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**Dr. Sachin Madhavrao Kanawade**
Dr. Vasantraodada Patil Shetkari Shikshan Mandal's Padmabhooshan Vasantraodada Patil Institute of Technology, Budhgaon, Tal- Miraj, Dist - Sangali, Maharashtra, India, Pin – 416304.

**Correspondence**
**Dr. Sachin Madhavrao Kanawade**
Dr. Vasantraodada Patil Shetkari Shikshan Mandal's Padmabhooshan Vasantraodada Patil Institute of Technology, Budhgaon, Tal- Miraj, Dist - Sangali, Maharashtra, India, Pin – 416304.

# Removal of ammonium and suspended solids from effluent of domestic wastewater plant

**Sachin Madhavrao Kanawade**

**Abstract**
A multipurpose filter column was studied as a polishing stage for the simultaneous removal of ammonium and suspended solids from a secondary domestic wastewater effluent. The multipurpose filter consisted of sand as the regular filter material, primarily for the purpose of suspended solids removal, and an ammonium selective natural zeolite, clinoptilolite, for the removal of ammonium. A Turkish clinoptilolite from the Bigadic region was used in the experiments. The capacity of the clinoptilolite was determined by isotherm analysis to be 10.4 mg/g for 20 mg/lt initial wastewater ammonium concentration at pH 7.3 with 0.5-1 mm diameter. In the continuous runs, the multipurpose filter unit was operated down flow with 50% of the unit consisting of clinoptilolite in the upper layer, and 50% sand in the lower both with a grain size range of 0.5-1 mm. The results have revealed that simultaneous removal of 100% of the ammonium and 75% of the suspended solids removal be achieved in the multipurpose filter unit for a working period of 38 hours. The success of this proposal could lend an alternative both for the upgrading of existing treatment plants and for polishing for ammonium and suspended solids rate by using one compact unit.

**Keywords:** Ammonium removal; clinoptilolite; filtration; ion exchange multipurpose filter; suspended solids removal.

## 1. Introduction
With the increasing population, development of industrialization and urbanization, the priority of pollution control and management of water resources are increasing day by day. Within that context, standards being imposed on wastewater discharges are getting more and more stringent in time. In line with this, the efforts directed towards development of highly efficient and economical technologies which require smaller areas are also increasing. In accordance with the Urban Wastewater Treatment Directive (91/271/EEC) of the European Union defining sensitive areas referring to the problem of eutrophication, control of nitrogen has become one of the main concerns in wastewater management. Together with nitrogen, more stringent standards are in place for suspended solids as well. According to the directive, the limits for total nitrogen and total suspended solids may go down to values as low as 10 mg/L and 35 mg/L, respectively as shown in Table 1. Maintaining those standards may not always be possible in conventional wastewater treatment plants with conventional treatment schemes. Upgrades and polishing units may be required for compliance. This work aims to investigate the possibility of polishing a secondary effluent from a domestic wastewater treatment plant using a multipurpose filter consisting of clinoptilolite and sand to treat ammonium and suspended solids in one single unit, where to processes namely ion exchange and filtration take place simultaneously.

Clinoptilolite is a natural aluminosilicate which is selective towards ammonium in the process of ion exchange. Ames (1967) had listed the selectivity rank of clinoptilolite as $Cs^{+} > Rb^{+} > K^{+} > NH4^{+} > Ba^{2+} > Sr^{2+} > Na^{+} > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^{+}$. As can be observed from the ranking, among cations expected in domestic wastewater, only potassium is preferred over ammonium. Additionally, the capacity of the clinoptilolite in the sodium form had been observed to be the highest (Koon and Kaufman, 1975). The effectiveness of clinoptilolite in removing ammonium from domestic wastewater had been demonstrated in a number of papers, many of which are included in the review by Hedstrom (2001).

The capacity of clinoptilolite towards ammonium were reported to be between 1-2.27 meq/gr clinoptilolite or 14-32 mg NH4 -N/gr clinoptilolite by various authors including (Semmens and Porter, 1979; Jorgensen *et. al*.,1979; Booker *et. al*., 1996; Beler Baykal and Guven, 1997; Nguyen, 1997) [19, 15, 8, 5, 17]. Another important factor affecting removal capacity is particle size (Hlavay, 1982) [12]. Smaller particle sizes favor ion exchange capacities however, very small particle sizes are not practical as the increased pressure drop leads to the clogging of the ion exchange column which necessitates a break in continuous operation.

