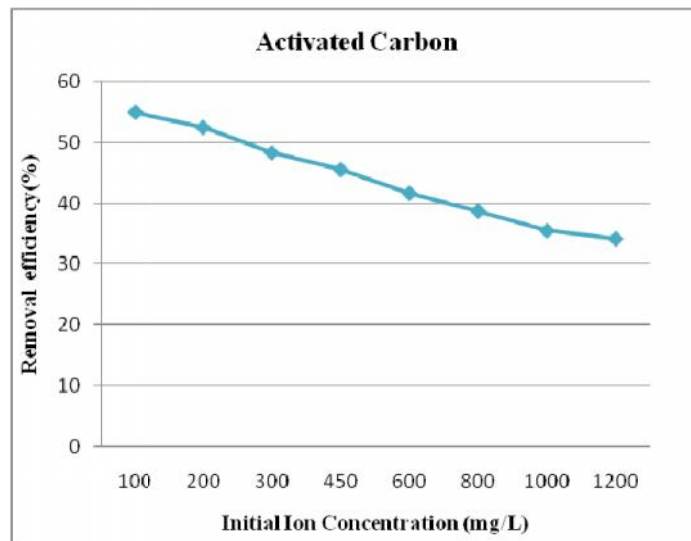


Fig 11

Effect of initial ion concentration on hardness removal by activated carbon: (Contact time 150 min, Dosage 4g/L).

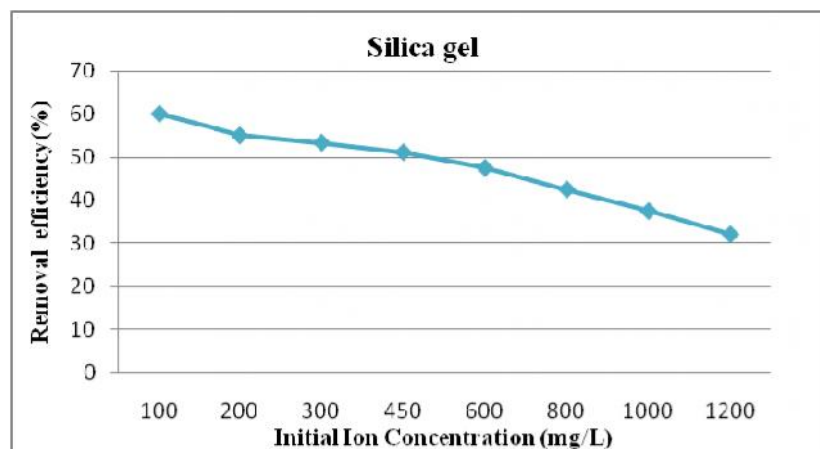


Fig 12

Effect of initial ion concentration on hardness removal by Silica gel: (Contact time 90 min, Dosage 6g/L).

