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REMOVAL OF HARDNESS (CA^{2+}, MG^{2+}) AND ALKALINITY FROM GROUND WATER BY LOW COST ACTIVATED CARBON USING *EICCHORNIA CRASSIPES* PLANT

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Keywords:

Hardness removal, low-cost activated carbon, Eicchornia crassipes, physicochemical parameters

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ABSTRACT

The study was carried out the physicochemical characteristics of ground water from Thirubhuvanam village of Thanjavur District, Tamilnadu (India). The physicochemical parameters such as TDS, EC, Calcium, Magnesium and Total alkalinity have been analyzed using Indian standard methods (IS: 3025) and removal of hardness (Ca^{2+}, Mg^{2+}) and alkalinity using *Eicchornia crassipes* carbon for purification of ground water. In present study various dose of *Eicchornia crassipes* carbon are taken and checked for the efficiency dose on ground water. After treatment of water sample with *Eicchornia crassipes* carbon were analyzed for different parameters like TDS, Mg^{2+}, Ca^{2+}, Alkalinity, electrical conductivity all parameters were reduced with increased dose of *Eicchornia crassipes* carbon.

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1. INDRODUCTION

Water hardness is the major amount of calcium and magnesium cations in water. Hardness is mostly expressed as milligram of calcium carbonate (CaCO3) equivalent per liter and also can be mentioned in term of carbonate (temporary) and noncarbonated (permanent) hardness. The hardness in water is naturally occurring in groundwater which weathering of limestone, sedimentary rock and calcium bearing minerals. They are also present locally from industrial effluent such as chemical and mining industry or the excessive use of lime to the soil in agriculture field. [2, 13]

In general, water supplies with total hardness higher than 200 mg/L can be tolerated by consumers but are considered as poor resources; while values higher than 500 mg/L are not acceptable for most of the domestic consumptions. Hardness in water refers to existing divalent ions, such as iron, manganese, calcium and magnesium. Among them, calcium and magnesium are known as the dominant species for water hardening [8]. Although it has been shown that water hardness doesn't have serious health impact, it has been demonstrated that hard water is responsible for the formation of deposits in boiler and household facilities, as well as diverse influence on cleaning performances of detergents [6]. Formation of precipitates may cause a decrease of heat transfer in boiler, a decrease of fluid rate, bursting of water pipeline, the formation of stain in dishes and clothes. Furthermore, high concentrations of magnesium in drinking water may induce a bitter taste [1]. In water purification and treatment plant, lime and soda ash are used for the removal of hardness. One of the main drawbacks of this process is the resulting waste, namely the large amount of liquid sludge produced, as well as the need for re-carbonation of the softened water [10, 7]. In addition, the use of additional chemicals to prevent sludge production is restricted and hence in most cases water hardness species cannot be fully removed [5]. A variety of methods have seen developed for the removal of toxic organic and inorganic constituents from water and waste water. The methods are adsorption, chemical precipitation, reverse osmosis membrane filtration, ion exchange and coagulation.

Increasing dose of *Phyllanthus emblica* wood carbon, increases the adsorption efficiency Ca^{2+}(71.7 %), Mg^{2+}(69.6 %) and total alkalinity (89.7 %), [3] Softening of hard water by removing ca^{2+} and Mg^{2+} cation was studied using natural and alkali modified pumices as adsorbents. Increasing the mass of adsorbent, the contact time (or) the initial ions concentration led to an increase of cations removal. The studied pumice adsorbent showed a higher selectivity for calcium adsorption if compared to magnesium [11].

Increasing dosage of *Moringa oleifera*, increases the hardness removal efficiency. The amount of dosage of *Moringa oleifera* required in a particular water sample depends on the number of hardness causing species present in water. *Moringa oleifera* as a coagulant is observed more effective for lower initial hardness and the removal efficiency decreases with increasing the initial hardness [4]. In this present study to access the activity of *Eicchornia crassipes carbon* on the removal of calcium, magnesium, total alkalinity, electrical conductivity and total dissolved solids from ground water.