**Table 1:** Requirements for discharges from urban waste water treatment plants (generated from 91/271/EEC).

| Parameters | Concentration | Minimum percentage of reduction |
|---|---|---|
| Biochemical oxygen demand ($BOD_5$ at 20 °C) without nitrification | 25 mg/l | 70-90 |
| Chemical oxygen demand (COD) | 125 mg/l | 75 |
| Total suspended solids | 35 mg/l (> 10 000 p.e.)<br>60 mg/l (2000-10000 p.e ) | 90 (more than 10000 p.e)<br>70 (2000-10000 p.e) |
| Total phosphorus | 2 mg/l P(10000-100000 p.e)<br>1 mg/l P (> 100 000 p.e) | 80 |
| Total nitrogen | 15 mg/l N(10000-100000 p.e)<br>10 mg/l N (> 100 000 p.e) | 70-80 |

Promising results were also obtained in terms of ammonium in systems incorporating clinoptilolite in filters (Beler Baykal *et. al*., 1994; Beler Baykal *et. al*., 1996; Beler Baykal *et. al*., 1997; Beler Baykal, 1998; Inan 2001) [4, 6, 5, 7, 13]. However, the emphasis in those papers was placed upon ammonium removal and the effect of adding clinoptilolite on filtration / suspended solids removal was not addressed. This paper is directed towards filling this gap in, by concentrating on the simultaneous removal of ammonium and suspended solids and investigating the mutual effect
of one process (ion exchange) upon the other (filtration). The grain size distribution of the clinoptilolite has a significant impact on the operating ammonium ion exchange capacity. Hlavay *et al*. (1982) [12] investigated grain sizes between 0.5-1.0, 0.3-1.6 and 1.6-4 mm. The smallest fraction resulted in the highest ammonium exchange capacity. When using smaller grain sizes, the higher ammonium exchange capacity is probably caused by a more favorable mass transfer into the zeolite (Hedström, 2001) [11]. The grain size distribution is also important for filtration performance. Ghosh *et al*. (1967) [10] indicated that the ratio between column diameter and grain diameter must be more than 40 in filters for effective operation. The use of sand in filters for domestic wastewater filtration is reported in a number of papers especially in the recent years (Jimenez *et. al*., 2000; Petala *et. al*. 2006; Adou *et. al*., 2007; Williams, 2007) [14, 18, 2, 21]. Filtration performance is investigated in these papers for different initial concentrations and filtration rates. However there is no paper was encountered about the use of clinoptilolite in filters as a filtration material. This paper summarizes an effort which investigates the use of a multipurpose filter for the simultaneous removal of ammonium and suspended solids as an alternative method for handling more stringent standards. The use of such filters in practice will make the removal of ammonium and suspended solids possible in only one unit. The success of the proposed approach is especially desirable for cases under land restriction for upgrading, and lends a quick and easy solution for treatment plants which already have filters.

## 2. Materials and Methods

Clinoptilolite is used as the ion exchanger and quartz sand is used as the filter material in the experiments. The grain sizes of sand and clinoptilolite are between 0.5-1 mm. The clinoptilolite is provided from Bigadic district of Turkey which has rich clinoptilolite reserves. The typical chemical analysis of the clinoptilolite is given in Table 2. Chemical pretreatment of clinoptilolite is executed to transform it to the sodium form which increases its ammonium exchange capacity. In the pretreatment process the clinoptilolite is washed with distilled water, dried and loaded with 1 M NaCl solution for 48 hours. After that, it is washed and dried again for filling the experimental column.

**Table 2:** Chemical Analysis of Bigadic Clinoptilolite (Celenli et. al., 1994)

| Bigadic Clinoptilolite (%) | |
|---|---|
| $SiO_2$ | 67.96 |
| $Al_2O_3$ | 10.74 |
| $K_2O$ | 3.01 |
| CaO | 0.74 |
| $Na_2O$ | 0.81 |
| $Fe_2O_3$ | - |
| MgO | 1.49 |
| TiO | - |
| Si | 15.36 |

The domestic wastewater which is used in the experiments is taken from the effluent of the secondary clarifiers of Bahcesehir Domestic Wastewater Treatment Plant. The treatment plant is an activated sludge system for 21000 population equivalent. Characteristics of the domestic wastewater of Bahcesehir Domestic Wastewater Treatment Plant is given in Table 3. The experimental setup is made up of one plexiglas column, one peristaltic pump, mono metric tubes and feed tanks. An automatic sampler is used for sampling at two hours intervals.