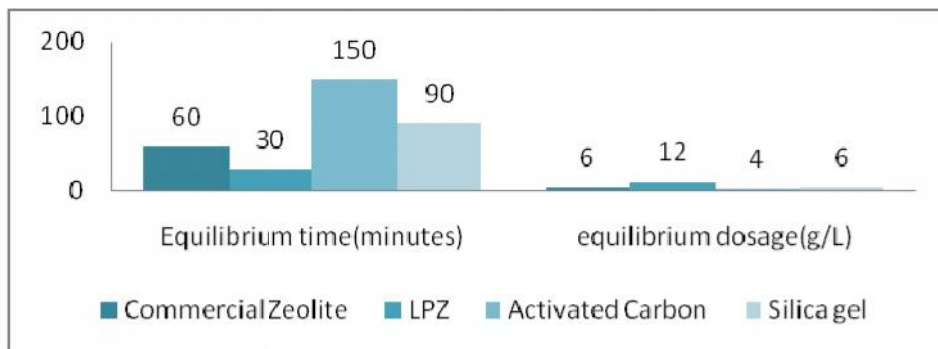


Fig 13.
Comparison of four adsorbents by their equilibrium time and dose

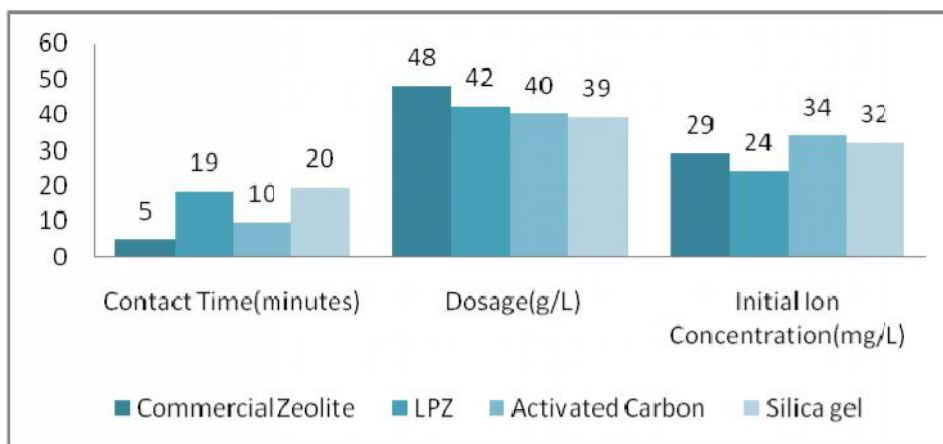


Fig 14
minimum percentages of removal efficiencies of four adsorbents

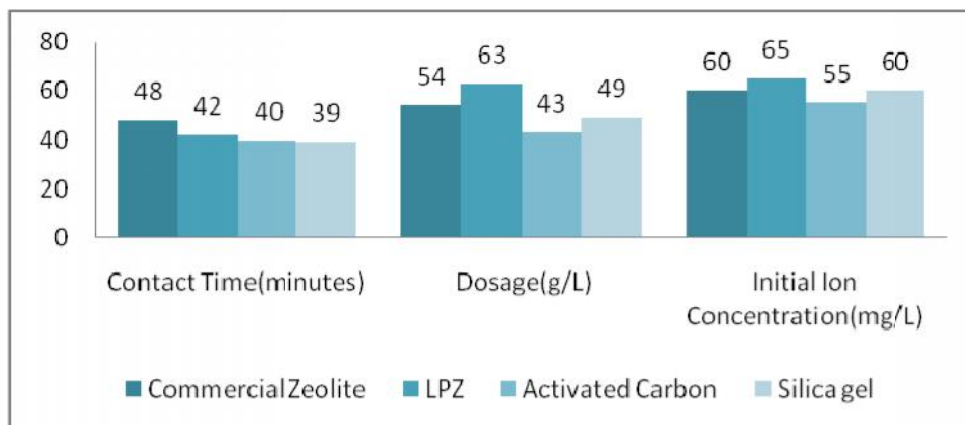


Fig 15
maximum percentages of removal efficiencies of four adsorbents when treated for Contact time, Dosage, Initial ion concentration.