2. MATERIALS AND METHODS

2.1 Study area:

The ground water samples were collected from Thirubhuvanam village in Thanjavur District.

2.2 Methodology:

The activated carbon was prepared by air dried stem part of *Eicchornia crassipes* plant powder with concentrated sulphuric acid in a weight ratio 1:1. The resulting black product was kept in a furnace maintained at 160^0 C for shows followed by washing with distilled water until it become free from excess acid and dried at 110^0 C for a period of 2 hours. The carbon product was grained well to fine powder and the portion retained between 90µ to 53µ sieves was used in all the adsorption experiments. This carbon is designated as *Eicchornia crassipes* carbon (ECC).

2.3 Characteristics of adsorbent:

2.3.1 Moisture content:

About 10 g of the sorbent was weighed in a Petri dish. The dish was placed in an electric oven maintained at $105^0 \pm 5^0$ C for about 4 hours. The Petri dish wash covered cooled in a desiccator and weighed. Heating, cooling and weighing was repeated at 30 minutes between the two consecutive weighing was less than 5 mg.

$$\text{Moisture content (\%)} = 100\,(M - X) / M \qquad (1)$$

Where,
M = Mass in grams of the sorbent taken for test.
X = Mass in grams of the sorbent after drying.

2.3.2 Ash content:

Two grams of adsorbent under examine was weighed accurately into a tarred porcelain crucible. The crucible and its contents were placed in an electric oven at $105^0 \pm 2^0$ C for about 4 hours. The crucible was removed from the oven and contents were ignited in an electric muffle furnace at $1000^0 \pm 4^0$ C for about 3 hours. The process of heating and cooling was repeated until the difference between two consecutive weighing was less than 5 mg.

$$\text{Ash on dry basis (\%)} = M_1 \times 100 / M\,(1 - X / 100) \qquad (2)$$

Where,
M_1 = Mass of the ash in grams.
M = Mass of the adsorbent taken for the test in grams.
X = Percentage of moisture content present in the adsorbent taken for the test.

2.3.3 pH:

10 g of the dried material was weighed and transferred into a one-liter beaker. 100 ml of freshly boiled and cooled water (adjusted to pH 7.0) was added and heated to boiling. After digesting for 10 minutes, the solution was filtered while hot, rejecting the first 20 ml of the filtrate. The remaining filtrate was cooled to room temperature and pH was determined using pH meter.

2.3.4 Decolourising power:

Decolorizing power of adsorbent is expressed in terms of milligrams (mg) of methylene blue adsorbed by 1 g of adsorbent. 0.1 g of the adsorbent was transferred to 50 ml glass stopper flask. 1 ml of methylene blue solution 0.15 % (w/v) was added from a burette and shaken for 5 minutes. Addition of methylene blue solution and shaking was continued till the blue colour persisted for at least 5 minutes.

$$\text{Decolorizing power (mg/g)} = [MB]\ w/v \times V \times 1000 / M \qquad (3)$$

Where,
V = Volume in ml of methylene blue solution consumed.
M = Mass of the adsorbent taken for the test in gram.

2.4 Adsorption studies

2.4.1 Effect of adsorbent dosage:

The ground water for study purpose was collected from Thirubhuvanam village in Thanjavur District. In this experiment were carried out by 100 ml of ground water sample with various doses of *Eicchornia crassipes* carbon of 50 mg to 150 mg weighed separately. The adsorption experiment was conduct on the magnetic stirrer for 120 minutes at 1280 rpm. After treatment the water quality parameters were analyzed, using Indian standard method (table-1). The efficiency dose of *Eicchornia crassipes* carbon was determined.

