

Chapter VIII

Adsorption Using Synthesized Bead Composites

Chapter VIII

Adsorption using Synthesized Bead Composites

Several materials have been reported as effective chelates viz., like, industrial by products, natural minerals, agricultural wastes and synthetic materials, for toxic substances. Functional groups such as carboxyl and hydroxyl in any plant material play an inevitable role in the removal of anions from aqueous matrices as well as wastewaters. However, the sorbing capability of these materials are not totally exploited due to their poor mechanical strength and chemical stability. Therefore, in recent years, composite materials synthesized from these eco-based raw materials in the form of beads, possessing better surface area, have gained much attention. This shall be due to their remarkable properties and synergistic nature¹. Thus, it is predicted that sequestering properties of sorbents' could be greatly enhanced, when delivered in composite form.

Keeping this fact under consideration, the present chapter explains the preparation of bioencapsulated beads using TCSS/ TETS as precursors and alginate/goethite/magnetite as dopants. Reason for choosing the mentioned modified materials as precursors among the four developed sorbents, is that Batch results show notable sorption characteristics of these sorbents against the other two materials (TVFH, TGGDB). Utilization of composite beads in adsorption process is favoured due to its stability, easy separation during filtration, biodegradability, nontoxic, low cost and hydrophilicity³.

8.1 Calcium Alginate/ Goethite/ Magnetite - Dopants

Calcium alginate is a biopolymer with a proficient cross-linking ability towards variable biomass and have been employed as effective pollutant trapper for wastewater samples. Alginate has been reported to be utilized effectively for the uptake of toxic anions².

Goethite (α -FeOOH) is one of the most common and stable crystalline iron hydroxides in natural systems. Metal oxide-based composites have recently gained considerable attention in sequestering anions, heavy metals and dyes, since they possess biocompatibility, water permeability, and ability to load large amounts of solid particles.

It has been reported to possess marked surface area ($100 \text{ m}^2/\text{g}$) and also exhibits selectivity in trapping pollutants from aquatic environments.

Magnetites are iron oxides prepared from ferrous and ferric salts in alkaline medium. These iron oxides when embedded with natural material tend to enhance the latter's sorptive nature. Therefore, magnetite serves as an ideal substitute in adsorption method as an alternate to their modified precursors.

8.1.1 Synthesis of Biomass Anchored Composite Beads

About 2 g of sodium alginate was weighed, dissolved in 100 mL double distilled water and swirled thoroughly at 60°C using magnetic stirrer to obtain a gel like substance. 2 g TCSS / TETS were added separately to two beakers containing the alginate gels, further the suspension was stirred for 2 hours, until the development of complete homogeneous mixture.

Goethite was prepared by dissolving 80 mL 0.2 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 500 mL double distilled water, followed by rapid addition of 20 mL 2.5 M KOH solution to maintain an alkaline pH environment. The resulting suspension was magnetically agitated for 6 hours maintaining a temperature of 40°C , until a yellow brown goethite precipitate was formed. The supernatant solution was decanted and later, goethite precipitate was washed thoroughly with double distilled water, dried for 24 hours in a at 60°C oven and finally powdered finely.

A ferrofluid mixture was obtained by dissolving 8 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 15 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, in double distilled water. pH of this mixture was adjusted with 5N NaOH solution to become alkaline (pH 11) and whisked vigorously at room temperature for an hour¹². A black precipitate formed was centrifuged. The settled precipitate was rinsed several times with double distilled water further, dried for 7 hours in an oven (70°C).

Alginate – precursors preparations were repeated to obtain homogeneous mixture with TETS / TCSS in two beakers each, 2g of synthesized Goethite and Magnetite were added to these four beakers, correspondingly. Later, the contents of the beakers were homogenized for 3 hours.

The homogeneous solutions from all the respective beakers were pipetted out using a micro dropper and introduced slowly into 100 mL 2% calcium chloride solution taken in six beakers, as single drop at a time, to form biocomposite beads. Further, these beads were rinsed repeatedly using double distilled water to remove excess calcium ions present on the beads' surface. The synthesized beads (TCSSCAB, TETSCAB, G@TCSSB, G@TETSB, M@TCSSB, M@TETSB) were dried out in hot air oven for 4 hours at 80 °C⁴. Schematic diagrams representing synthesis of TETSCAB, G@TETSB, M@TETSB are shown in figures 8.1, 8.2 and 8.3.



