Hardness (Ca^{2+}, Mg^{2+}) uptake from ground water by activated *Phyllanthus emblica* wood powder

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Abstract:

The present study was done to evaluate the water purifying property of activated *Phyllanthus emblica* wood powder. Ground water sample was collected from Thirubhuvanam village, was analyzed for physicochemical parameters. Activated *Phyllanthus emblica* wood powder was examined as natural alternative material for ground water treatment. The results were compared with the BIS of drinking water quality guide line. All parameters were reduced with increased dose of activated *Phyllanthus emblica* wood powder.

Keywords: Hardness removal, physicochemical parameters, *Phyllanthus emblica*, ground water treatment.

1. INTRODUCTION

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 hardness [13]. Calcium is the most abundant mineral in the human body. Calcium plays vital roles in the structure and function of the human body [16]. However, there is a significant association between calcium level in drinking water and colorectal, gastric and breast cancer [17]. Magnesium is a naturally occurring mineral that is found in food and other medical products. The adult human body contains about 25 g of magnesium, about 60% of this quantity is present in bones and 40% is Present in muscles and other tissues. However, taking too much supplemental magnesium can result in symptoms of toxicity. These symptoms include a fall in blood pressure, confusion, abnormal cardiac rhythm, muscle weakness, difficulty breathing and deterioration of kidney function [6].

In order to removal the divalent ions (Ca2+, Mg2+) various methods have been widely applied for water softening includes, electrochemical processes [8], Enzyme catalyzed [10], Nano filtration [3], electro- dialysis [12], ultrasound [9], ultra- filtration [1], ion-exchange [5][11], membranes [7]. The two major methods which are typically used to remove hardness form water are lime soda softening and ion exchange softening. The first method is used mostly for municipal purposes [2].

The primary drawbacks of the lime soda method include the production of a large volume of sludge that requires post-treatment, excessive use of chemicals (such as lime soda ash, and caustic soda) and the addition of acids for pH adjustment, which increases operating expenses [14]. The ion exchange process is primarily employed for residential water softening. Experimental studies have found the sodium level in softened water was 2.5 time higher than municipal water [18].

After treatment of water sample with *Phyllanthus emblica carbon* were analyzed for different parameters like TDS, Mg2+, Ca2+, Alkalinity, electrical conductivity all parameters were reduced with increased dose of *Phyllanthus emblica* carbon [4].

Softening of hard water by removing Ca2+ and Mg2+ 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 [5].

The objective of this study to evaluate the water purifying property of activated *Phyllanthus emblica* wood powder.

2. MATERIALS AND METHODS

2.1 Study area:

The ground water sample was collected Thirubhuvanam village from Thanjavur district.

2.2 Methodology:

The activated bio material was prepared by air dried *Phyllanthus emblica* wood powder soaked with 0.1 M NaOH at 24 hours. The material was washed with distilled water until it become free from excess base and dried at 110^0C for 2 hours. Then the material soaked with 0.1 M acetic acid at 3 hours, followed by washed with distilled water until it become free from excess acid and dried at 110^0C for a period of 2 hours. The adsorbent and its portion retained 120 µ - 1 µ sieves were used in all the adsorption experiment. The material was designated as activated *Phyllanthus emblica* wood powder (APEWP).

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.

Moisture content (%) = 100 (M – X) / M (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 1000^0C ± 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.

Ash on dry basis (%) = M_1 ×100 / M (1-X / 100) (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.

Decolorizing power (mg/g) = [MB] w/v × V × 1000 / M (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 APEWP adsorbent of 100 mg to 400 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 APEWP adsorbent was determined.

2.4.2. Effect of contact time:

400 mg of APEWP adsorbent was mixed with 100 ml of ground water, and kept on magnetic stirrer for 30min, 60 min, 90 min, 100 min and 120 min time variation at 1280 rpm speed. The adsorption experiments were conduct at room temperature 29.7 ± 2^0 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:

$Q_e = V (C_i – C_f) / M$ (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).

2.4.4. Radish seed phytotoxicity assay:

To evaluate phytotoxic properties of adsorbent (APEWP), Radish seed phytotoxicity assay was performed.

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 6th 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.

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.

3.1.1 Effect of adsorbent dosage:

The ground water following drinking water quality parameters were analyzed after the treatment of various doses 100 mg/100 ml to 400 mg/100 ml.