2.4.2 Effect of contact time:

100 mg of *Eicchornia crassipes* carbon was mixed with 100 ml of ground water, and kept on magnetic stirrer for 30min, 60 min, 90 min and 120 min time variation at 1280 rpm speed. The adsorption experiments were conduct at room temperature 29.7^0 C. After the treatment water quality parameters were analyzed, using Indian standard methods.

2.4.3 Adsorption Capacity Measurement:

The adsorption capacity of the calcium, magnesium and alkalinity was measured using following relation:

$$Q_e = V (C_i - C_f) / M \qquad (4)$$

Where, Q_e, V, C_i, C_f and M are representing the adsorption capacity, volume of the sample, initial concentration, final concentration and amount of adsorbent used in gram (Table-4).

2.5 Radish seed phytotoxicity assay:

To evaluate phytotoxic properties of adsorbent (ECC), Radish seed phytotoxicity assay was performed [12]

Root length determination:

Whatman No. 1 filter paper kept on Petri dish and 5 ml of treatment water were added. Filter paper was dried at room temperature for reducing extra solvent. 5ml of double distilled water was added and then 20 radish seed were placed on Petri dish followed by tightly sealed and maintained at room temperature ($29^0 \pm 2^0$C). Root length was measured after 2, 4 and 6^{th} days of interval. Only double distilled water containing Petri dish was used as control. Raw water containing Petri dish was used separately. Each assay was carried out in three times [9].

3. RESULTS AND DISCUSSION

3.1 Characteristics of adsorbent:

Physical parameters of adsorbent are very important for adsorption technique. The results are given about table number – 2.

3.2 Effect of adsorbent dosage:

The ground water following drinking water quality parameters were analyzed after the treatment of various doses 50 mg/100 ml to 150 mg/100 ml.

3.2.1 Total Dissolved Solid:

The initial total dissolved solid observed was 278 mg/l. It was observed that the use of *Eicchornia crassipes* carbon showed decrease in TDS of ground water (278 mg/l to 190 mg/l)with increased dose at 50mg/100ml to 150mg/100ml respectively,(Table-3),(Fig-1).

3.2.2 Electrical Conductivity:

The initial electrical conductivity observed was 0.60 mS / cm in ground water. It was observed that the use of *Eicchornia crassipes* carbon showed decrease in electrical conductivity (0.60 – 0.42 mS/cm) of ground water with increased dose, (Table-3),(Fig-2).

3.2.3 Calcium (Ca^{2+}):

The initial calcium (Ca^{2+}) observed was 36.87 mg/l in ground water. It was observed that the use of *Eicchornia crassipes* carbon showed decrease in calcium of ground water with increased dose at 50 mg/100 ml to 150 mg/100 ml. (Table-3), (Fig-3).

3.2.4 Magnesium (Mg^{2+}):

Magnesium during the present research work was observed to be 14.09 mg/l for ground water sample. It was observed that after treatment with *Eicchornia crassipes* carbon; Mg^{2+} was decreased with increase dose of *Eicchornia crassipes* carbon. After treatment the magnesium concentration is 6.07 mg/l, (Table-3), (Fig-4).

3.2.5 Total Alkalinity:

The initial concentration of total alkalinity observed was 72.33 mg/l in ground water. It was observed that the use of *Eicchornia crassipes*carbon showed decrease in total alkalinity of ground water with increased dose at 50mg/100ml to150mg/l,(Table-3), (Fig-5).

Adsorption efficiency of calcium, magnesium, and alkalinity are given in the table-4. Before and after treatment of *Eicchornia crassipes* carbon and its concentration variation of calcium, magnesium and alkalinity are shown in the figure-7.

3.3 Effect of contact time:

The percentage of hardness (Ca^{2+}, Mg^{2+}) and total alkalinity removal was increases with increases in contact time. In this method calcium ion reduced from 36.87 mg/l to 10.01 mg/l. Magnesium and total alkalinity are reduced from 14.09 mg/l to 6.07 mg/l and 72.33 mg/l – 9.80 mg/l respectively, (Table-5). After treatment the concentration of TDS, EC, Ca^{2+}, Mg^{2+} and total alkalinity are shown in the figure-6.