**Table 3:** Wastewater Characterization of Bahcesehir Domestic Wastewater Plant

| Parameters | Influent | Effluent |
|---|---|---|
| $NH_4$ –N (mg/l) | 50-85 | 19-24 |
| Total Kjehldal Nitrogen (mg/l) | 80-114 | 30-43 |
| COD | 400-800 | 40-58 |
| $BOD_5$ | 180-455 | 25-35 |
| Total Suspended Solids | 230-300 | 40-97 |
| pH | 7-8 | 7-7.5 |

The suspended solids analysis made by a straining system and Ammonium analysis is made by using an ion meter which has ± 0.1 mV accuracy and a Jenway 924 328 model ammonia electrode. (Standard Methods, 1995). The experimental setup is shown in Figure 1. The experimental work consists of batch and continues experiments. The batch mode is used for isotherm studies for determining the ion exchange capacity of the clinoptilolite. Different weights of clinoptilolite samples are contacted with known ammonium concentrations at a constant temperature (25°C). The initial concentration of ammonium was regulated by adding $NH_4Cl$ into original wastewater sample if necessary. After 24 hours shaking period the solution and clinoptilolite phases are separated and the ammonium concentrations in solutions are measured. By using the difference between the first and last ammonium concentrations of solutions, ammonium concentrations in the solid phase are calculated and isotherm curves are plotted.