Figure 8.1 TETSCAB

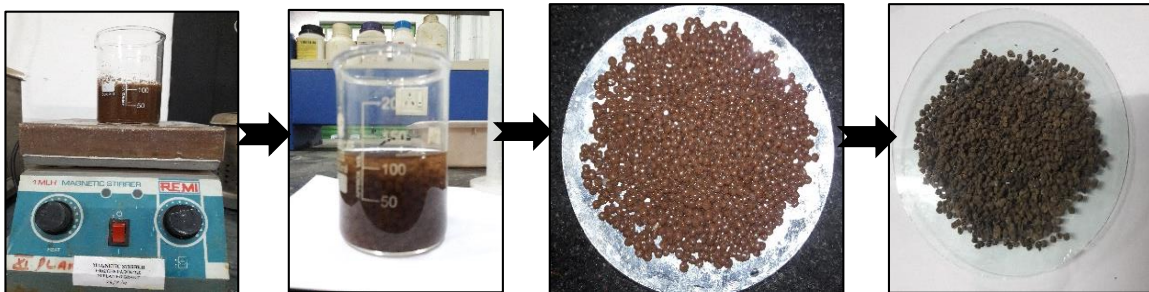


Figure 8.2 G@TETSB

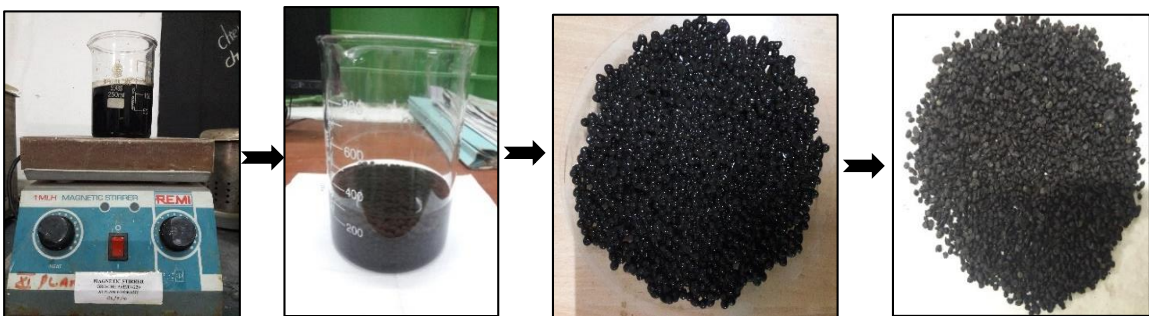


Figure 8.3 M@TETSB

8.1.2 Batch Verification – Biocomposite Beads

Batch verification was done to assess the sorption capacities of the prepared biobeads for aqueous anionic species. Important factors such as pH environment, initial anionic concentration, preset time frames and temperature conditions were maintained as predetermined in previous chapters, but for different doses of beads. The variation in dose ranges was halved against those optimized doses of the precursors, required for the present study. The supernatant solutions were filtered after agitating in mechanical shaker and the residual sample concentrations were recorded complexometrically (listed in Tables 8.1 & 8.2) using UV-Visible Spectrophotometer as per the procedure as mentioned in chapter III.

Requirement of beads' dose for effective anion chelation is Magnetite (50 mg) > Goethite (75 mg) > Alginate (100 mg), as evident from the tables. Reduction in sorption process at higher doses reflect the swelling nature of the beads' due to crowded number. The synthesized beads expressed excellent chelating properties, however marginal increase in percentage removal of anions by M@TETSB is observed at a lesser dosage itself and thence, characterization studies were restricted to these beads alone.

Table 8.1 Impact of TCSS Beads - Aqueous Solutions

Beads' dose (mg)	Percentage Removal (%)								
	TCSSCAB			G@TCSSB			M@TCSSB		
	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻
25	68.9	66.8	67.3	84.3	83.7	85.6	88.7	82.7	83.8
50	77.5	74.3	77.8	91.3	90.2	89.8	97.4	96.2	96.8
75	84.8	81.8	83.4	96.8	95.4	96.4	94.3	91.3	92.5
100	95.6	94.9	95.2	93.4	91.8	92.7	90.9	89.4	90.4
125	90.3	89.8	90.1	91.5	90.6	90.2	88.3	84.5	87.6