3.4 Radish seed Phytotoxicity Assay:

The results were compared with control. The phytotoxicity was inhibited by after ground water treatment of *Eicchornia crassipes* carbon. Mean data of root length inhibition by treatment water of *Eicchornia crassipes* carbon are give in table – 6 and Fig – 8.

3.5 Kinetic Models:

3.5.1 Largergren pseudo first order equation:

Pseudo-first order rate equation is commonly used to the adsorption of liquid/solid system based on adsorbent capacity. According to this model, one adsorbate species reacts with one active site on surface. The differential form of the equation is expressed as,

$$dq_t /dt = k_1 (q_e - q_t) \qquad (5)$$

Integrating equation (5) for the boundary conditions t= 0 –t and q_t = 0 –q_t gives:

$$\ln (q_e / q_e - q_t) = k_1 t \qquad (6)$$

Equation (6) can be rearranged to obtain the following linear form:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (7)$$

In order to obtain the rate constants, the values of ln (q_e- q_t) were linearly correlated with *t by* plot of ln (q_e- q_t) versus *t* to give a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively.

3.5.2 Pseudo second order equation:

The kinetic of sorption was analyzed by means of the pseudo-second order model, which is expressed as follows:

$$dq_t / d_t \;\; k_2 (q_e - q_t)^2 \qquad (8)$$

Where k_2 is the rate constant (g/mg min). Integration of Eq. (8) at the boundary, qt=0 at t=0 and qt=qt at t=t and then rearrangement to a linear form gives (Eq. 9):

$$t / q_t = 1/k_2 \, q_e^2 + 1 / q_e \, t \qquad (9)$$

The value of q_e can be determined from the slope of the plot t/qt vs. t, respectively. The adsorption data were tested with pseudo first order kinetic model. The results are shown in figure-9.

The lagergren pseudo first order mechanism shows poor linear plots. The same data were tested with pseudo second order kinetic mechanism and results are shown in figure-10. The plots have better linearity and the adsorption capacity of calcium, magnesium and total alkalinity are given in table - 7.

TABLES

Table-1: Methods used for chemical study of ground water.

Parameters	Methods	Reference
Calcium	EDTA- Titrimetric method	IS:3025(Part 40)
Magnesium	EDTA- Titrimetric method	IS:3025(Part 46)
Total Alkalinity	Titrimetric method	IS:3025(Part 23)
Total Dissolved Solids	Gravimetric method	IS:3025(Part 16)
Electrical Conductance	Conduct metric method	IS:3025-1964

Table-2: Texture properties of the *Eicchornia crassipes* based activated carbon.

Parameters	Capacity
Moisture content	3.47 **%**
Ash content	10.41 **%**
pH	6.92
Decolorising	105 mg/g
Size	90 µ - 53 µ

Table-3: Parameter studied before and after treatment of groundwater with various dose of *Eicchornia crassipes* carbon

Parameters	**Before Treatment**	**After treatment of water at various dose of *Eicchornia crassipes* carbon**				**BIS Standards**
	0 mg / 100 ml	50 mg/100 ml	100 mg/l00 ml	125 mg/100 ml	150 mg/100 ml	
Total Dissolved Solids (mg/l)	278	221	180	184	190	500 mg/l
Electrical Conductivity (mS/cm)	0.60	0.51	0.42	0.43	0.44	-
Calcium (mg/l)	36.87	23.04	10.01	10.01	12.02	75 mg/l
Magnesium (mg/l)	14.09	9.11	6.07	6.07	7.29	30 mg/l
Total Alkalinity (mg/l)	72.33	39.23	13.48	13.48	14.71	200 mg/l

Table-4: Removal efficiency of Calcium, Magnesium and Total Alkalinity.

