# N-Cetyl-N,N,N-tri methyl ammonium bromide based Tin(IV) Phosphate, A New Surfactant based Hybrid Ion Exchanger: Synthesis, Ion exchange and Physico-chemical Characterization

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**_Abstract_**
*N-Cetyl-N,N,N-tri methyl ammonium bromide based Tin (IV) Phosphate has been reported as a new class of hybrid ion exchanger. It has been characterized by some physico-chemical studies such as FTIR analysis, SEM study and elemental analysis. Its method of synthesis along with ion exchange characterization has also been reported in this study including ion exchange capacity, concentration study, elution study, recycling study and thermal stability.*

*The antimicrobial activity of N-Cetyl-N, N, N-tri methyl ammonium bromide based Tin (IV) Phosphate on some microorganisms such as Staph Awrens, E. coli ESS 2231, Protect vulgaris and Aspergillus fumigatus has also been studied to prove the antimicrobial nature of the reported material. Based on the above study it has been concluded that the present material can be of great importance in environmental pollution control.*

**Keywords:** Hybrid ion exchanger, N-Cetyl-N,N,N-tri methyl ammonium bromide, Tin(IV) phosphate, Ion exchange studies, Characterization.

## Introduction

Hybrid ion exchangers[3,4] synthesized by combining organic and inorganic species have opened the entryway of sufficient chances for the specialists and experts in recent days. As organic ion exchangers are very reproducible and exhibit chemical stability, yet, they do not show resistance towards heat. Besides, they lose their ion exchange properties on being presented to solid radiations. Inorganic ion exchangers laid out their place in analytical chemistry from their resistance towards heat and radiations and their particular selectivity for various metal ions.

Nonetheless, the primary disadvantage of these materials has been their chemical and mechanical stability. The disadvantages and benefits of both, organic and inorganic ion exchangers have made researchers to investigate on organo-inorganic or hybrid ion exchangers. Such materials[5,6,15,18] have been introduced and synthesized in the research laboratories which have demonstrated their value in chemistry by showing promising ion exchange behaviour.

The surfactant molecules diminish the interfacial tensions[12,16,17] when present between solid and liquid phases and, in this way, assist with wetting the surface appropriately and work with the exchange of metal ions effectively and promptly from the surface. Encouraged by this, a number of surfactant based hybrid ion exchangers[7-11,13,14] have been synthesized in these laboratories, depicting promising ion exchange characteristics.

In the present work, synthesis and studies are reported on N-Cetyl-N,N,N-tri methyl ammonium bromide based tin (IV) phosphate (CTAB-SnP). Studies include some physico-chemical characterization by FTIR analysis, SEM study and elemental analysis along with ion exchange characterization such as ion exchange capacity, concentration study, elution study, thermal stability and adsorption study for some heavy metal ions. The antimicrobial activity has also been explored.

## Material and Methods

**Reagents and Chemicals:** Tin chloride ($SnCl_4.5H_2O$) and N-Cetyl-N,N,N-tri methyl ammonium bromide were obtained from CDH, India whereas phosphoric acid ($H_3PO_4$) was purchased from E. Merck, India. All other chemicals and reagents were of AnalaR grade.

**Instruments/Apparatus used:** FTIR studies were carried out on Nicolet iS5 FTIR spectrometer whereas SEM study was performed using JEOL JSM 840, SM. Elemental analysis (C, H, N) was carried out by Heraeus Carlo Erba-1108 analyzer while tin and phosphorus were determined by Inductively coupled plasma atom emission spectrometer.

**Preparation of the reagents solution:** Solutions of tin(IV) chloride, N-Cetyl-N,N,N-tri methyl ammonium bromide and phosphoric acid were prepared in demineralized water (DMW).