Table 8.2 Impact of TETS Beads - Aqueous Solutions

Beads' dose (mg)	Percentage Removal (%)								
	TETSCAB			G@TETSB			M@TETSB		
	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻
25	73.4	70.5	71.8	88.3	85.3	87.2	95.7	93.7	94.8
50	86.3	83.7	85.6	93.8	90.5	93.6	99.8	99.4	99.5
75	94.8	92.3	93.1	98.9	97.3	97.8	97.3	96.3	96.5
100	97.6	96.8	97.9	95.7	93.7	93.4	94.4	92.4	93.9
125	91.6	90.7	90.8	92.7	90.9	91.7	92.6	90.5	91.2

8.2 M@TETSB Characterization

8.2.1. Magnetic Nature

Magnetic property of M@TETSB were tested by placing a magnet externally near the watch glass containing beads. Magnets were found to attract the beads in no time, which demonstrates the high magnetic sensitivity¹⁴ of M@TETSB (fig 8.4).



Figure 8.4 Magnetic Beads

8.2.2 BET

M@TETSB recorded greater percentage removal of anions against G@TETSB and TETSCAB, which shall be due to better surface area of these magnetite beads. Therefore, BET analysis was restricted to these beads, whose surface area was calculated to be 163.2 m²/g. This appreciable is was higher when compared to similar synthesized beads using few other eco-based precursors as reported in literature¹⁵ (table 8.3).

Table 8.3 Surface Characterisation

Adsorbents	BET-Surface Area (m²/g)
Ca based beads ¹⁶	34.1
Chitosan Soyabean husk beads ¹⁷	147.8
Copper chitosan beads ¹⁸	28.5
Palm seed-based biochar beads ¹⁹	135.0
chitosan/Al ₂ O ₃ /Fe ₃ O ₄ beads ²⁰	72.3
M@TETSB (current study)	163.2

8.2.3 FT-IR Spectral Study

Presence of iron hydroxide salts in the magnetite doped TETS was verified through FT-IR spectral study. Figure 8.5 shows the occurrence of new peaks at 585 cm⁻¹ and 1630 cm⁻¹ corresponding to FeO and Fe₃O₄. Further, a broad peak at 3398 cm⁻¹ is characteristic of FeO-OH, Fe(OH)₂ and Fe(OH)₃ derived from Fe₃O₄ magnetic particles²¹. Other notable peaks in the spectra are identical to that of its counterpart in figure 5.11.