3.1.2. Total Dissolved Solid and Electrical Conductivity:

The initial concentration total dissolved solid observed was 278 mg/l and electrical conductivity observed was 0.60 mS/cm in ground water. TDS was observed that the use of APEWP adsorbent showed decrease in TDS (278 – 219 mg/l) of ground water with increased dose at 100 mg/100ml to 400 mg/l. The TDS variation of before and after treatment of ground water with various dose of APEWP are shown in table-3 and fig- 1.

Electrical conductivity was observed that the use of APEWP adsorbent showed decrease an EC 0.60 to 0.47 mS/cm of ground water with increased dose from 100 mg/100 ml to 400 mg/100 ml.(Table- 3) and (Fig- 2).

3.1.3. Calcium (Ca^{2+}):

The initial calcium (Ca^{2+}) observed was 36.87 mg/l in ground water. It was observed that the use of APEWP adsorbent showed decrease in calcium of ground water with increased dose from 100 mg/100 ml to 400 mg/100 ml (Table- 3), (Fig- 3). In human body hypper calcimia causes coma and death, if calcium level rises to 160 mg/100 ml. In this adsorption technique is very useful tool for removal of high concentration of calcium from ground water.

3.1.4. Magnesium:

Magnesium during the present research work was observed to be 14.09 mg/l from ground water sample of Thirubhuvanam village. Treatment of APEWP adsorbent was given ground water sample in different dose 100 mg/100 ml to 300 mg/100 ml. After treatment the concentration of magnesium ion is 9.72 mg/l (Table- 3), (Fig- 4). In ground water above 400 mg/l of magnesium causes nausea and muscular weakness.

3.1.5. Total alkalinity:

The initial concentration of total alkalinity observed was 72.33 mg/l in ground water. It was observed that the use of APEWP adsorbent showed decrease in total alkalinity of ground water with increased dose from 100 mg/l to 400 mg/100 ml (Table-3), (Fig-5). Adsorption efficiency of calcium, magnesium, and alkalinity are given in table-4 and the concentration variation of ground water of before and after treatment is shown in fig- 7.

3.2. 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 18.03 mg/l. Magnesium and total alkalinity are reduced from 14.09 mg/l to 9.72 mg/l and 72.33 mg/l – 36.78 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.

3.3.Radish seed Phytotoxicity Assay:

The results were compared with control. The phytotoxicity was inhibited by after ground water treatment of activated *Phyllanthus emblica* wood powder. Mean data of root length inhibition by treatment water of APEWP adsorbent are give in table – 6 and Fig – 8.

3.4. Kinetic Models:

3.4.1 Pseudo second order equation:

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

$dq_t / d_t \;\; k_2 (q_e - q_t)^2$ (5)

Where k_2 is the rate constant (g/mg min). Integration of Eq. (5) at the boundary, *qt*=0 at *t*=0 and *qt*=*qt* at *t*=*t* and then rearrangement to a linear form gives (Eq. 6):

$t / q_t = 1/k_2 q_e^2 + 1 / q_e t$ (6)

The value of q_e can be determined from the slope of the plot *t/qt* vs. *t*, respectively. The pseudo second order kinetic mechanism and results are shown in figure-9. The plots have better linearity and the adsorption capacity of calcium 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 activated *Phyllanthus emblica* wood powder adsorbent.

Parameters	Capacity
Moisture content	12.03 **%**
Ash content	10 **%**
pH	7.16
Decolorising	45 mg/g
Size	120 µ - 1µ

Table-3: Parameter studied before and after treatment of groundwater with various dose of APEWP adsorbent.

Parameters	**Before Treatment**	**After treatment of water at various dose of APEWP adsorbent.**						**BIS Standards**
	0 mg /100 ml	100 mg/100ml	200 mg/l00 ml	300 mg/100 ml	400 mg/100 ml	420 mg/100 ml	500 mg/100ml	
TDS (mg/g)	278	246	236	228	220	219	224	500 mg/l
EC (mS/cm)	0.60	0.54	0.51	0.49	0.47	0.47	0.48	-
Ca^{2+} (mg/g)	36.87	30.05	26.05	22.04	18.03	18.03	20.03	75 mg/l
Mg^{2+} (mg/g)	14.09	13.36	10.93	9.72	9.72	9.72	9.72	30 mg/l
TA (mg/g)	72.33	58.84	44.13	41.68	36.78	36.78	41.68	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	18.03	4.71	51 %
Mg^{2+}	14.09	9.72	1.45	31 %
Total Alkalinity	72.33	36.78	8.88	49.1 %