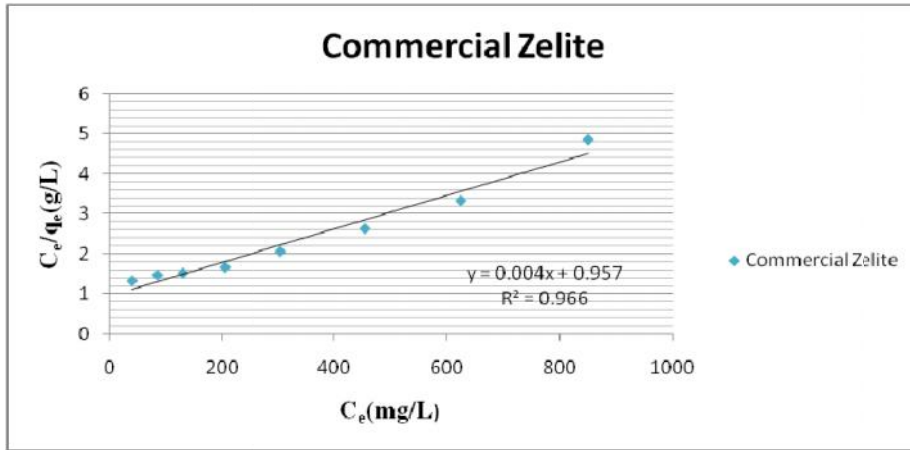


Fig 16
Langmuir adsorption isotherm for Commercial Zeolite

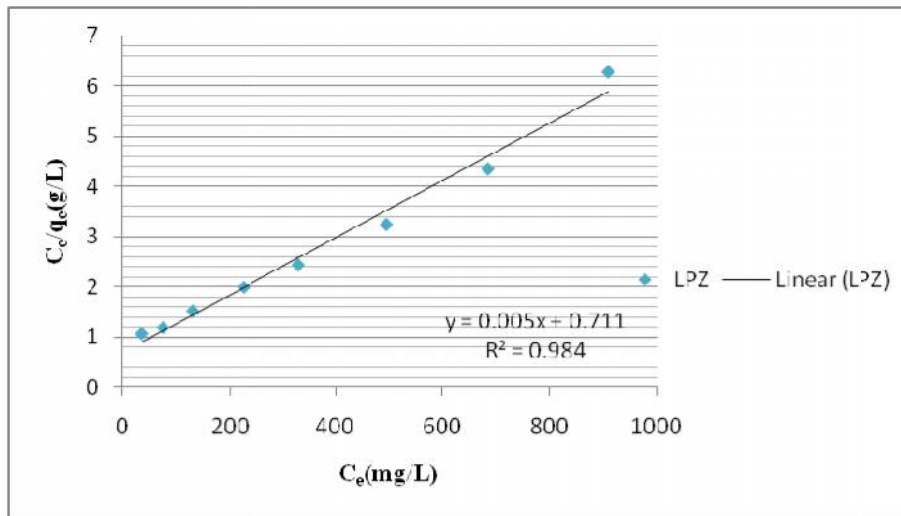


Fig 17
Langmuir adsorption isotherm for LPZ.

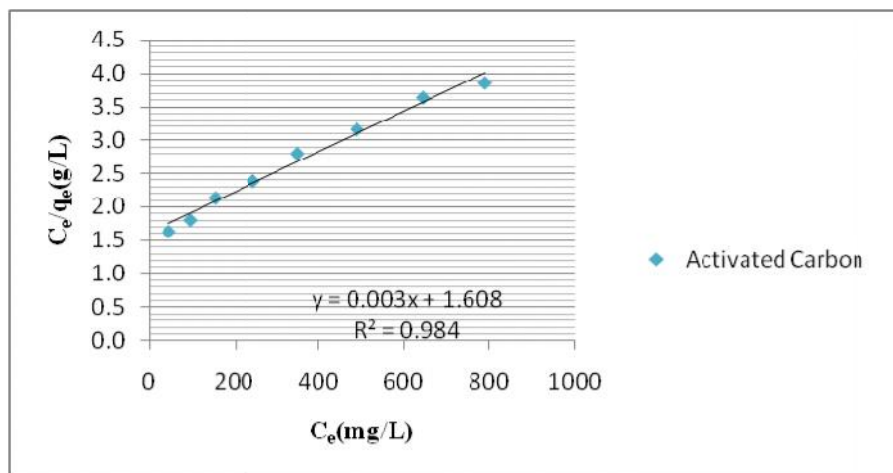


Fig 18
Langmuir adsorption isotherm for Activated Carbon.

