## **RESEARCH ARTICLE**

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# **Determination and Treatment of Fluoride in Temple Tank by Adsorption using** *Citrullus Lanatus*

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# ABSTRACT

Now-a-days, there is not only a drastic change in population but also simultaneously towards in modern industrialization activities, consequently lead to contamination of both the ground and surface fresh water resources by various waste-stuffs coming out from domestic, municipal, agricultural, industrial and medicinal areas. The groundwater resources are extraordinarily essential for drinking, irrigation, public water supply, industrial utilization and other developmental activities. Generally, the contaminated groundwater resources will create 80-85 % impact on human health, which also affects the entire ecological systems. In this research work, we examined the physico-chemical properties of Thiruparankundram Murugan Temple Tank (TMT) and Vandiyur Mariamman Teppakulam (VMT) of Madurai District in Southern Tamil Nadu. The water samples of each station were collected and investigated, for which the seasonal dissimilarity studies were carried out during April 2019–March 2020. The water quality and physico-chemical parameters like pH, temperature, colour, turbidity, EC, TDS, TH, DO, Cl, F, SO<sub>4</sub>, TSS, trace metal contents, *etc* of the samples were analyzed and compared with the standard WHO, BIS and APHA reports. Furthermore, the low cost–effective activated carbon material, derived from *Citrullus lanatus* (Watermelon) was utilized as an adsorbent for the effective removal of fluoride content in the study areas. This study revealed that the activated carbon, derived from *Citrullus lanatus* is a valuable adsorbent for the removal of fluoride than other carbon materials.

*Keywords* – Adsorption, Citrullus lanatus, Fluoride ion, Physico–chemical parameters, Water quality

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#### I. INTRODUCTION

Generally, water is an essential natural resource for all life supporting activities for humans, animals as well as higher plants in the ecosystems *i.e.*, no life without water (H<sub>2</sub>O) [1, 2]. The unique property of water as the most common universal liquid is widely utilized for drinking, irrigation, power generation, domestic purpose and other developmental activities [3-5]. In every year, approximately 60 - 65 % of groundwater (say major source of freshwater) resources are fully utilized to our regular domestic activities, agricultural and industrial purposes, globally. Due to the fast industrialization, human population, urbanization and rapid socio-economic development activities, the demand of groundwater has been increasing day by day but, the overexploitation, deterioration and high contamination of such resources are now in front of critical challenges [2, 6]. The contamination

groundwater quality is of becoming an environmental issue and the nation should adopt stringent water quality requirements to control the pollution from various sectors. The addition of organic as well as inorganic pollutant materials from non-pointed and pointed sources like domestic and municipal sewages, solid garbage, food wastes, farm effluents and agricultural wastes (including artificial fertilizer residues, insecticides, herbicides, pesticides and farmyard wastes), electroplating, pesticide, fertilizer and beverage industries wastes are directly dumped into groundwater bodies without any further treatment will cause pollution. Due to the undesirable rapid changes of groundwater resource bodies, the periodical analysis on physico-chemical, biological and microbiological parameters are mandatorily checked for those polluted sources. However, the polluted water bodies are up-taken by human, plants and animals, which all will lead to cause a serious health related issues [7-10]. In

addition to these, the disposal of the dead bodies, discharge of various industrial effluents, domestic and municipal sewage wastes and agricultural runoff, may damage our ecological systems as well as pose serious health hazards to human and other living species. Due to weathering, volcanic processes and some industrial (say fertilizer, iron work, ceramic, glass, brick, electroplating, *etc.*) wastewater contains high concentration of fluoride content, which enters eventually into the groundwater sources as well as pollute critically [11–13].