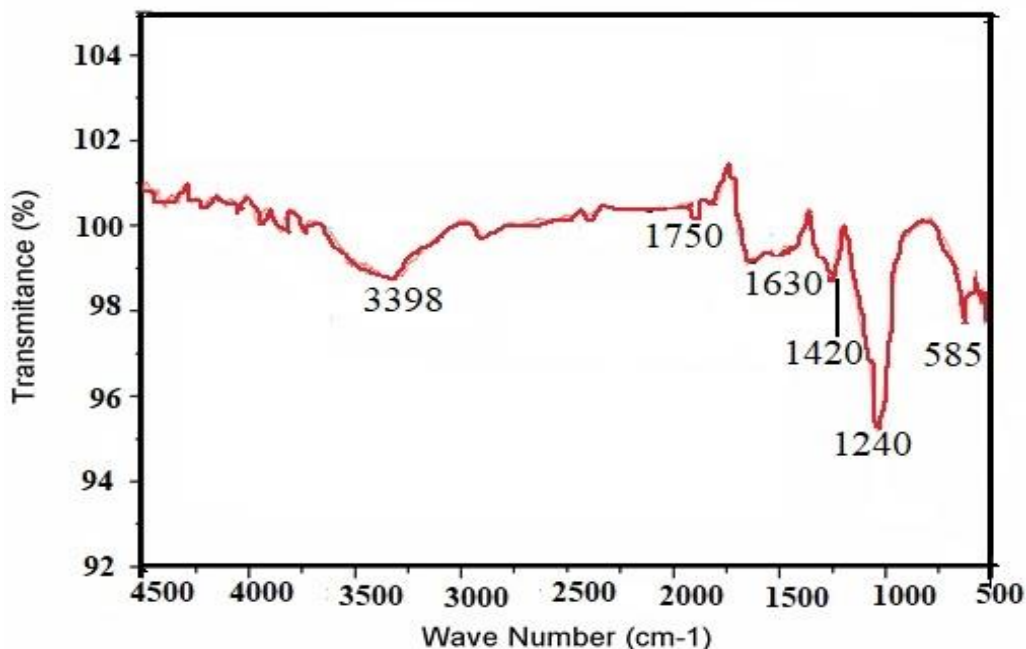


Figure 8.5 FT-IR Spectra – M@TETSB

8.2.4 SEM/ EDAX Analyses

Phosphate removal was almost 100 % by M@TETSB. Therefore, these beads along with anion laden beads were subjected to SEM analysis to explore their surface morphology, depicted in figures 8.6 & 8.7. Also, the elemental composition of phosphate laden magnetite beads was studied using EDAX technique. Figure 8.6 shows the surface of the magnetite beads to be cubical in nature. However, change in the surface texture due to the chelation of phosphate ions by beads surface is evident from the flower like appearance²² as seen in figure 8.7.

Figure 8.8 reflects the distribution of marked peaks at 0.2, 0.5, 2.0 and 2.6 keV specified to the presence of carbon, oxygen, phosphorus and chlorine atoms. Two altered energy at 6.4 and 7.0 keV, also one peak at 4 keV corresponds to the presence of Fe and Ca ions in the spectra. These fine spectral lines confirm phosphate sorption, doping of ferrofluid in the magnetite beads, along with the bead formation taking place in CaCl₂ base.

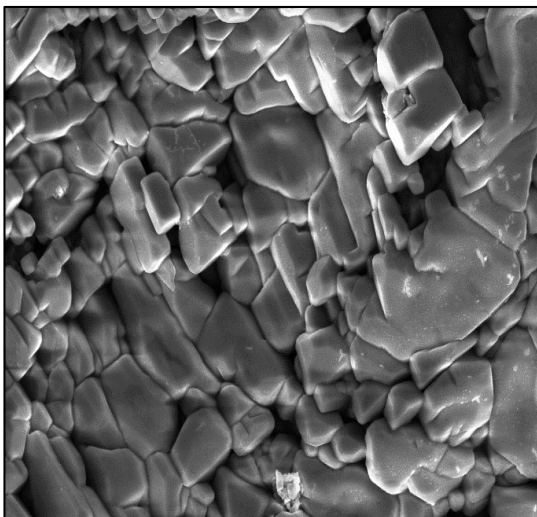


Figure 8.6 SEM - M@TETSB

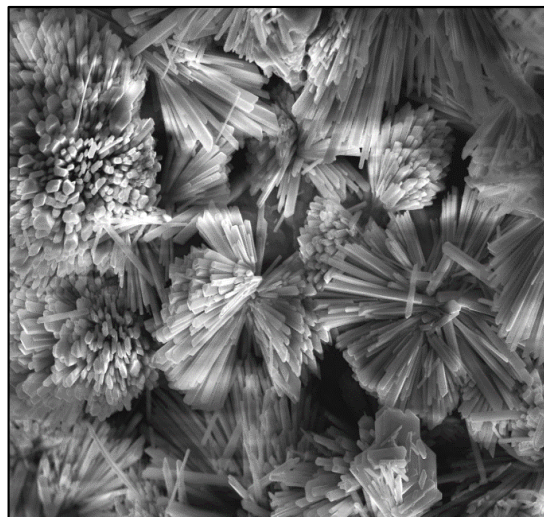


Figure 8.7 SEM - PO₄³⁻ - M@TETSB

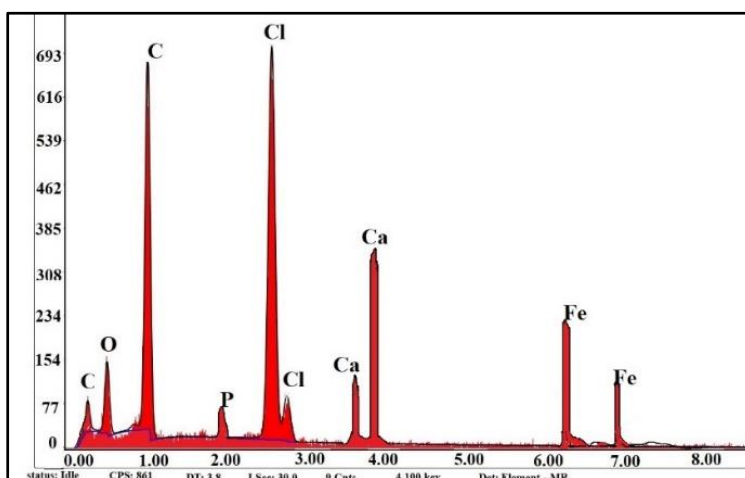


Figure 8.8 EDAX - PO₄³⁻ - M@TETSB

8.2.5 TG - DTA Analyses

The stable nature of any adsorbent material against temperature parameter is essential to prospect its thermal withstanding capacity when tested at field conditions. In this context, thermal stability of M@TETSB was verified under nitrogen atmosphere using TGA and DTA methods at a heating range of 900 °C. The corresponding thermogram, represented in figure 8.9 demonstrates three stages of step-down process. The first one starting from 30 °C dips down upto 250 °C, representing the presence of water molecules in the magnetite beads. Further, decline in the curve, within the range of 250 °C