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	241	234	218	221	220	500 mg/l
EC	0.60	0.52	0.50	0.47	0.47	0.47	-
Ca^{2+}	36.87	21.04	20.03	18.03	18.03	18.03	75 mg/l
Mg^{2+}	14.09	13.36	12.15	11.54	9.72	9.72	30 mg/l
Total Alkalinity	72.33	49.04	41.68	36.78	36.78	36.78	200 mg/l

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

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	8.7 mm	33.4 mm	44.5 mm

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

Parameters	C_0 mg/l	C_e mg/l	Pseudo Second order kinetic model		
			Qe (Exp) (mg/g)	Qe (Theo) (mg/g)	R^2
Ca^{2+}	36.87	18.03	4.71	12.04	0.991
Total Alkalinity	72.33	36.78	8.88	5.23	0.998

FIGURES

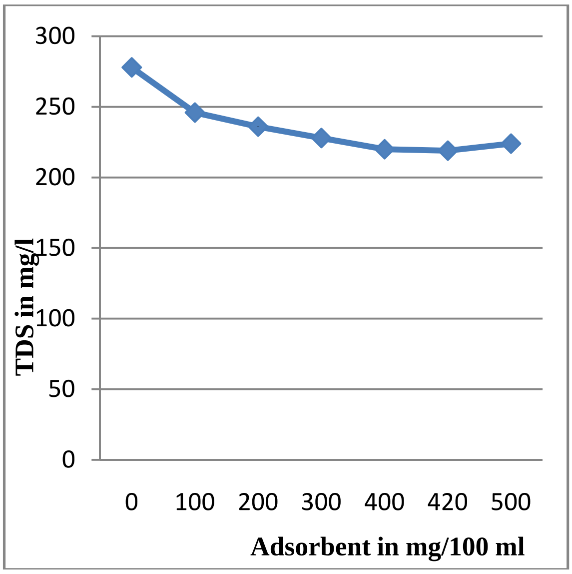

Fig-1: TDS of ground water before and after treatment of APEWP.

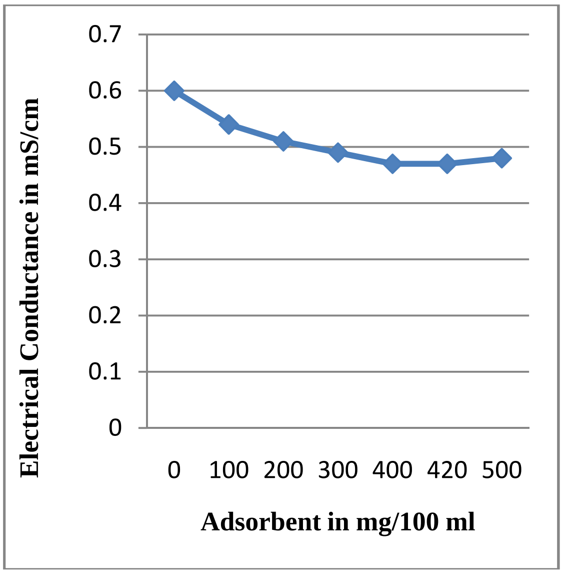

Fig-2: EC of ground water before and after treatment.

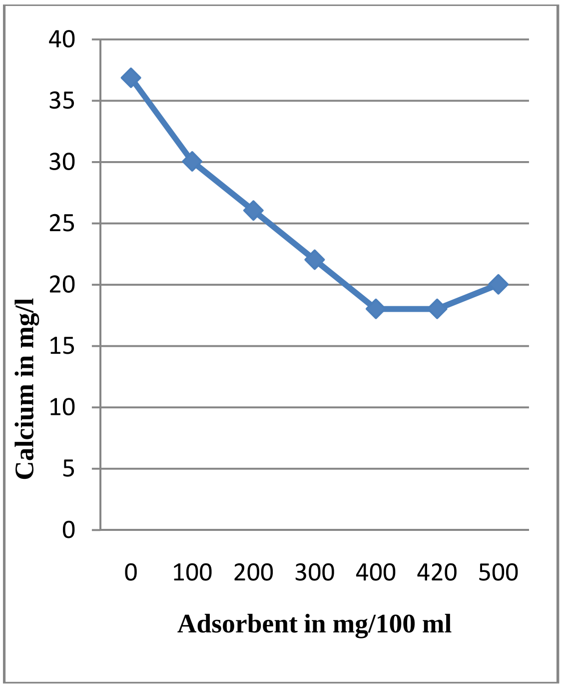

Fig-3: Ca^{2+} of ground water before and after treatment of APEWP.