According to WHO, the permissible limit value of fluoride content [14] present in the drinking water is 1.5 mg/L, but the excessive concentration of fluoride content leads to some health problems like thyroid disorder, brain damage, Alzheimer's syndrome, osteosclerosis (brittle bones), cancer, dental as well as skeletal fluorosis and infertility [15, 16]. In order to reduce the fluorine content or defluoridation of water, we have been executing certain top most advanced techniques viz. nanofiltration, reverse osmosis (RO), coagulation, electrocoagulation. electrochemical oxidation. adsorption, precipitation, ion exchange and membrane processes [17, 18]. Among them, adsorption technique is widely acceptable and convenient one due to low cost, ease of operation as well as maintenance, efficient removal and more eco-friendly than the other processes [18, 19]. Recently, the low-cost, efficient and eco-friendly available cheap adsorbents like activated carbon derived from coconut fiber shell and dust, bael shell, Cocos nucifera shell, tea ash, sugarcane bagasses, coffee husk, rice straw, banana peel, Conocarpus erectus, etc [20-25] are widely utilized for defluoridation of water by adsorption processes. Furthermore, the study of water quality parameters is more essential for all the groundwater sources to assess the water quality, to prevent the various water pollutions, creating awareness about water quality and also human health. Hence, there is always a need and concern over the protection and management of groundwater quality for future generation [26].

From the systematic observations as well as deeper investigations of the ground and surface water resources on our recent works [2, 27-29], the present investigation is concerned to reduce the fluoride content present in the temple pond water sources, especially in Thiruparankundram Murugan Temple Tank or Teppakulam (TMT) (say Saravana Poigai Pond) and Vandiyur Mariamman Teppakulam (VMT) of the Madurai district from April 2019 to March 2020 by adsorption method using activated carbon, derived from Citrullus lanatus (watermelon). In this work, various physicochemical water qualities like colour, odour, temperature, electrical conductivity, pH, turbidity, dissolved oxygen (DO), alkalinity, total dissolved solids (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD), calcium (Ca), chloride (Cl), fluoride (F), magnesium (Mg), iron (Fe), nitrate, nitrite, sodium (Na), sulphate (SO<sub>4</sub>), *etc.*, have been discussed in detail. Also, to study the defluoridation process, the contact time, adsorbent dosage, initial fluoride concentration, temperature and pH were optimized and further desorption studies were also carried out to check the reusability of adsorbent.

# II. EXPERIMENTAL METHOD

# 2.1. Study area

Madurai city is the third largest city (longitude: 78°7'28.1884" E; latitude: 9°56'20.7348" N) in Southern Tamil Nadu, it houses the world famous Sri Meenakshi Sundareshwarar temple and is situated on the banks of the river Vaigai. Thiruparankundram, Thirumalai Nayakar Mahal, Gandhi Museum, Pazhamudhir Solai, Maghamalai, Algar Koil, Vandiyur Mariamman Teppakulam and Kazimar Periya Pallivasal are some of the major tourism as well as holistic places in this district. Regarding the boundary, north is bounded by Dindigul district; east is Sivaganga district and south as well as west is bounded by Virudhunagar and Theni districts respectively and it covers an area of about 3,741.73 sq. Km and is a thickly populated district of south Tamil Nadu in India i.e., as per census of 2011, total population is 3,041,038 with a sex-ratio of 990 females, for every 1,000 males and it is the ninth largest population dense district in Tamil Nadu. It is administratively divided into 13 Panchayat Union or Blocks and 420 Village Panchayats. The geographical information of this Madurai district is simple and flat as well as hill area. The river Vaigai flows towards the northwest to southeast direction through the district and it is hot drier during the summer season. Madurai district have got benefits from south-west Monsoon as well as from north east monsoon, in getting rainfall and the mean humidity varies from 50-68 %. Normally, this district receive rainfall from South-West (June to September) and North-East (October to December) monsoons and the annual rainfall is irregular and intermittent, over this district and the average rainfall varies from about 500-900 mm. Generally, Madurai district has a hot and dry climate; the summer season starts from March to July month (hottest period), the moderate climate season from August to October and cool climate from November to February. Temperature during summer period may vary from 27.0 °C to 42 °C,

whereas in the winter seasons, the temperatures range between 29.6 °C and 18 °C.