to 450 °C, shall contribute to the degradation of polymeric unit (alginate). Later, the final step down had occurred between 450 °C to 600 °C, referring to continuous denaturing of the beads/ decomposition of organic moieties²³. Seldom substantial variation was perceived beyond 600 °C upto 900 °C. This show that M@TETSB is thermally stable almost upto 500 °C.

A low endothermic peak at 47 °C is noted in DTA curve, implying moisture vaporization from the surface of the beads. Complete loss of water molecule is indicated by a steep rise in the peak at 393 °C, beyond which a continuous decline of this curve is obvious until 900 °C. From this, it is inferred that the endothermic nature of the beads had come to halt²⁴.

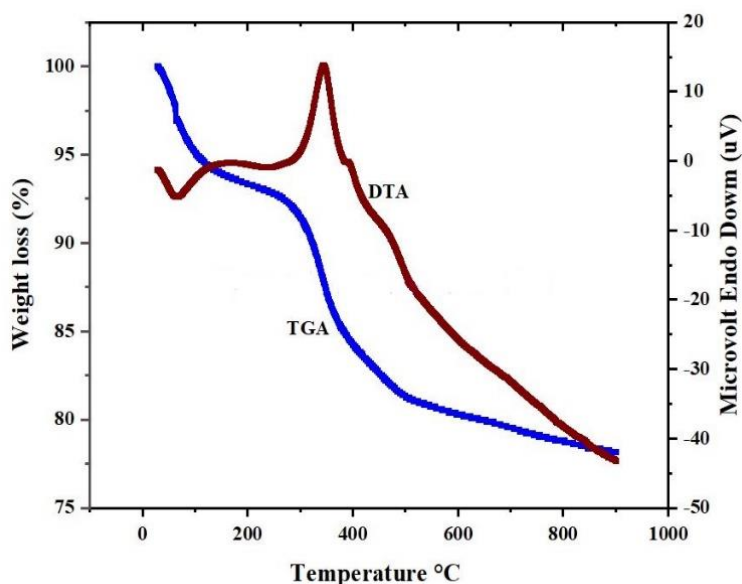


Figure 8.9 TGA/DTA – M@TETSB

8.2.6 VSM Analyses

Vibrating sample magnetometer is an instrument employed to assess the magnetic property of any magnetized material. This is done through the observation of magnetic moment, as a response of applying ascending and descending magnetic field (G) to the material²⁵. The data of this magnetic field forms hysteresis loop at room temperature. Magnetite and M@METSBS were subjected to VSM study and the hysteresis curves obtained from related data are shown in figures 8.10 & 8.11. Non- appearance of expected

loops in the curves indicate the absence of diamagnetic nature, concluding that both the materials exhibit paramagnetic property. Magnetization and coercivity values calculated from the graphical representation confirm these values are lower for magnetite beads than the magnetite dopants (Table 8.4). These reduced values reflect the enhancement in magnetic separation and reusability of exhausted beads²⁶.