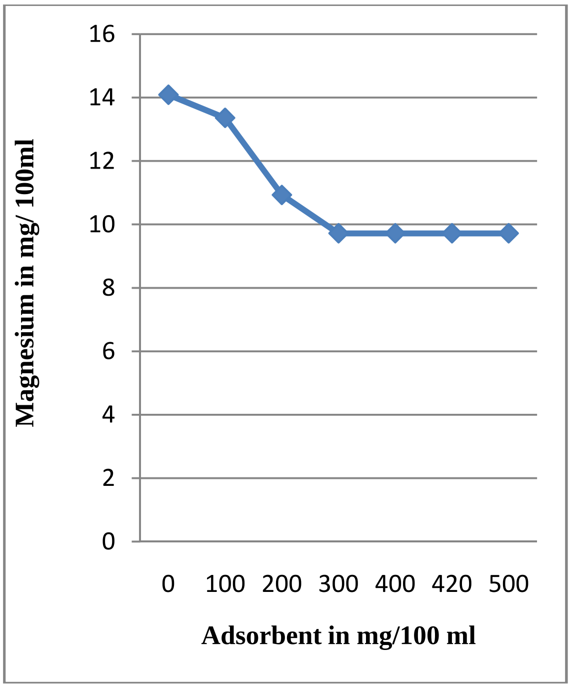

Fig-4: Mg^{2+} of ground water before and after treatment.

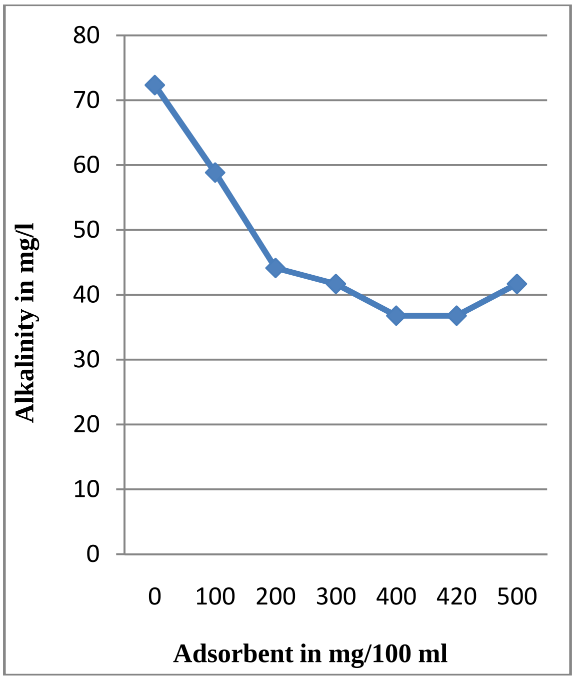

Fig-5: TA of ground water before and after treatment of APEWP.

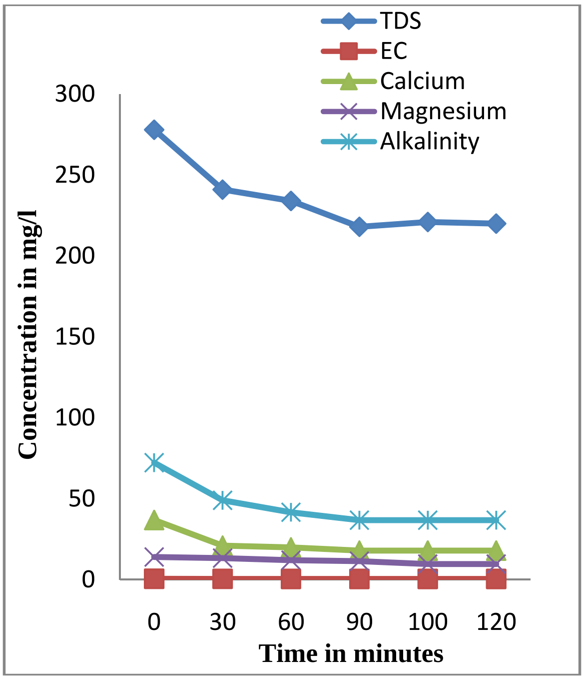

Fig-6: Concentration of TDS, Ca2+, Mg2+ and TA adsorbed on APEWP for various times.