**Fig.1.**Location of sampling stations at Thiruparankundram Murugan Temple (TMT) and Vandiyur Mariamman Temple Teppakulam (VMT) in Madurai District.

study In this area (Fig. 1). Thiruparankundram Murugan Temple pond or (9°53'25"N; 78°4'15"E) Teppakulam in Thiruparankundram block is one of the Six Abodes of Murugan Temple in the World. The temple pond receives water from river Vigai. The Vandiyur Mariamman Teppakulam is associated with the Vandiyur Mariamman Temple and it was built in 1645 AD, during the rule of King Thirumalai Nayak. Generally, the tank is well connected to river Vaigai through an ingenious system of underground Channels. These two pond areas are surrounded by more than a dozen of dyeing, chemical, agrochemical and many core industries, the wastes coming from these sources are not proper treatment and it is directly dumped in to the Teppakulam, so, the entire Teppakulam water was polluted, which leads to affect the entire ecological system in the study areas. Hence, the present study was carried out to cover a detailed impact made by the domestic sewage and industrial effluents on the physicochemical properties of the Teppakulam water bodies for the period of April 2019 to March 2020 at the different localities.

### 2.2. Materials and Methods

Water samples were collected from two pond stations for analyzing various physicochemical parameters and handling were adopted based on the standard methods [30–33]. The distance between two sampling stations was kept more than 10 - 12 Km and the temperature of the samples was measured in the field itself at the time of sample collection as per standard method [30-32]. After collection of the samples, the bottles were tightly sealed, suitably labeled, preserved and immediately kept in dark boxes. The samples were kept in refrigerator maintained at 4 °C and analyzed for various parameters at their earliest (Scheme 1). The collected water samples were analyzed by both classical and automated instrumental methods, prescribed by the standard methods [30-33] and the mean value of analytical data parameters among the two stations were compared and tabulated.

### 2.3. Preparation of activated carbon materials derived from Citrullus lanatus (Watermelon seeds)

The watermelon (Citrullus lanatus) seeds were collected from local market of various fruit shops in Madurai District. In this work, two steps of activation processes were involved (Fig. 2), in the first stage, optimization of the carbonization products at different temperature were carried out, at different time periods and then activated the carbonized materials in powder form with KOH (acting as activation agent). The collected watermelon seeds were washed several times with CO<sub>2</sub> free double distilled water and dried in open air for 5 - 8 days to reduce their moisture contents. The moisture free watermelon seeds were then crushed and pulverized into powder, using a laboratory milling machine for reduction of size and then dried in an air oven for 24 h at 65–75 °C to obtain constant weight. In order to study the optimum conditions for the adsorbents preparation, the moisture free air stable watermelon seeds powder were carbonized at different temperatures (200, 250, 300, 350, 400, 450 and 500 °C), in a muffle furnace at different time periods (15, 30, 45 and 60 min). The carbonized watermelon seed carbon materials (CWS - particle size of 250 µm) was then removed from the muffle furnace and cooled in open air for 40-60 min and then weighed.



Scheme 1. Flow chart of methodology and physicochemical analyses.

In the second stage, the chemical activations of the above carbonaceous materials with KOH (activation agent) solution at various concentrations (0.20, 0.40, 0.60, 0.80 and 1.00 M), separately to produce activated carbonized watermelon seed carbon materials (ACWS) with particle size of 250  $\mu$ m. The above processes were repeated, until a constant weight was obtained and then it was stored, after drying in *vacuo* over anhydrous CaCl<sub>2</sub>. The obtained CWS and ACWS materials were structurally characterized by FTIR, *p*XRD and SEM studies.



**Fig. 2.** General route for the preparation of carbonized and activated watermelon seed (CWS and ACWS) materials.

# III. RESULTS AND DISCUSSION 3.1. Physico–chemical analysis of study areas

In the present studies, two ponds or Teppakulam stations namely Thiruparankundram Murugan Temple pond in Thiruparankundram block and Vandiyur Mariamman Teppakulam in Madurai East block of Madurai District from April 2019 to March 2020, in every month and the results were compared with the WHO and other standard reports [14, 30-33]. Madurai district has non-unique advantage of rainfall, during both the south-west and north-east monsoons, monthly rainfall varies from 14.0 mm (minimum - March) to 850.00 mm (maximum - November) and the mean annual rainfall will be 817.24 mm for the period of our study. Fortunately, there was a little rainfall in the month of January and the mean humidity varies from 50-68 %. The mean monthly temperature varies with a maximum of 42.08 °C in the month of May to a minimum of 22.60 °C in December. Fig. 3 explains the variation of monthly rainfall and temperature of our study areas.