Parameters	**C_0 mg/l**	**C_e mg/l**	**Q_e mg/g**	**% of Removal**
Ca^{2+}	36.87	10.01	26.86	72.8
Mg^{2+}	14.09	6.07	8.02	56.9
Total Alkalinity	72.33	13.48	58.85	81.3

Table-5: Parameter studied before and after treatment of water at various time

Parameters	**Before Treatment**	After treatment of water at various time					**BIS Standards**
		30 min	60 min	90 min	100 min	120 min	
TDS	278	185	183	181	180	180	500 mg/l
EC	0.60	0.43	0.42	0.42	0.42	0.42	-
Ca^{2+}	36.87	13.02	12.02	10.01	10.01	10.01	75 mg/l
Mg^{2+}	14.09	7.29	7.03	6.07	6.07	6.07	30 mg/l
Total Alkalinity	72.33	19.61	14.71	9.80	9.80	13.48	200 mg/l

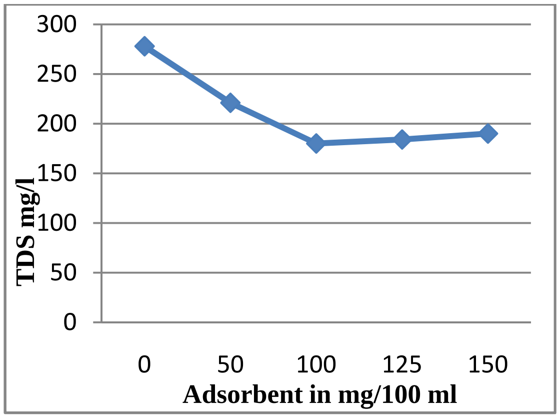
Table-6: Analysis of mean data of root length inhibition by treatment water of ECC.

Variables	**2- Day**	**4- Day**	**6- Day**
Control	10.9 mm	58.4 mm	74.4 mm
Ground water	8.4 mm	42.2 mm	42.5 mm
Treatment water	10.4 mm	56.9 mm	70.4 mm

Table **– 7:** Pseudo First and second order kinetic parameters for the present work

Parameters	**C_0 mg/l**	**C_e mg/l**	**Pseudo first order kinetic model**			**Pseudo Second order kinetic model**		
			Qe (Exp) (mg/g)	**Qe (Theo) (mg/g)**	**R^2**	**Qe (Exp) (mg/g)**	**Qe (Theo) (mg/g)**	**R^2**
Ca^{2+}	36.87	10.01	26.86	5.32	0.975	26.86	28.57	0.996
Mg^{2+}	14.09	6.07	8.02	1.29	0.923	8.02	8.84	0.987
Total Alkalinity	72.33	13.48	58.85	35.48	0.950	58.85	71.42	0.996

FIGURES



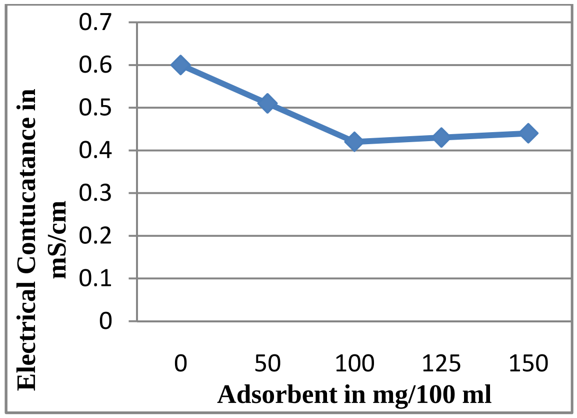
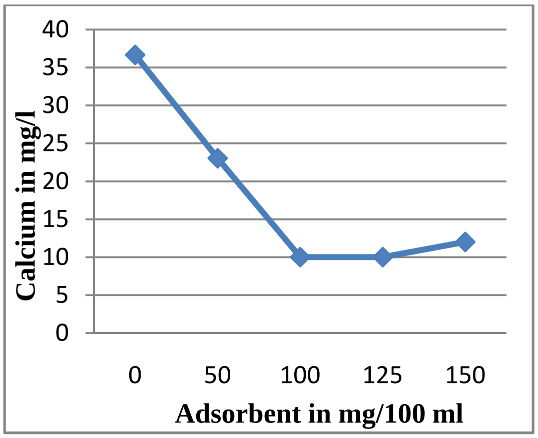


Fig-1: TDS of ground water before and after treatment of ECC. Fig-2: EC of ground water before and after treatment of ECC.