Table 8.4 VSM - Parameters

Parameters	Magnetite	M@TETSB
Magnetization	26.93	11.84
Coercivity	63.52	37.69

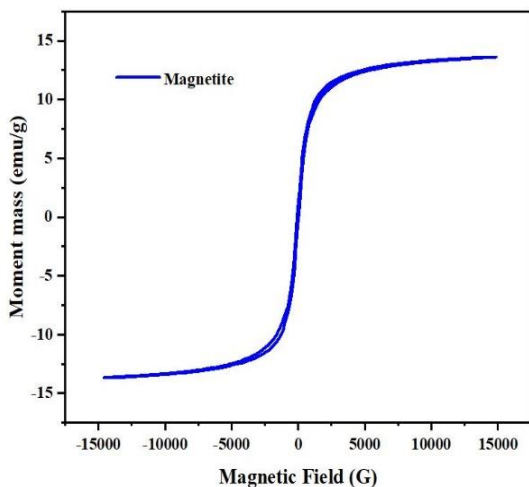


Figure 8.10 VSM – Magnetite

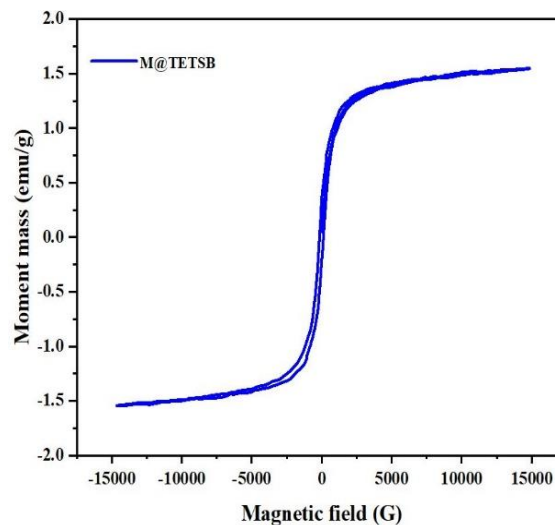


Figure 8.11 VSM – M@TETSB

8.2.7 XRD Analyses

XRD patterns recorded in 2 theta regions between 5 – 90 °C for magnetite doped TETS and its dopant are picturized in figure 8.12. The reflections (red in colour) observed at 28.45, 30.14, 40.52, 51.73, 63.45 and 78.49 °C correspond to the dopant associated with the crystal planes of (222), (311), (400), (422), (511) and (440). This suggests the pure magnetic nature of the latter²⁷. A replica pattern is evidenced for XRD analysis of beads too, which propound the surface enrichment of magnetite with TETS, with least alteration in its crystalline nature.

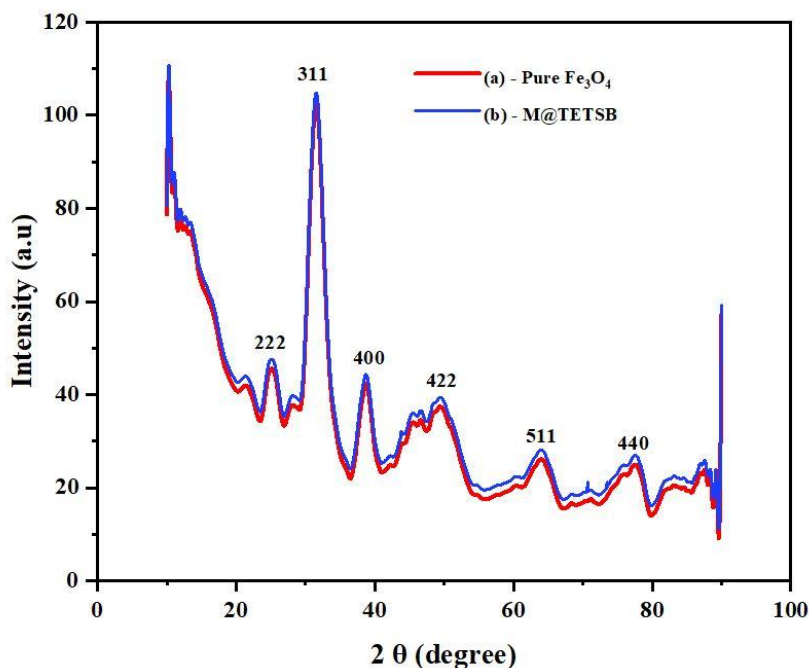


Figure 8.12 XRD – Magnetite/M@TETSB

8.3 Effluent Analysis – M@TETSB

Based on the Batch results, experimental setup was upscaled by testing the nature of beads against effluent samples.

PO_4^{3-} , NO_3^- and SO_4^{2-} ions enriched laundry effluent sample was collected from Perfect Laundry Unit, located at Ootacamund, Tamil Nadu, India. The concentrations of the anions in the native sample examined at Seed Enviro Laboratory, Coimbatore, Tamil Nadu, India were alarming, exceeding the permissible limits. In this view, the raw sample was subjected to serial dilutions to match the concentrations of the laboratory solutions. Followingly, Batch equilibration studies were restricted using M@TETSB for the diluted sample, since these beads registered better sorption characteristics, under identical optimized conditions. The residual concentrations corresponding to the three anions were determined and listed in table 8.5. The results show that the percentage removal of anions in the diluted effluent sample to be lesser than the anion chelation which had occurred in corresponding aqueous solutions (Table 8.2). The fact behind decreased anionic sequestration shall be due to the presence of other ions interfering the sorption process.