Some of the important physico-chemical parameters are found and compared with the WHO permissible values (**Table 1**). **Table 1**, clearly shows that the majorities of pond water bodies are slightly basic in nature, due to the presence of bicarbonate  $(HCO_3^-)$  and carbonate  $(CO_3^{2-})$  ions. The maximum (9.05) and minimum (6.57) pH values were recorded at Vandiyur Mariamman Temple and the observed pH values are also within the permissible limit of drinking water of WHO [14, 30–33]. The observed electrical conductivity (EC) values are higher than the permissible limit, which clearly indicating the presence of high amount of dissolved inorganic substances in ionized forms those are upcoming from various industries near to the study areas.



**Fig. 3.** Climate of the study area, during April 2019 – March 2020.

Moreover, all the ponds show high amount of dissolved oxygen (DO), during the month of September to December due to heavy rainfall and fresh water mixing in the pond. The desirable limit of total hardness (TH) is 300 mg/L and WHO is 500 mg/L, according to Indian standard but in the study area, the TH values are within the acceptable limit. In our present study, the amount of chloride and sulphate ions are within the WHO values but the fluorine values exceed the WHO value and also the concentration of F content is maximum in summer and minimum in monsoon seasons. The concentrations of Na, K and Ca values were somewhat found higher than the WHO or other standard permissible limit values, because of high consumption of salts (say NaCl or KCl), which causes hypertension and increases the risk for stroke, left ventricular hypertrophy osteoporosis, renal stones and asthma [34, 35]. Also, the discharge of industrial wastes, domestic sewage and agricultural wastes are added to the concentration of sulphate. The concentration of inorganic phosphate content values is somewhat low in pre and post monsoon seasons due to the decreased land drainage, sewage and fertilizer disposal from the surface run off.

The toxic and heavy metal contents level is below the WHO values, except lead (Pb) and mercury (Hg), if the metal concentration level is higher than WHO values that may cause some ill effect to human as well as animals like kidney and bone damages, carcinogenic, cancer, nervous disorder, *etc* [37–38]. This variation is probably due to various factors mainly, the trace metal contents from the soil and crops, geographical location, fertilizers and fungicides applied in the area, environmental pollutions due to automobile emissions, industrial effects, weathering of rocks and other agricultural activities.

# 3.2. Characterization of CWS and ACWS materials

Table 2, clearly shows that changes in the carbonization temperature with constant time and mass, the percentage of ash, fixed carbon, charcoal yield, moisture and volatile matter contents also varied *i.e.*, change in the carbonization temperature alternatively changes the proximate content of the watermelon seeds. The results indicate that, the optimum condition for the carbonized watermelon seed with 400  $^{\circ}$ C at 60 min in 0.5 M KOH medium shows better results.

| Table 1. | Hydroche | emical parame | ters for T | Thiruparankundram Murugan Temple Teppakulam (TMT) and e Teppakulam (VMT) in Madurai District during April 2019 – |       |    |         |          |        |       |        |   |
|----------|----------|---------------|------------|--|-------|----|---------|----------|--------|-------|--------|---|
|          | Vandiyur | Mariamman     | Temple     | Teppakulam   | (VMT) | in | Madurai | District | during | April | 2019 - | - |
|          | March 20 | 020.          |            |  |       |    |         |          |        |       |        |   |