**Synthesis of the ion exchange material:** Samples of N-Cetyl-N,N,N-tri methyl ammonium bromide based tin(IV) phosphate were synthesized by adding one volume of 0.3M tin(IV) chloride solution to a mixture of 0.6M $H_3PO_4$ and N-Cetyl-N,N,N-tri methyl ammonium bromide (1:1) dropwise with constant stirring. The resulting slurry was kept for 24 hrs. Then, it was filtered and washed with demineralized water till pH~4. It was dried and cracked into small granules by putting in demineralized water and converted into $H^+$-

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form by treating with 1M $HNO_3$ for 24 h and finally washed with demineralized water to remove excess of acid, dried at $45^0$C and sieved to 50-70 mesh sized particles. Three samples were synthesized by varying the concentration of N-Cetyl-N,N,N-tri methyl ammonium bromide (below CMC, at CMC and above CMC). Sample-3 was selected for further studies as per the highest ion exchange capacity, obtained. Table 1 reveals the samples synthesized with their corresponding ion exchange capacity.

**Ion exchange capacity (IEC):** The ion exchange capacity of the material has been determined by the column process as usual by taking 1 g of the material (in $H^+$-form) in a glass column of internal diameter ~ 1cm, fitted with glass wool at its bottom. 250 ml of 1M $NaNO_3$ solution was used as eluant, maintaining a very slow flow rate (~ 0.5 ml $min^{-1}$). Then, the effluent was titrated against a standard alkali solution to determine the total $H^+$ - ions released. Table 2 depicts the ion exchange capacity of the synthesized material for few metal ions and also, the comparison in ion exchange capacities with other surfactant based hybrid ion exchange material is reported in table 3.

**Concentration behavior:** Concentration behavior was studied to determine the optimum concentration of the eluent (Table 4). For that, different concentrations of eluent ($NaNO_3$) were passed in the columns of the synthesized material and ion exchange capacities were determined by column process[7].

**Elution behavior:** Elution study was conducted to check how much eluant is required for the complete exchange of $H^+$-ions by passing different fractions of 10 ml of eluant ($NaNO_3$) and ion exchange capacities were determined by column process as usual. Histogram in figure 1 exhibits the result of elution study.

**Table 1**
**Synthesis of various samples of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate**

| Sample No. | Concentration of CTAB (M) | $Na^+$- ion exchange capacity (meq/dry g) |
|---|---|---|
| Sample-1 | 0 | 1.30 |
| Sample-2 | 0.0001 | 1.75 |
| Sample-3 | 0.001 | 2.55 |
| Sample-4 | 0.01 | 2.20 |

**Table 2**
**Ion exchange capacity of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate for some metal ions**

| Metal ion solutions | $Na^+$- ion exchange capacity (meq/dry g) |
|---|---|
| LiCl | 2.20 |
| $NaNO_3$ | 2.55 |
| KCl | 2.65 |
| $MgCl_2$ | 2.00 |
| $CaCl_2$ | 2.70 |
| $SrCl_2$ | 2.85 |
| $BaCl_2$ | 3.10 |

**Table 3**
**A comparison in ion exchange capacity of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate with other hybrid ion exchangers, prepared earlier**

| Name of the materials | $Na^+$- ion exchange capacity (meq/dry g) |
|---|---|
| CTAB based Sn(IV) phosphate (present work) | 2.55 |
| Acrylamide Th(IV) phosphate[5] | 2.00 |
| Pectin Ce(IV) phosphate[5] | 1.78 |
| Pectin Th(IV) phosphate[5] | 2.15 |
| Cellulose acetate Th(IV) phosphate[5] | 1.70 |
| Acrylonitrile Zr(IV) phosphate[5] | 2.08 |
| Acrylamide Sn(IV) phosphate[5] | 2.10 |
| Dodecyl pyridinium chloride based Sn(IV) phosphate[11] | 2.39 |

**Table 4**
**Variation of ion exchange capacity of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate with eluant concentrations**

| Concentration of $NaNO_3$(M) | $Na^+$- ion exchange capacity (meq/dry g) |
|---|---|
| 0.2 | 1.50 |
| 0.4 | 1.90 |
| 0.6 | 2.20 |
| 0.8 | 2.35 |
| 1.0 | 2.55 |
| 1.2 | 2.15 |