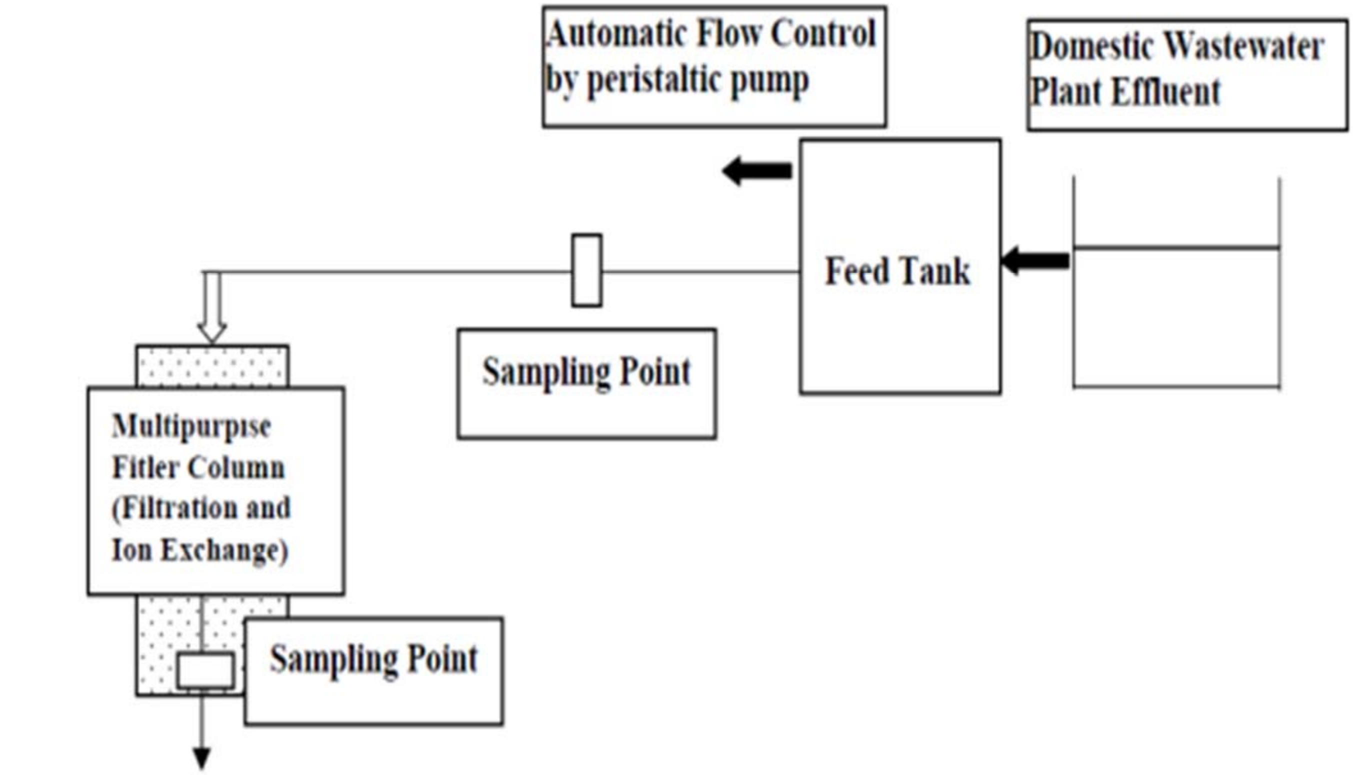


**Figure 1:** The Experimental Setup.

A multi-purpose column consisting of clinoptilolite and sand is used in continuous runs operating at 10 minutes hydraulic retention time. Total bed height of the system is 50 cm. The bed height of clinoptilolite and sand is 25 cm. each and clinoptilolite is placed on the upper layer. The contact time for clinoptilolite is 5 minutes. With the onset of clogging, the multi-purpose filter is backwashed and the effluent ammonium and suspended solids concentrations are monitored both before and after backwashing. Backwashing is maintained for 10 minutes at a backwash rate of 13.75 m/hours.

Conditions of the column study are given in Table 4.

**Table 4:** Conditions of the column study

| | |
|---|---|
| $T_h$ Hydraulic Retention Time for Sand+Clinoptilolite System | 10 min. |
| $T_c$ Contact time for zeolite | 5 min. |
| Column Diameter | 3 cm |
| Total Bed Height | 50 cm |
| Bed height of clinoptilolite | 25 cm |
| Porosity (for 0.5-1 mm sand) | 0.36 |
| Uniformity coefficient (for 0.5-1 mm sand) | 1.34 |
| Porosity (for 0.5-1 mm clinoptilolite) | 0.45 |
| Uniformity coefficient (for 0.5-1 mm clinoptilolite) | 1.90 |
| Influent Ammonium Concentration | 20 mg/l |
| Influent Suspended Solids Concentration | 72 mg/l |
| Surface Area | 7.07 $cm^2$ |
| Bed Volume | 353 ml |
| Filtration Rate | 2.95 $m^3$ /$m^2$hours |
| Backwashing rate | 13.75 m/hours |

## 3. Results and Discussion

The isotherm study results for 0.5-1 mm grain sized clinoptilolite are given in Figure 2. The isotherm curves are drawn for ammonium removal both from domestic wastewater and deionized water to observe the effect of different cations in domestic wastewater which may compete with the target ions, i.e. ammonium for the exchangeable ion on the surface of the clinoptilolite. As can be seen from Figure 2 the removal from deionized water is more than from domestic wastewater. This is because of the presence of cations other than ammonium in the domestic wastewater. The whole removal capacity of clinoptilolite can be used for ammonium ions in deionized water, because no other cations exist.