Table 8.5 Impact M@TETSB - Effluent

Beads' dose (mg)	Percentage Removal (%)		
	M@TETSB		
	PO ₄ ³⁻	NO ₃ ⁻	SO ₄ ²⁻
25	62.2	60.5	61.6
50	75.2	72.8	74.7
75	88.6	84.6	87.1
100	94.4	90.7	92.5
125	87.7	84.9	85.9
150	83.1	80.6	81.5

8.4 References

- [1] Javad Kazemi, Vahid Javanbakht et al., Alginate beads impregnated with magnetic Chitosan@Zeolite nanocomposite for cationic methylene blue dye removal from aqueous solution, *International Journal of Biological Macromolecule*, (2019) 1 – 35
- [2] Venkata Subbaiah Munagapati, Dong-Su Kim, Equilibrium isotherms, kinetics, and thermodynamics studies for congo red adsorption using calcium alginate beads impregnated with nano-goethite, *Ecotoxicology and Environmental Safety*, 141 (2017) 226 - 234
- [3] Ilango Aswin Kumar, Natrayasamy Viswanathan, Fabrication of metal ions cross-linked alginate assisted biocomposite beads for selective phosphate removal, *Journal of Environmental Chemical Engineering*, (2017) 1 -34
- [4] Mohammad E. Hossain, Cody L. Ritt, Tala B. Almeelbi and Achintya N. Bezbaruah, Biopolymer Beads for Aqueous Phosphate Removal: Possible Applications in Eutrophic Lakes *Journal of Environmental Engineering*, 144 (5) (2018) 1- 11
- [5] Soodamani Periyasamy, Venkatrajan Gopalakannan, Natrayasamy Viswanathan, Fabrication of Magnetic Particles Imprinted Cellulose based Biocomposites for Chromium (VI) removal, *Carbohydrate Polymers*, (2017) 1- 28
- [6] G.V. Krishna Mohan, A. Naga Babu, K. Kalpana and K. Ravindhranath, Zirconium-Treated Fine Red Mud Impregnated in Zn-Alginate Beads as Adsorbent in Removal of Phosphate from Water, *Asian Journal of Chemistry*, 29, No. 11 (2017), 2549-2558
- [7] Hanna Siwek, Artur Bartkowiak and Małgorzata Włodarczyk, Adsorption of Phosphates from Aqueous Solutions on Alginate/Goethite Hydrogel Composite Water 11 (2019) 1 – 13
- [8] Yong-Un Han, Chang-Gu Lee, Jeong-Ann Park, Jin-Kyu Kang, In Lee, Song-Bae Kim, Immobilization of Layered Double Hydroxide into Polyvinyl Alcohol/Alginate Hydrogel Beads for Phosphate Removal, *Environmental Engineering Research*, 17(3) (2012) 133-138

- [9] Xiangqian Li, Huizhong Xu, Zhe-Sheng Chen, and Guofang Chen, Biosynthesis of Nanoparticles by Microorganisms and Their Applications, *Journal of Nanomaterials*, (2011) 1-16
- [10] Rana M, Akhtar N, Rahman S, Jamil HM, Asaduzzaman SM, Extraction of Hydroxyapatite from Bovine and Human Cortical Bone by Thermal Decomposition and Effect of Gamma Radiation: A Comparative Study, *International Journal of Complement Alternative Medicine*, 8(3) (2017) 00263 226
- [11] Figueiredo, A. Fernando, G. Martins, J. Freitas, F. Judas, and H. Figueiredo, Effect of the calcination temperature on the composition and microstructure of hydroxyapatite derived from human and animal bone, *Ceramics International*, 36(8) (2010) 2383-2393
- [12] Lau, K.-t. Lau, H. Ku, F. Cardona, and J.-H. Lee, Analysis of heat-treated bovine cortical bone by thermal gravimetric and nanoindentation. *Composites Part B: Engineering*, 55 (2013) 447- 453
- [13] Ravulapalli Sujitha and Kunta Ravindharnath, Extraction of Phosphate from Polluted Waters using Calcium Alginate Beads Doped with Active Carbon Derived from *A.aspera* plant as Adsorbent, *Journal of Analytical Methods in Chemistry*, 4(5), 2017, 1-13
- [14] Yanan Shang, Kangying Guo, Xing Xu, Zhongfei Ren, Baoyu Gao, Cellulose based multifunctional hybrid material for sequestering phosphate in stratified water purification columns, *Cellulose*, 25 (2018) 5877–5892
- [15] Baskaran Ramalingam, Thanusu Parandhaman, Priyadarshani Choudhary, Sujoy K Das, Biomaterial Functionalized Graphene-Magnetite Nanocomposite: A Novel Approach for Simultaneous Removal of Anionic Dyes and Heavy-Metal Ions, *ACS Sustainable Chemistry & Engineering*, (2018) 1 – 37
- [16] Jayachandran Venkatesan, Baboucarr Lowe, Panchanathan Manivasagan, Kyong Hwa Kang, Elna P. Chalisserry, Sukumaran Anil, Dong Gyu Kim and Se-Kwon Kim, Isolation and Characterization of Nano-Hydroxyapatite from Salmon Fish Bone, *Materials*, 8 (2015) 5426-5439