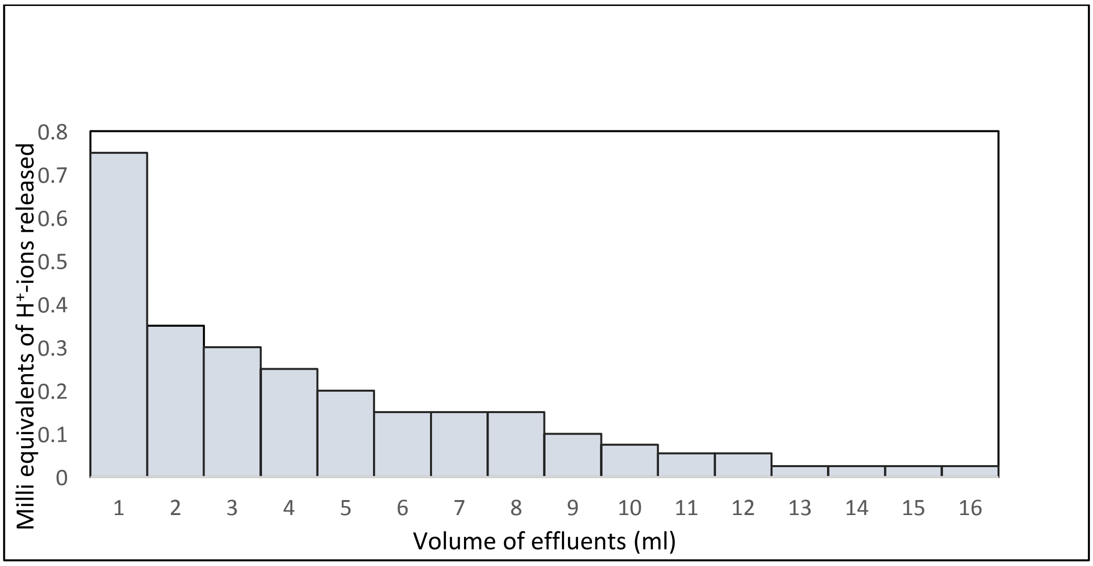


**Figure 1: Histograms showing the elution behaviour of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate**

**Thermal study:** Several 1.0 g samples of the synthesized material were heated at various temperatures in a Muffle furnace for 1 h each and their ion exchange capacities were determined by the column process (explained before) after cooling them to room temperature. The results of thermal studies are shown in table 6.

**Recycling Study:** Recycling study has been performed to check the utility of the synthesized material in terms of multiple uses by taking 1 g of the synthesized ion exchange material ($H^+$-Form) in the column. Determine the ion exchange capacity as usual by passing 1M $NaNO_3$ as an eluant and titrating against standard alkali solution. Number of cycles were repeated by regenerating the exchange material using standard HCl solution.

**Antibacterial and antimicrobial Study:** Agar well diffusion method has been used to determine the antimicrobial activities and minimum inhibitory concentrations (MIC) of CTAB-SnP against some bacteria like *Staph Awrens*, *E. coli* ESS 2231, *Protect vulgaris* and *Aspergillus fumigatus*.

## Results and Discussion

**Ion exchange capacity (IEC):** The reported surfactant based hybrid ion exchanger, CTAB based tin(IV) phosphate has been found to exhibit the highest ion exchange capacity (2.55 meq/dry g) among other hybrid ion exchange materials[5,11] (Table 3). In fact, it reveals higher ion exchange capacity than other cationic surfactant based ion exchangers i.e. DPC based tin(IV) phosphate[11]. The reason might be the enhanced interlayer distances in the layers of tin(IV) phosphate as a result of adsorption of N-Cetyl-N,N,N-tri methyl ammonium bromide being a polar molecule in the layers of tin(IV) phosphate.

**Concentration behavior:** The eluant concentration for complete elution of $H^+$-ions from the matrix of synthesized ion exchanger has been found to be 1 M as depicted in table 4.

**Elution behavior:** The histograms shown in figure 1 reveal that only 160 ml of 1M $NaNO_3$ is required for the complete elution of $H^+$-ions from the exchanger matrix.

**Thermal study:** A gradual decrease in the ion exchange capacity (Table 5) has been found on heating the synthesized exchange material on varying temperatures from $45^0$C to $500^0$C. The results reveal that the exchanger is quite stable up to $200^0$C showing 92.2% retention of its ion exchange capacity. But, it starts degradation in the capacity up to $400^0$C showing 45.1% retention of its ion exchange capacity before showing 9.8% at $500^0$C.