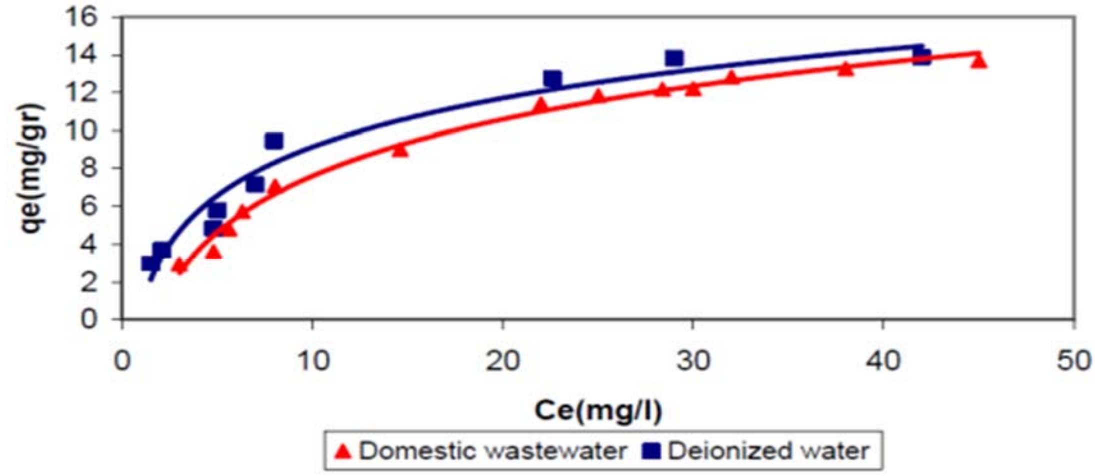


**Figure 2:** Isotherm curves for domestic wastewater and deionized water.

As the result of batch isotherm experiments, the capacity of Bigadic clinoptilolite was determined as 10.4 mg/g for 20 mg/lt initial wastewater ammonium concentration at pH 7.3 with 0.5-1 mm diameter zeolite. This result is compatible with the results of similar studies for determining the capacity of Bigadic clinoptilolite before (Inan 2001) [13]. The search for the compatibility of the data with various isotherm models have revealed that the best fit is obtained by the Langmuir model ($R^2$=0.9737). Figure 3 shows the results of the isotherm model tests for compatibility with the Langmuir and Freundlich isotherm.