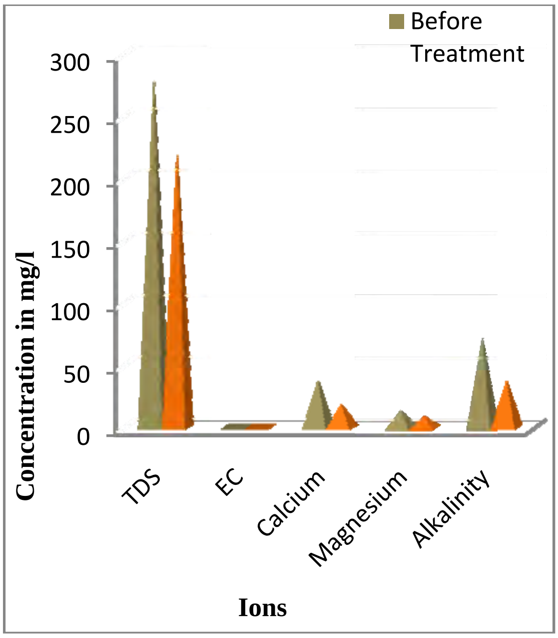

Fig - 7: Concentration variation of ground water before and after treatment of APEWP.

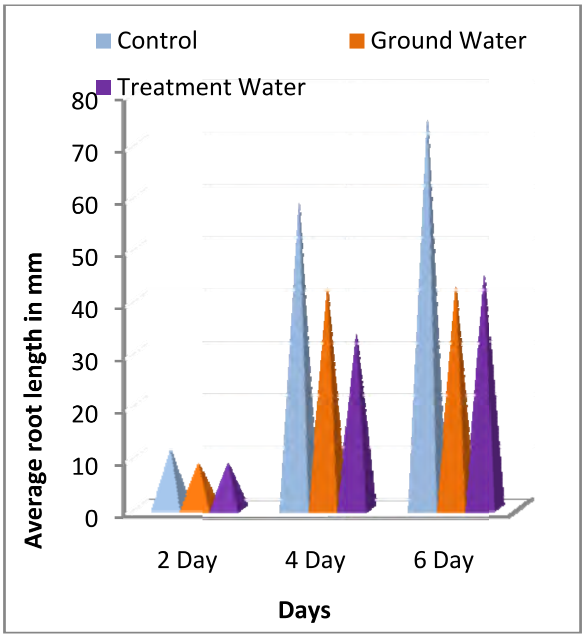

Fig-8: Regular root length inhibition by treatment water of APEWP. Data compared with Control and ground water.

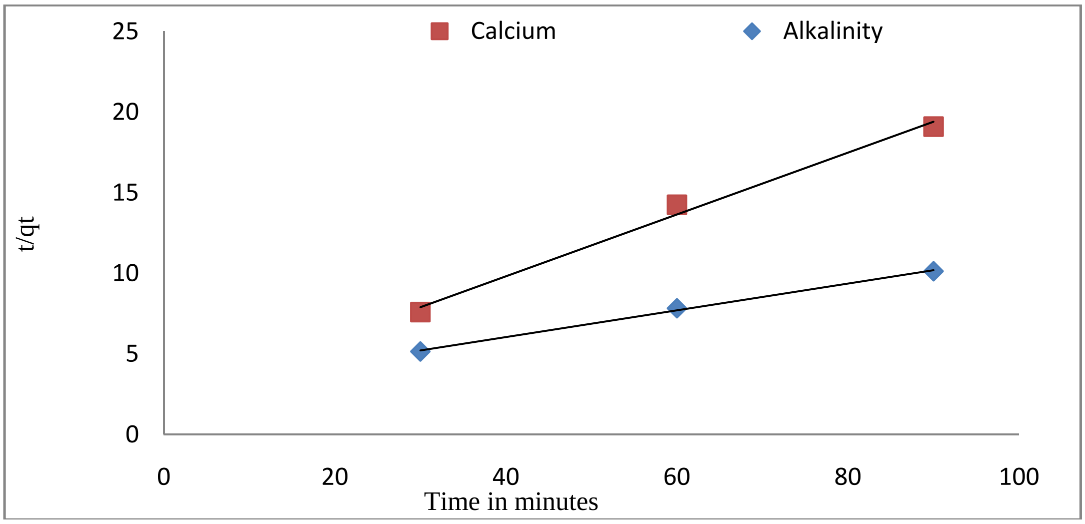

Figure-9: Pseudo Second Order kinetic model

CONCLUSION

In present study concluded the various dose of activated *Phyllanthus emblica* wood powder (APEWP) adsorbent are taken and checked for the adsorption efficiency on ground water. After treatment of water sample were analyzed for different parameters like total dissolved solids, electrical conductivity, calcium, magnesium and total alkalinity were reduced with increased dose of APEWP adsorbent.

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