**Table 5**
**Thermal stability of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate after heating at various temperatures for 1 h each**

| Drying temperature ($^0$C) | Na+- ion exchange capacity (meq/dry g) | Change in colour | % Retention of ion exchange capacity |
|---|---|---|---|
| 45 | 2.55 | Off white | 100 |
| 100 | 2.45 | Off white | 96.1 |
| 200 | 2.35 | Pale white | 92.2 |
| 300 | 2.10 | Brown white | 82.3 |
| 400 | 1.15 | Brown white | 45.1 |
| 500 | 0.25 | Balckish | 9.8 |

**Table 6**
**Recycling studies on N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate**

| Number of recycles (After regeneration) | $Na^+$- ion exchange capacity (meq/dry g) |
|---|---|
| 1 | 2.55 |
| 2 | 2.55 |
| 3 | 2.45 |
| 4 | 2.35 |
| 5 | 2.15 |
| 6 | 1.80 |
| 7 | 0.90 |
| 8 | 0.25 |

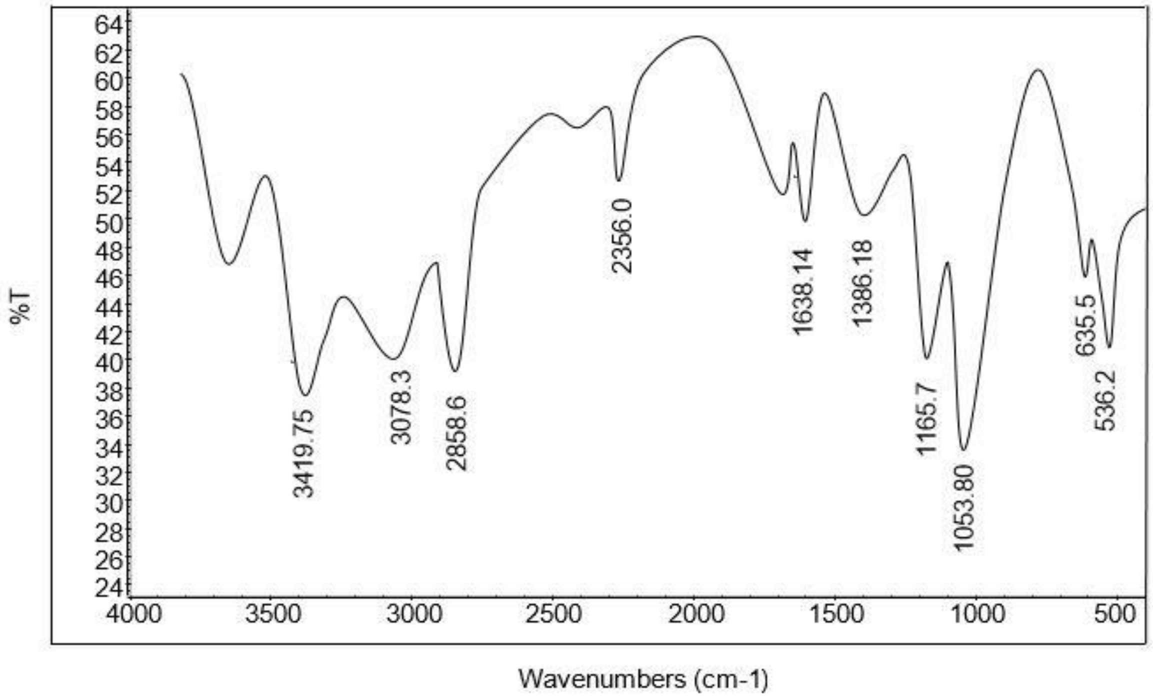


**Figure 2: FTIR Spectra of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate**

**Table 7**
**Elemental analysis of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate**

| Elements | Percentage (in 0.25g of the material) |
|---|---|
| Tin | 38.36 |
| Phosphorus | 27.15 |
| Carbon | 4.65 |
| Hydrogen | 1.85 |
| Nitrogen | 1.35 |

**Recycling study:** Recycling studies (Table 6) of the synthesized ion exchange material determine that the material can be used 4-5 times without losing much of its ion exchange capacity.