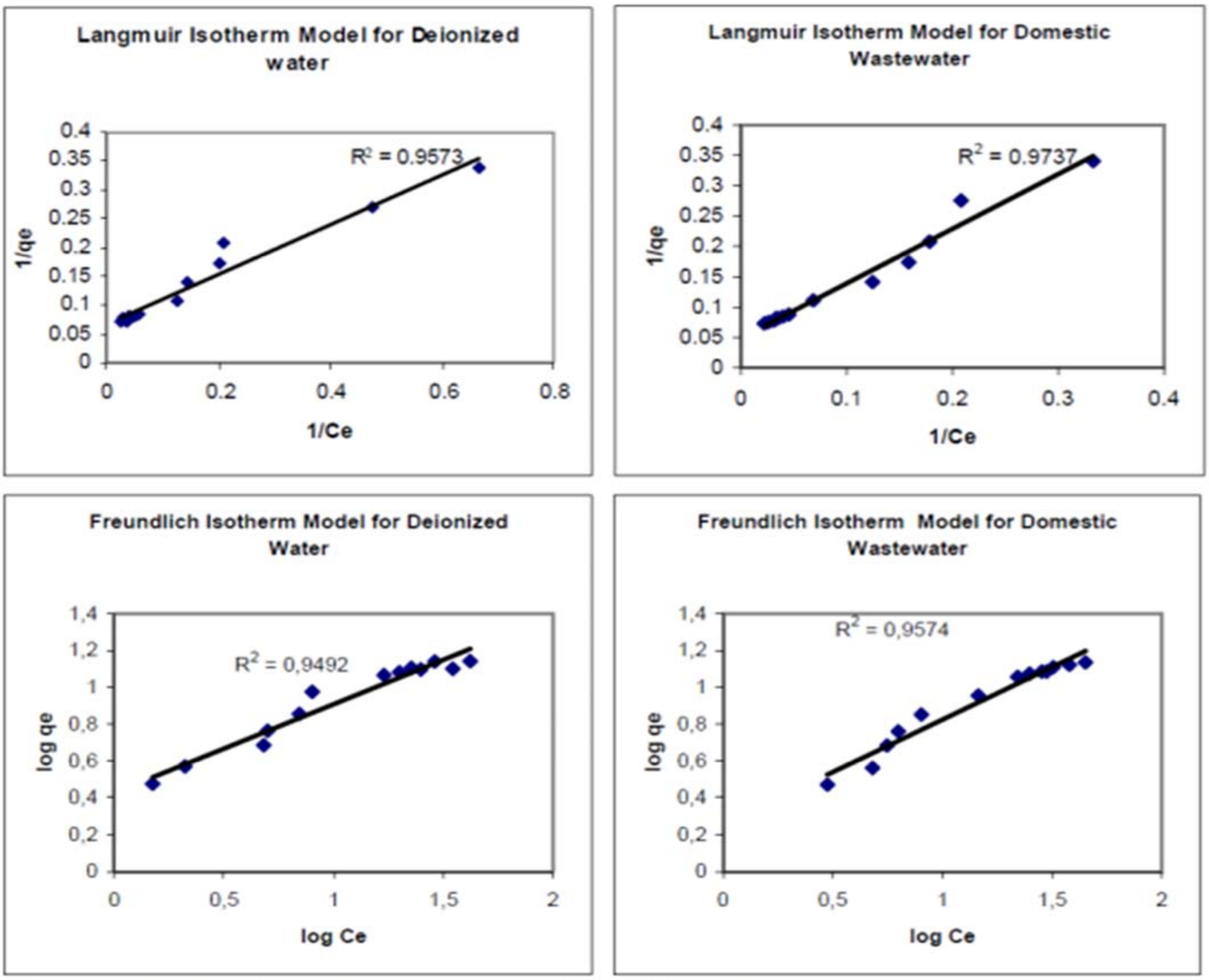


**Figure 3:** Langmuir isotherm models for deionized water and domestic wastewater.

A sample of many trials for suspended solids and ammonium removal in the multi-purpose filter is given in Figure 4. As can be seen from the figure, suspended solids removal is achieved as %75 for 48 hours until clogging. This is an important result for the multipurpose system since the filtration process is continuing successfully although a portion of the filter is filled with clinoptilolite. After backwashing, system performance is observed to continue at the same level. It is also observed that the zeolite is still at the upper layer after the backwashing due to its lower density ($\rho$ = 2.54 g/cm$^3$ for sand and $\rho$ = 2.32 g/cm$^3$ for clinoptilolite) % 100 ammonium removal is achieved in the multi-purpose filter for 38 hours. The backwashing at the 48. hour has no positive effect on the ammonium removal performance and ammonium removal is just zero at 56. hour. Figure 4 indicates the need for regeneration after 40 hours, the exact time of which will be dictated by the exact targeted concentration, for regaining the ion exchange capacity. Backwashing and regeneration are also important aspects of this proposal and results concerning these with different alternatives will be the subject of another paper. It is observed that from the experimental multi-purpose column studies, 100% ammonium removal and 75% suspended solids removal can be achieved in one single unit as a multipurpose filter. With these removal performances, the effluent concentration for ammonium will be 0 mg/lt (The initial concentration is 20 mg/lt for ammonium) and the effluent concentration for suspended solids will be 18 mg/lt (The initial concentration is 72 mg/lt for suspended solids) for this study. These results are compatible with the standards for ammonium and suspended solids which were given in Table 1. This shows that the multipurpose systems can be an alternative for wastewater treatment plants which are similar to Bahcesehir Domestic Wastewater Treatment Plant studied in this work.