|   | Units    | WHO<br>values | Thiru                   | paranku  | lurugan     | Vandiyur Mariamman |                         |          |          |                   |
|---|----------|---------------|-------------------------|----------|-------------|--------------------|-------------------------|----------|----------|-------------------|
| D                                       |          |               | Temple Teppakulam (TMT) |          |             |                    | Temple Teppakulam (VMT) |          |          |                   |
| Parameters                              |          |               | Min                     | Max      | Mean        | Std.<br>deviation  | Min                     | Max      | Mean     | Std.<br>deviation |
| Appearance                              |          |               | Clear                   | with lig | ht green ir | n colour           | Clear                   | with lig | ght gray | in colour         |
| Odour                                   |          |               |                         |          | Nil         |                    |                         |          | Nil      |                   |
| Temperature                             | °C       |               | 22.60                   | 42.08    | 31.45       | 0.25               | 23.8                    | 41.86    | 32.90    | 0.390             |
| pH                                      |          | 6.50-9.20     | 6.28                    | 8.25     | 7.62        | 0.31               | 6.57                    | 9.05     | 7.59     | 0.28              |
| EC                                      | µS/cm    | 500-1500      | 425                     | 1525     | 962         | 25.26              | 486                     | 1561     | 985      | 29.10             |
| Turbidity                               | NT units | 5.00          | 3.20                    | 5.60     | 4.85        | 0.61               | 3.56                    | 5.78     | 4.90     | 0.82              |
| TDS                                     | mg/L     | 500-2000      | 760                     | 1560     | 1105        | 25.62              | 850                     | 1400     | 1208     | 32.20             |
| Total alkalinity                        | mg/L     | 250-500       | 95.50                   | 380.90   | 230.70      | 32.21              | 79.80                   | 408.30   | 280.60   | 33.50             |
| DO                                      | mg/L     | 6–8           | 5.86                    | 9.01     | 7.43        | 0.39               | 5.57                    | 9.28     | 7.65     | 0.41              |
| BOD                                     | mg/L     | 5.0           | 6.43                    | 10.64    | 8.55        | 1.43               | 7.24                    | 10.98    | 9.21     | 1.68              |
| COD                                     | mg/L     | 10.0          | 12.68                   | 22.07    | 17.45       | 1.23               | 10.24                   | 22.68    | 17.82    | 1.38              |
| TH                                      | mg/L     | 500           | 280.10                  | 480.40   | 390.30      | 10.80              | 232.40                  | 494.00   | 385.30   | 11.20             |
| Cl                                      | mg/L     | 250-600       | 149.00                  | 230.08   | 180.90      | 8.06               | 170.50                  | 286.00   | 220.20   | 16.51             |
| F <sup>-</sup>                          | mg/L     | 1.5-2.0       | 1.35                    | 2.22     | 1.86        | 1.35               | 1.40                    | 2.35     | 2.02     | 1.62              |
| $SO_4^{2-}$                             | mg/L     | 200-600       | 185                     | 520      | 385         | 12.1               | 196                     | 540      | 420      | 10.60             |
| Ammonia NH <sub>3</sub>                 | mg/L     | 5-10          | 4.20                    | 7.60     | 6.00        | 1.40               | 4.60                    | 8.10     | 6.90     | 1.90              |
| Nitrate as NO <sub>2</sub> <sup>-</sup> | mg/L     | 0.001         | Trace                   | < 0.001  | < 0.001     |                    | Trace                   | < 0.001  | < 0.001  |                   |
| Nitrate as NO <sub>3</sub> <sup>-</sup> | mg/L     | 45            | 21                      | 40       | 32          | 2.10               | 24                      | 43       | 34       | 2.60              |
| $PO_4^{2-}$                             | mg/L     | 0.1-0.5       | 0.12                    | 0.45     | 0.32        | 0.85               | 0.15                    | 0.47     | 0.36     | 0.92              |
| Na                                      | mg/L     | 50-200        | 143.28                  | 208.68   | 184.25      | 5.68               | 140.02                  | 212.35   | 196.25   | 6.21              |
| K                                       | mg/L     | 10-12         | 4.90                    | 12.05    | 8.24        | 2.15               | 5.23                    | 12.47    | 9.06     | 2.39              |
| Ca                                      | mg/L     | 75-200        | 65                      | 185      | 146         | 10.25              | 80                      | 190      | 160      | 11.66             |
| Mg                                      | mg/L     | 30-150        | 35                      | 139      | 105         | 8.95               | 40                      | 142      | 110      | 9.21              |
| Fe                                      | mg/L     | 0.30          | 0.14                    | 0.25     | 0.21        | 0.35               | 0.17                    | 0.27     | 0.22     | 0.42              |

Table 2. Carbonization of CWS Ematerial, at different temperature and time period.