**IR study:** The IR studies[2] (Figure 2) reveal the presence of metal-oxygen and metal-hydroxide bonds along with the external water molecules, phosphate groups, ammonium and amine groups in the matrix of synthesized hybrid ion exchange material. Peaks at 536.2 $cm^{-1}$ and 1053.8 $cm^{-1}$ confirm the presence of phosphate group in the material. Peaks around 1638.14 $cm^{-1}$ and at 3419.75 $cm^{-1}$ reveal the presence of external water molecules. The bands beyond 3419.75 $cm^{-1}$ are because of –OH groups present in the matrix of ion exchanger. The peaks[1] at 2858.6 $cm^{-1}$, 2356.0 $cm^{-1}$ and 1386.18 $cm^{-1}$ reveal the presence of methyl and methylene groups respectively in the matrix of synthesized material whereas peaks at 3078.3 $cm^{-1}$ and 1165.7 $cm^{-1}$ depict the presence of ammonium and C-N stretching of amine group in the material respectively.

**Elemental analysis:** The elemental analysis (Table 7) reveals the presence of N-Cetyl-N,N,N-tri methyl ammonium bromide in the matrix of hybrid ion exchanger i.e. CTAB based tin (IV) phosphate.

**Scanning electron microscopy (SEM) study:** Although, tin(IV) phosphate is non fibrous in nature but the synthesized hybrid ion exchanger has been found fibrous. SEM study (Figure 3) reveals its fibrous nature. It may be perhaps due to the intercalation of tin(IV) phosphate with the polar N-Cetyl-N,N,N-tri methyl ammonium bromide molecules.

**Antibacterial and antimicrobial Study:** Antibacterial activity data (Table 8) reveals that CTAB based tin(IV) phosphate shows afficacy against *Staph awrens*, *E. coli* ESS 2231, *Protect vulgaris* and *Aspergillus fumigatus*.