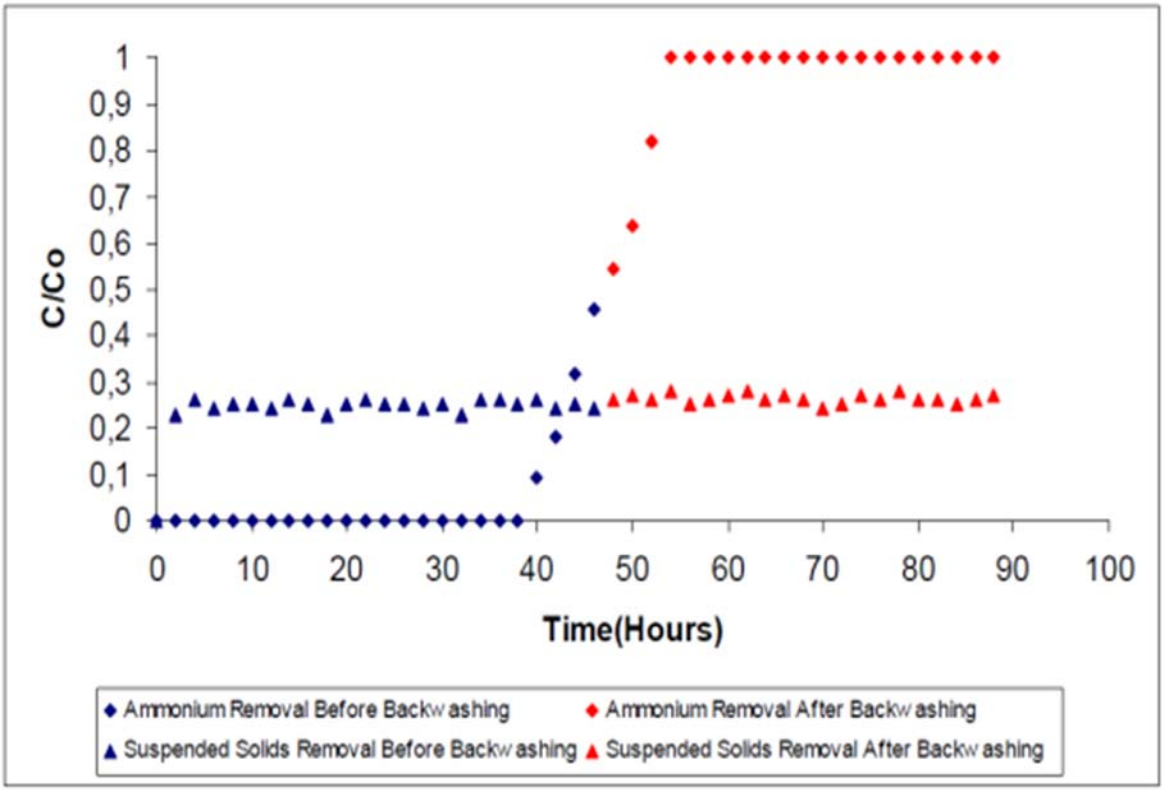


**Figure 4:** The ammonium and suspended solids removal performances of multipurpose column.

## 4. Conclusions

This study is aimed especially to determine the performance of ammonium and suspended removal together in a multi-purpose filter by using a domestic wastewater plant effluent. The capacity of Bigadic clinoptilolite was determined by the isotherm analysis as 10.4 mg/g for 20 mg/lt initial wastewater ammonium concentration at pH 7.3 and 0.5-1 mm diameter zeolite. As a result, it is observed that from the experimental multi-purpose column studies, ammonium removal and suspended solids removal can be achieved together in a single unit. 100% removal is provided for ammonium and 75% removal for suspended solids. This study is directed towards the investigation of the use of a multipurpose filter treating ammonium and suspended solids simultaneously as an alternative method for handling more stringent standards of ammonium and suspended solids. By using multipurpose filters in practice it will be possible to remove ammonium and suspended solids in only one unit with no additional land requirement and for those plants which already have filters, no additional equipment. The multipurpose filters can be an alternative both for the upgrading of existing treatment plants or polishing stage for ammonium and suspended solids with high removal efficiencies.

## 5. Acknowledgements

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**Author's Biography:**

**Dr. Sachin Madhavrao Kanawade** was born in 11 March 1978 at Nashik, Maharashtra, India. His native place is Nimgaonpaga, Tal-Sangamneer, Dist-A'Nagar, Maharashtra, India. He received his Bachelor's Degree in Chemical Engineering from Pravara Rural Education Society's Pravara Rural Engineering College, Pravaranagar (Loni) which is affiliated to Pune University in India in Nov.2001.Then he worked as a Production Officer in different Multinational Chemical Industries in India (2001 to 2008) like M/S Watson Pharma Ltd, Ambernath, MIDC, Mumbai, MS,M/S Glenmark Pharmaceuticals Ltd, Mohol, Dist. Solapur, MS, M/S Sun Pharmaceutical Industries Ltd, A. Nagar, MIDC,MS for 7 years.

Then he changes his field. He joined K. K. Wagh College, Nasik, MS, India in 2008 & worked as Lecturer for 2 years. At the same time he received his Master of Engineering in Environmental Engineering from Pravara Rural Education Society's Pravara Rural Engineering College, Loni in Dec.2010.Then he joined Pravara Rural Education Society's Sir Visvesvaraya Institute of Technology, Chincholi, Tal-Sinnar, Dist-Nasik, M.S. India in 2010 & worked as Assistant Professor in Chemical Engineering Department for 5 years. In the same period he completed his PhD Degree in Chemical Engineering in session 2011 – 2014 from Kumar Bhaskar Varma Sanskrit and Ancient Studies University Nalbari, Assam, India.

Presently he is Associate Professor at Dr. Vasantraodada Patil Shetkari Shikshan Mandal's Padmabhooshan Vasantraodada Patil Institute of Technology, Budhgaon, Tal – Miraj, Dist–Sangali, Maharashtra, India in Chemical Engineering Department.

Presently he is Reviewer / Editorial Board Member / Advisory Board Member of 64 different International Journals of different fields. He having 21 International Professional Membership of different Organizations

He published 47 Technical Research Papers in different International Journals like International Journal of Wastewater Treatment & Green Chemistry, International Journal of Chemical Engineering, International Journal of Environmental Pollution Control & Management, International Journal of Multidisciplinary Approach & Studies, International Journal of Chemical Engineering & Applications, International Journal of Chemistry & Material Science & International Journal of Engineering Studies and Technical Approach etc

His research topic includes & interested in Chemical

Engineering, Environmental Engineering, Wastewater Treatment by Adsorption, Advanced Separation Process, Chemical Engineering Design, Mass Transfer, Chemical Process Synthesis, Chemical Engineering Thermodynamics etc.