| Temp.<br>(in °C) | Time<br>(in min) | Mass<br>(in g) | Ash content<br>(in %) | Volatile content<br>(in %) | Moisture content<br>(in %) | Fixed carbon<br>(in %) | Charcoal<br>yield (in %) |
|------------------|------------------|----------------|-----------------------|----------------------------|----------------------------|------------------------|--------------------------|
| 200              | 15               | 5              | 18.5                  | 33.6                       | 2.2                        | 45.2                   | 52.5                     |
| 250              | 15               | 5              | 22.4                  | 27.4                       | 2.1                        | 47.8                   | 46.2                     |
| 300              | 15               | 5              | 24.8                  | 24.3                       | 1.7                        | 48.5                   | 40.5                     |
| 350              | 15               | 5              | 26.8                  | 20.6                       | 1.9                        | 49.9                   | 40.1                     |
| 400              | 15               | 5              | 28.1                  | 18.2                       | 1.8                        | 51.5                   | 35.5                     |
| 450              | 15               | 5              | 28.9                  | 18.0                       | 2.0                        | 50.8                   | 33.9                     |
| 500              | 15               | 5              | 29.2                  | 17.6                       | 1.9                        | 50.9                   | 32.0                     |
| Temp.            | Time             | Mass           | Ash content           | Volatile content           | <b>Moisture content</b>    | <b>Fixed carbon</b>    | Charcoal                 |
| (in °C)          | (in min)         | (in g)         | (in %)                | (in %)                     | (in %)                     | (in %)                 | yield (in %)             |
| 400              | 15               | 5              | 28.1                  | 18.2                       | 1.8                        | 51.5                   | 35.5                     |
| 400              | 30               | 5              | 28.4                  | 15.5                       | 2.1                        | 53.2                   | 34.9                     |
| 400              | 45               | 5              | 29.2                  | 12.8                       | 2.4                        | 54.8                   | 34.4                     |
| 400              | 60               | 5              | 28.1                  | 11.6                       | 2.6                        | 57.4                   | 34.0                     |

So, in this work, we have synthesized the CWS and ACWS materials at optimum experimental conditions (Temp. 400 °C; Time: 60 min and 0.5 M KOH) for the entire process. The synthesized CWS and their ACWS materials, under the optimum

condition was further structurally characterized by various spectral (FTIR, powder XRD and SEM) studies.



Fig. 4. FTIR spectra of CWS and ACWS materials, before and after activation.

The FTIR spectral studies clearly indicate there is no appreciable change in the absorption peaks of carbonized watermelon seed material (CWS) and their activated CWS material. The major peaks observed at 652 and 810 cm<sup>-1</sup> are assigned to bending vibration of v (=C–H), Further, the peaks at 1053, 1658 and 3450 cm<sup>-1</sup>, correspond to stretching of v (=C–O), v (=C–C) and v (–OH) cm<sup>-1</sup> bonds, respectively. It was found that the fluoride ions exist in the pond waters are easily bound to the –OH and –CO functional groups, present in the CWS and ACWS [39, 40].

The powder X-ray diffraction as well as SEM analyses is useful to determine the structure, particle size, porosity and morphology of the CWS and ACWS materials. From the pXRD pattern, we have come to know that the observed characteristic strong absorption peaks were responsible for the so formed CWS and ACWS materials. It confirms that those materials have uniform carbon phase with no impurity and the observed average crystalline sizes are in the range of 20-35 µm. Similar way, the SEM analysis determines the surface morphology, purity, phase identification and particle size of materials and their SEM pictographs were taken in an accelerating voltage, ranging from 10 to 20 kV. The SEM pictographs (Fig. 5) clearly indicate that the synthesized low cost adsorbent materials, CWS and ACWS have uniform matrix with smooth interface as well as homogeneous phase identity. The SEM images of ACWS materials show that the activated carbon particles are highly porous in nature along with the particle size of about 25 µm, which was not observed with CWS material.



Fig. 5. SEM photographs of CWS and ACWS materials.

# **3.3.** Adsorption studies for the removal of fluorine or fluoride ion

From the adsorption studies, we have to found the equilibrium time for a maximum adsorption of fluoride content, under the optimum conditions of ACWS material in this study areas. In this study, the prepared 50 mg of activated ACWS material was utilized for 50 mL of 10 mg/L fluoride solution. **Fig. 6a** clearly depicts that the amount of fluoride adsorption (in mg/g) increased with increased agitation time initially, then gradually became sluggish and approached to nearly a constant value within 120 min. It clearly illustrated that, initially the availability of the active sites on the adsorption surface is limited, owing to strong binding of fluoride ions towards AWSM material.



Fig. 6 (a) Effect of agitation time and (b) effect of adsorbent dosage on % adsorption as well as adsorption capacity of F<sup>-</sup> ions on activated carbon materials of watermelon seeds at optimum conditions.