- [17] H. Thagira Banu, P. Karthikeyan, and Sankaran Meenakshi, Zr⁴⁺ ions embedded chitosan-soya bean husk activated bio-char composite beads for the recovery of nitrate and phosphate ions from aqueous solution *International Journal of Biological Macromolecules*, (2019) 1 -44
- [18] Byungryul, Ka-Young Jung, Sang-Hyup Lee, Seunghak Lee and Jae-Woo Choi, Effective Phosphate Removal from Synthesized Wastewater Using Copper–Chitosan Bead: Batch and Fixed-Bed Column Studies, *Water Air Soil Pollution* (2014) 1 – 12
- [19] Mustafa Gazi, Akeem Adeyemi Oladipo & Kola A. Azalok, Highly efficient and magnetically separable palm seed-based biochar for the removal of nickel, *Separation Science and Technology*, (2016) 1 -28
- [20] Farahnaz Bozorgpour, Hossein Fasih Ramandi, Pooya Jafari, Saman Samadi, Shabnam Sharif Yazd, Majid Aliabadi, Removal of nitrate and phosphate using chitosan/Al₂O₃/Fe₃O₄ composite nanofibrous adsorbent: Comparison with chitosan/Al₂O₃/Fe₃O₄ beads, *International Journal of Biological Macromolecules*, 93 (2016) 557 - 565
- [21] Weixiao dou, Zhen Zhou, Lu-Man Jiang, Aijian Jiang, Rongwei Huang, Xiaoce Tian, Wei Zhang, Dongqing Chen, Sulphate Removal from Wastewater using Ettringite Precipitation Magnesium ion Inhibition and Process Optimisation, *Journal of Environmental Management*, 2(7), 2017, 34 - 46
- [22] Xin Liu, Lingfan Zhang, Removal of Phosphate Anions using the Modified Chitosan Beads: Adsorption Kinetics, Isotherm and Mechanism Studies, *Power Technology*, 14(2), 2015, 6- 26
- [23] J. Singh, A. Ali, V. Prakash, Removal of Lead (II) from Synthetic and Battery Wastewater using Agricultural Residue in Batch/Column Mode, *Journal of Environmental Science and Technology*, 13(2), 2013, 22- 36

- [24] A. Naga Babu, G.V.Krishna Mohan, K. Kalpana, and K. Ravindharnath, Removal of Lead from water using Calcium Alginate Beads Doped with Hydrazine Sulphate-Activated Red Mud as Adsorbent, *Journal of Analytical Methods in Chemistry*, 3(4), **2017**, 2-15
- [25] Per Olof Persson and Bent Hultman, Phosphorus Removal and Recovery from Wastewater using Magnetite, *Industrial Ecology*, 7(2), **2010**, 4- 10
- [26] Abinashi Sigdel, Jeongwon Park, Hyoeun Kwak, Pyung-Kyu Park, Arsenic removal from aqueous solutions by adsorption onto hydrous iron oxide-impregnated alginate beads, *Journal of Industrial and Engineering Chemistry*, XXX (**2016**) 1 – 10
- [27] Perumal Karthikeyan and Sankaran Meenakshi et al., In situ fabrication of magnetic particles decorated biopolymeric composite beads for the selective remediation of phosphate and nitrate from aqueous medium, *Journal of Environmental Chemical Engineering*, (**2019**) 1 – 38.