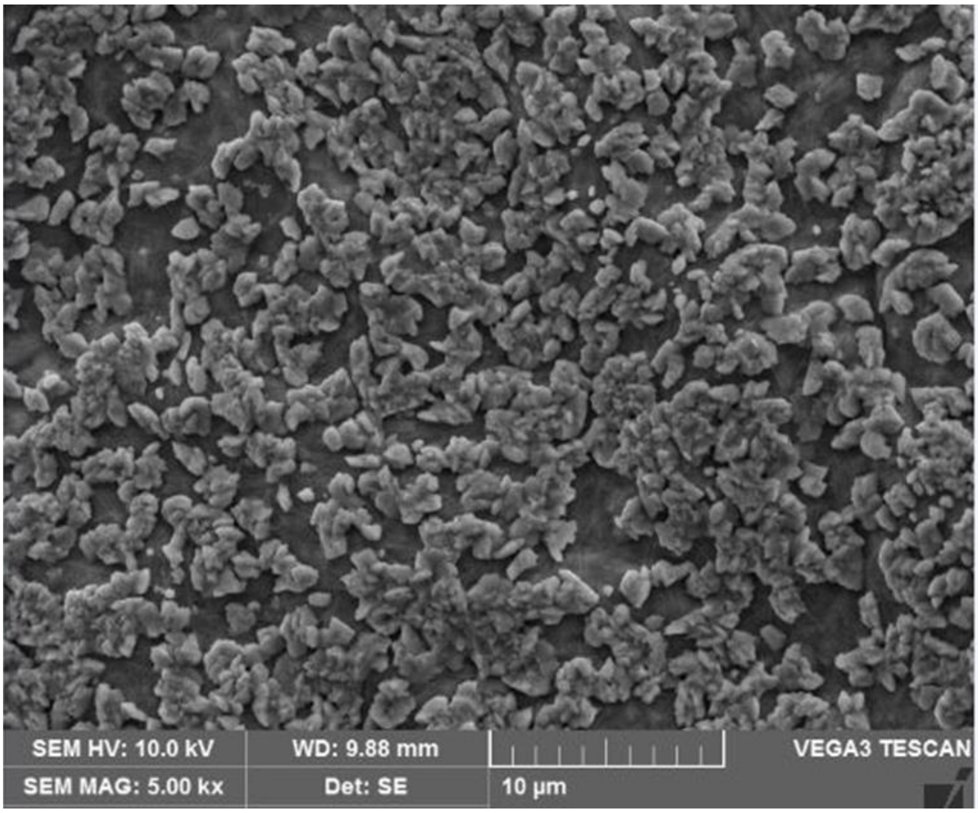


**Figure 3: SEM photograph of N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate**

**Table 8**
**Antibacterial study on N-Cetyl-N,N,N-tri methyl ammonium bromide –Tin (IV) Phosphate**

| Antibacterial activity | |
|---|---|
| Conc. (μg/ml) | 94 |
| Staph Awrens | 22 |
| Conc. (μg/ml) | 118 |
| *E. coli* ESS 2231 | 17 |
| Conc. (μg/ml) | 250 |
| Protect Vulgaris | 24 |
| Conc. (μg/ml) | 122 |
| *Aspergillus Fumigatus* | 20 |

## Conclusion

The synthesized material has shown the highest ion exchange capacity among other hybrid ion exchange materials. The presence of N-Cetyl-N,N,N-tri methyl ammonium bromide in matrix of tin(IV) phosphate has played a key role in enhancement of ion exchange capacity of the material which in turn, may be due to an increment in the distances of the layers of tin(IV) phosphate that makes feasible exchange of ions. The material has been found thermally stable, reusable showing antibacterial characteristics.

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## References

1. Kalsi P.S., Spectroscopy of Organic Compounds, 5th Edition **(2002)**

2. Rao C.N.R., Chemical Applications of Infrared Spectroscopy, Academy Press, New York **(1963)**

3. Somya A. and Vargas-Bernal R., eds., Hybrid Nanomaterials: Hybrid Ion Exchangers, IntechOpen, London, UK **(2020)**

4. Somya A., Metal Phosphates: Their Role as Ion Exchangers in Water Purification, In Gupta R.K., eds., Metal Phosphates and Phosphonates, Engineering Materials, Springer, Cham., https://doi.org/10.1007/978-3-031-27062-8_19 **(2023)**

5. Somya A., *Res. J. Chem. Environ*., **23(3)**, 96 **(2019)**

6. Somya A. and Upadhyay V., *Res. J. Chem. Environ.*, **24(7),** 107 **(2020)**

7. Somya A. and Singh M., *Curr. Anal. Chem*., **18(3)**, 383 **(2022)**

8. Somya A. and Maheria K., *Bull. Mater. Sci*., **43**, 163 **(2020)**

9. Somya A., Rafiquee M.Z.A., Varshney K.G. and Al-Lohedan H.A., *Desalination Water Treat*., **56**, 638 **(2015)**

10. Somya A., Rafiquee M.Z.A. and Varshney K.G., *Colloids Surf. A Physicochem. Eng. Asp*., **336**, 142 **(2009)**

11. Somya A. and Upadhyay V., *Res. J. Chem. Environ*., **21(1)**, 18 **(2017)**

12. Somya A., Rafiquee M.Z.A. and Upadhyaya V., *Res. J. Chem Environ*., **22(6)**, 45 **(2018)**

13. Varshney K.G., Rafiquee M.Z.A. and Somya A., *Colloids Surf. A Physicochem. Eng. Asp*., **317**, 400 **(2008)**

14. Varshney K.G., Rafiquee M.Z.A. and Somya A., *J. Therm. Anal. Calorim.*, **90**, 663 **(2007)**

15. Varshney K.G., Rafiquee M.Z.A., Somya A. and Drabik M., *Ind. J. Chem*., **45A**, 1856 **(2006)**

16. Varshney K.G., Rafiquee M.Z.A. and Somya A., *Colloids and Surface A: Physicochemical and Engineering Aspects (USA)*, **301**, 224 **(2007)**

17. Varshney K.G., Rafiquee M.Z.A. and Somya A., *Colloids and Surface A: Physicochemical and Engineering Aspects (USA)*, **301**, 69 **(2007)**

18. Varshney K.G., Tayal N. and Gupta U., *Coll. Surf. A: Physico. Eng. Asp*., **145**, 71 **(1998)**.

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