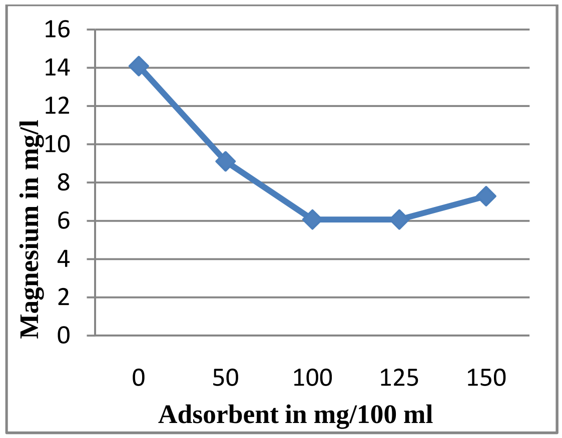
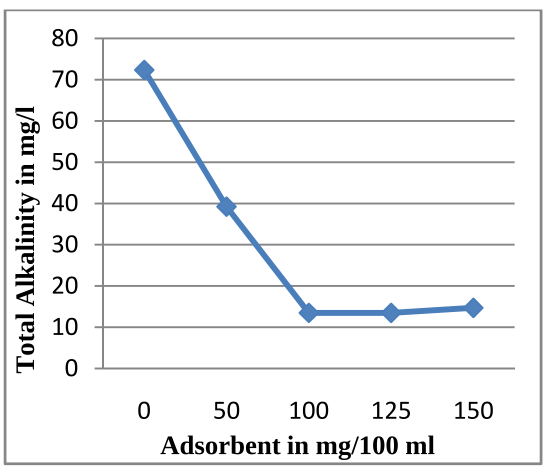


Fig-3: Ca^{2+} of ground water before and after treatment of ECC. Fig-4: Mg^{2+} of ground water before and after treatment of ECC.



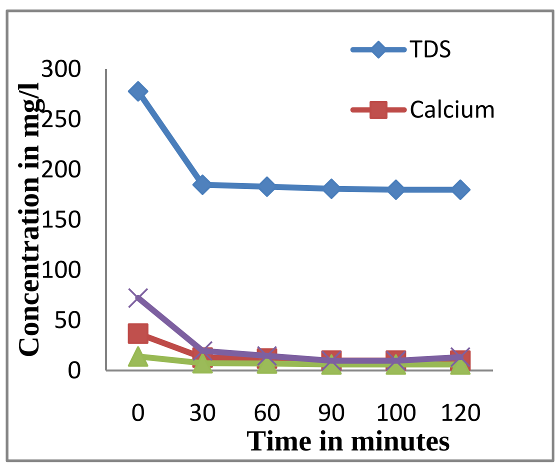
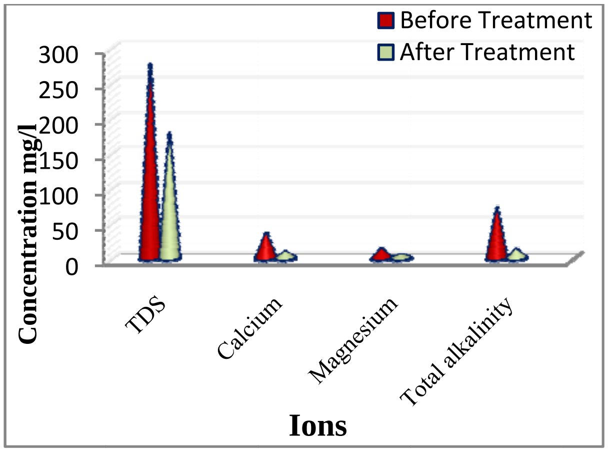


Fig-5: TA of ground water before and after treatment of ECC. Fig-6: Concentration of TDS, Ca^{2+}, Mg^{2+} and TA adsorbed on ECC for various times.