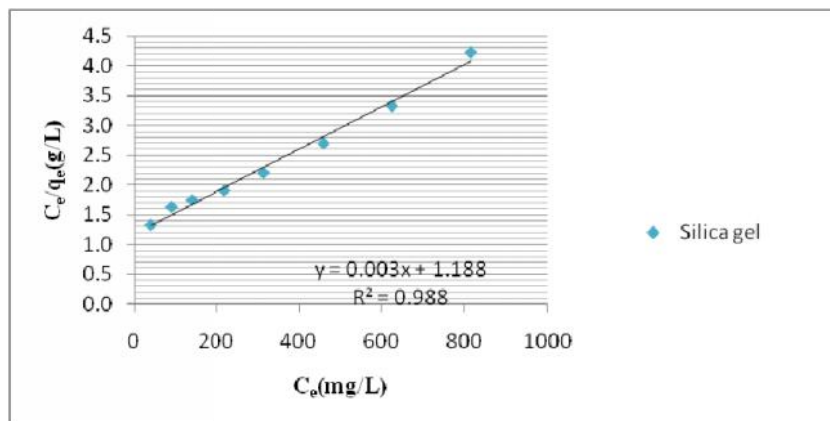


Fig 19
Langmuir adsorption isotherm for Silica gel.

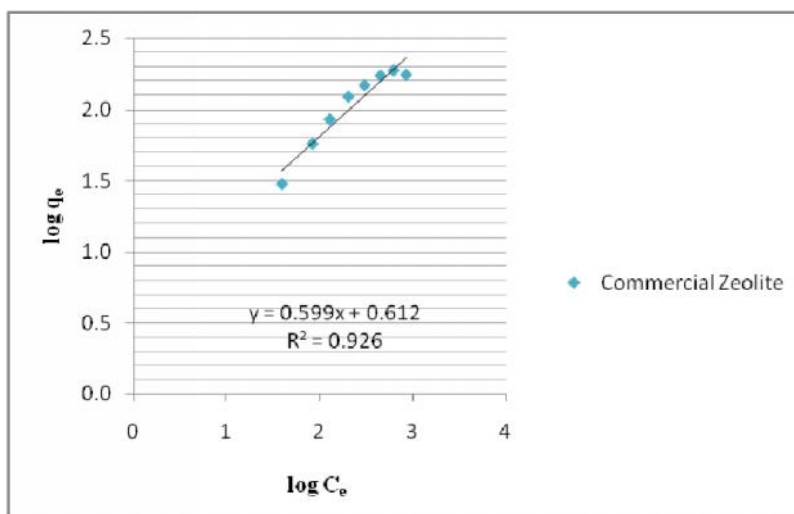


Fig 20
Freundlich adsorption isotherm for Commercial Zeolite.