The effect of adsorbent dosage was studied by varying the amount of ACWS material from 50 to 500 mg per 50 mL of fluoride solution, under the optimized agitation time (in 120 min) period. **Fig. 6b** clearly demonstrates that by increasing the amount of activated adsorbent ACWS doses, the percentage of removal of fluoride content also increases, whereas the adsorption capacity ( $q_e$ ) values decrease gradually *i.e.*, increase in the adsorbent dosage, the unsaturation of adsorption sites may lead to drop in the adsorption capacity, whereas at higher adsorbent dose, the agglomeration of adsorbent particles may reduce the surface area, accompanied by an increase in the diffusional path length [10, 23]. Generally, the adsorption is strongly dependent on pH of the solution that mainly controls the adsorption of fluoride ions on the surface of ACWS materials. Under the optimum experimental conditions, the removal of fluoride ion content decreases with increase of pH. In this work, the synthesized activated carbon (ACWS) materials, derived from watermelon seeds have a positive charge at lower pH (< 4.0). Moreover, it was found that the fluoride ions present in the study areas have got strongly chemisorbed to the prepared ACWS materials those involved in the ligand exchange reaction mechanisms [10, 23, 41]. It can be represented as:

$$-C-OH + H^{+} - C-OH_{2}^{+}$$

$$-C-OH_{2}^{+} + F^{-} - - C-F + H_{2}O$$

where, -C-OH represents the surface hydroxyl group of activated CWS material and the combination of the above equations in the combined form can be given as:

$$-\text{C-OH} + \text{F}^- + \text{H}^+ \longleftarrow -\text{C} - \text{F} + \text{H}_2\text{O}$$

From this mechanism, the fluoride ions present in the Teppakulam water bodies are effectively removed by the cost–effective as well as, cheaply available waste biomass material, watermelon seeds *i.e.*, the activated ACWS material surface have some positive sites of adsorption, which chemisorbed strongly the fluoride ions of the water bodies to remove the ions more effectively than the other methods.

#### **IV. CONCLUSION**

The people of Madurai district mainly have been depending upon the source of surface and groundwater from the river Vaigai and their concerned ponds or lakes for their agricultural, domestic and industrial development activities. In the present study, we summarize the various physico-chemical parameters of the two ponds or Teppakulam stations, namely Thiruparankundram Temple Murugan Teppakulam (TMT) in block Thiruparankundram and Vandiyur Mariamman Teppakulam (VMT) in Madurai East block of Madurai district, during the study period of April 2019 to March 2020. The observed pH value in Vandiyur Mariamman Temple Teppakulam (VMT) is slightly alkaline in nature that is due to the presence of bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate  $(CO_3^{2-})$  ions. High amount of DO is measured in the month of September to December, due to heavy rainfall and fresh water mixing in the pond. The

chloride, sulphate, TH, TDS and TSS amounts are within the WHO values, while the fluoride ion values are exceeding the WHO value and also the concentration of fluoride content is maxima in summer and minima in monsoon season. So, we have synthesized the low cost, eco-friendly as well as cheaply available and effective activated carbon adsorbent materials derived from watermelon seeds viz carbonization followed by activation with KOH solution at optimum experimental conditions (Temp. 400 °C; Time: 60 min and 0.5 M KOH). The synthesized activated CWS material has widely been utilized to remove the fluoride ions in the study areas through adsorption process. The observed heavy as well as trace toxic metals such as Fe, Cr, Ni, Mg, Mn, Cd and Al were below the WHO permissible limits except, Pb and Hg. From the observed various physico-chemical values in the present study areas, it has been concluded that the pond water bodies in Madurai district is slightly contaminated and possibly safe for drinking, agricultural and household purposes, at present.

### **V. RECOMMENDATIONS**

Even though the Thiruparankundram Murugan Temple pond or Teppakulam (TMT) in Thiruparankundram block and Vandiyur Mariamman Teppakulam (VMT) resources in Madurai district is currently plenty, conventional methods for water management practices like rainwater harvesting might be necessary in order to restrict any surprising water demand as a result of industrialization or population increase, in future.

### DISCLOSURE STATEMENT

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