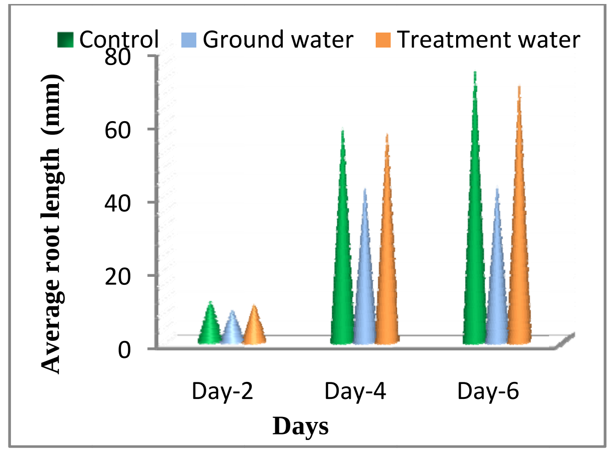


Fig - 7: Concentration variation of ground water before and after treatment of ECC.

Fig-8: Regular root length inhibition by treatment water of ECC.
Data compared with Control and ground water.

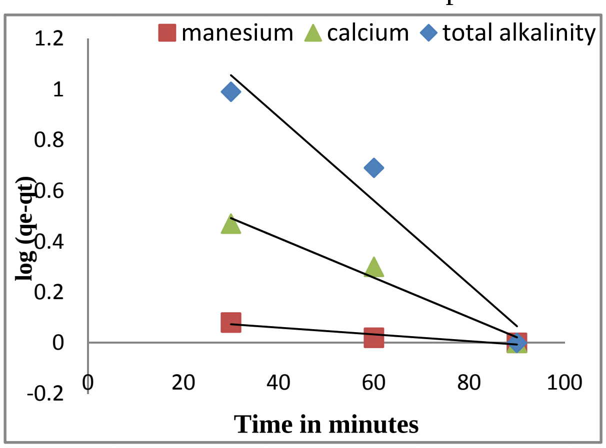


Figure-9: Pseudo First order kinetic model

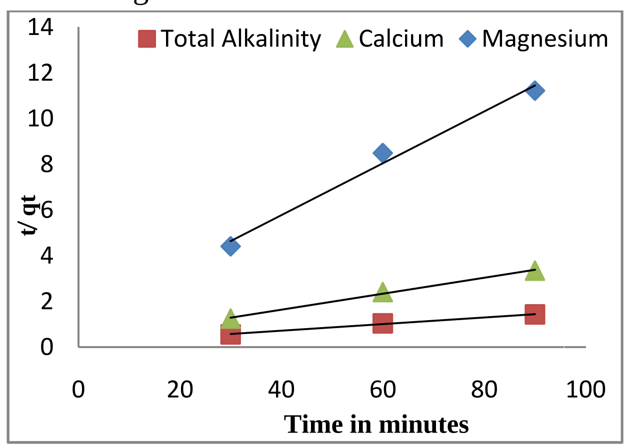


Figure-10: Pseudo Second Order Model

CONCLUSION

In present study was concluded that various dose of *Eicchornia crassipes* carbon are taken and checked for the efficiency dose on ground water. After treatment of water sample with *Eicchornia crassipes* carbon were analyzed for different parameters like TDS, Electrical conductivity, calcium (72.8 %), magnesium (56.9 %) and total alkalinity (81.3 %) were reduced with increased dose of *Eicchornia crassipes* carbon.

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