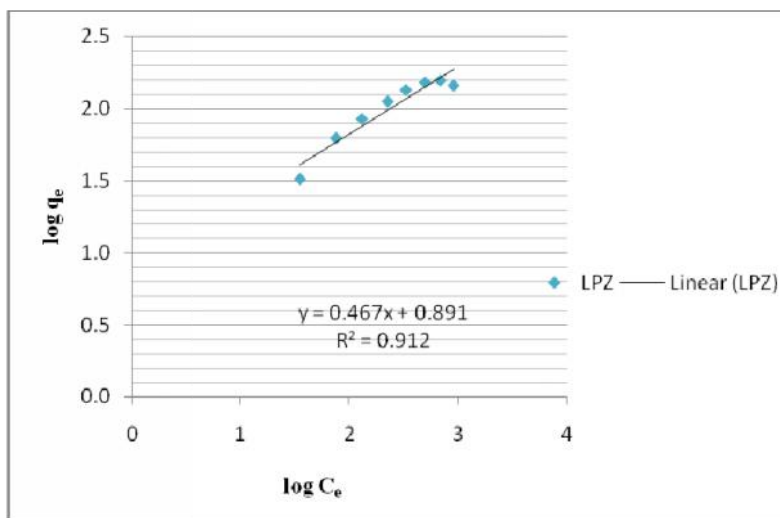


Fig 21
Freundlich adsorption isotherm for LPZ

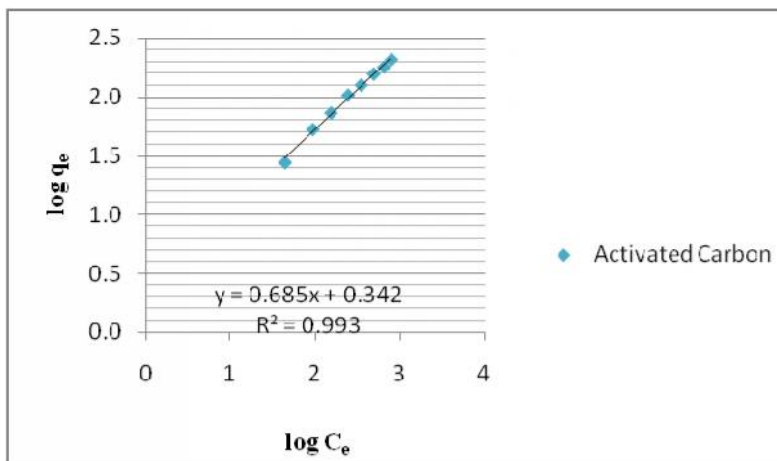


Fig 22
Freundlich adsorption isotherm for Activated carbon.

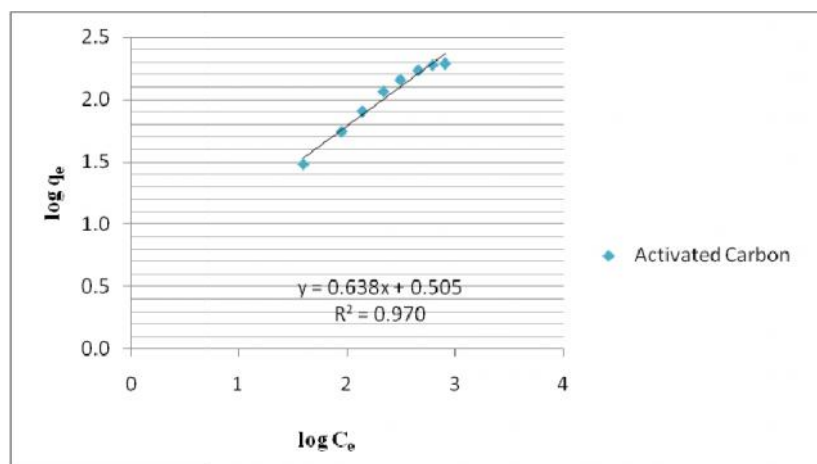


Fig 23
Freundlich adsorption isotherm for Silica gel.

Table 1
Chemical Composition of Fly Ash

| Compound | Composition of Fly Ash (%) |
|--------------------------------|----------------------------|
| SiO ₂ | 59.96 |
| Al ₂ O ₃ | 26.15 |
| Fe ₂ O ₃ | 5.85 |

Table 2
Langmuir adsorption parameters of four adsorbents:

| S.No | Parameter | Adsorbent | | | |
|------|----------------|--------------------|-------|------------------|------------|
| | | Commercial Zeolite | LPZ | Activated Carbon | Silica gel |
| 1 | R ² | 0.966 | 0.984 | 0.984 | 0.988 |
| 2 | q _m | 250 | 200 | 333 | 333 |
| 3 | K _L | 0.957 | 0.711 | 1.608 | 1.188 |

Table 3
Freundlich adsorption of four adsorbents:

| S.No | Parameter | Adsorbent | | | |
|------|----------------|--------------------|-------|------------------|------------|
| | | Commercial Zeolite | LPZ | Activated Carbon | Silica gel |
| 1 | R ² | 0.926 | 0.912 | 0.993 | 0.970 |
| 2 | N | 1.669 | 2.141 | 1.460 | 1.567 |
| 3 | K _f | 0.612 | 0.891 | 1.342 | 1.505 |

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