Removal of Sulphate from contaminated water bodies of River Rushikulya using Natural adsorbent

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Abstract

Due to heavy discharge of textile, steel and paper industries into nearby river water directly with partial treatment, the contamination in river water is a big concern day by day. One of the bulk contaminating elements found in river and ground water is sulphate which has a long listed hazardous impact on the health of human and living bodies. The bulk amount of gypsum released from plants is big contributor for sulphate level up in water bodies. In this research, Rushikulya River, which is a most well-known river in Odisha, is selected for study. The river water sample was collected from ten different sites along this river.

The samples were analysed in laboratory and sulphate found was attempted to remove on treating with a natural composite matrix prepared from bagasse waste and coir pith. It is found that with the medium acidic range from 5 to 6 and with a dose of 4:6 ratio composite matrix, it is possible to remove sulphate up to 97% from the water sample taken.

Keywords: River water, Sulphate ion, Agro-based waste, Composite matrix, SEM.

Introduction

Due to development of industries on river belt, the level of sulphate contamination in river water is increasing gradually. The heavy pesticide usage in agriculture and the addition of industrial effluents directly into water, make it unhealthy to be used as drinking water[20,21]. Seeing the high-level sulphate in river water, earlier research was carried out for removal of sulphate using advance methodologies i.e. Electro-dialysis, Reverse Osmosis and Nanotechnologies etc.[1]

Fang et al[11] have studied the removal of high-concentration sulphate ions from the sodium alkali FGD wastewater using ettringite precipitation method, factor assessment, feasibility and prospect. The method was feasible for treating high concentration sulphate from waste water and potential method as a commercial application in future.

Ricci et al[22] experimented on integration of nano-filtration and reverse osmosis for metal separation and sulfuric acid recovery from gold mining effluent. Here the viability of implementing sequential stages of microfiltration (MF), nano-filtration (NF) and reverse osmosis (RO) to recover sulfuric acid, to separate noble metals and to produce high quality reuse water from a gold mining effluent, specifically from a pressure-oxidation process effluent[22]. Additionally, lime demand for neutralization of the proposed treatment streams and current lime demand were compared. It was observed that the NF attained high sulfuric acid permeation, equivalent to 82% and a substantial acid purification of approximately 77% in relation to feed solution.

Moreover, the RO increased the acid content by 99% in relation to feed solution considering a recovery rate of 50%. The neutralization of the MF and NF concentrates allowed for a 20% reduction in lime consumption in relation to current demand[23,25]. Lopez. et al[17] have studied the recovery of sulphuric acid and added value metals (Zn, Cu and rare earths) from acidic mine waters using nano filtration membranes. The membrane chemistry of the active layer (nature and acid-base membrane properties) and structure (single/double layer) were found to be strong parameters in the membrane separation performance. Ion transport data were modelled according to a Solution-Electro-Diffusion model coupled with ion reactive transport and the membrane permeances to ions were determined[17].

Luptakova et al[18] have studied on the sulphate's removal from acid mine drainage. AMD is characterized by low pH and high content of heavy metals and sulphates. For the purposes of experiments, a few variants of the selective medium DSM-63 culture media were used in term of the sulphates and sodium lactate contents in the selective medium as well as sulphates in the studied AMD[15,16,18]. Maree et al[19] have investigated on biological removal of sulphate from industrial effluents and concomitant production of sulphur. Sulphate wastes can be treated by the biological sulphate process for the production of reusable water and/or the recovery of valuable by-products such as elemental sulphur, sodium bisulphide and heavy metals[19,26,27]. Arnold et al[2] have studied the Technologies for sulphate removal with valorisation options. Although this process successfully removes the metals and increases the pH to neutral levels, the resulting effluents contain high levels of sulphate (1500 - 2000), well above the permittable discharge levels. In British Columbia, Canada, a 30-day average sulphate concentration guideline of 65 has been proposed and other provinces are also considering lower limits for sulphate[2].

Ahmet Aygun et al[3] have studied the removal of sulphate from landfill leachate by crystallization. The present study explores the applicability of response surface methodology (RSM) in conjunction with central composite design (CCD) matrix to statistically optimize ettringite crystallization

https://doi.org/10.25303/296rjce075083

process for the removal of sulphate from landfill leachate[3-6]. Geldenhuys et al[12] have studied an integrated limestone/lime process for partial sulphate removal. They focus on two topics namely (1) an innovative process for the neutralization and partial sulphate removal of acid streams produced during coal mining and processing and (2) optimization of this integrated neutralization process by adding small amounts of synthetic organic polymers.

The sulphate level was reduced to 1094, which is less than the original aim of 1200. Chemical costs associated with neutralization, using limestone instead of lime, are reduced by 69% in the integrated limestone/lime process[7-9]. There are a number of successive or simultaneous stages involved in the agglomeration of particles. To get optimum neutralisation of the acid water and partial sulphate removal below the saturation level of gypsum (i.e. 1500), maximum sludge recovery was needed. The higher is the concentration of seed crystals, the larger is the surface area[12,28].

Fajtl et al[10] have studied gypsum precipitation – a medium to control sulphate pollution of freshwater sediment leachates. This experiment was to determine the effects of pH values and calcium supplements (as $CaCl_2$) on the formation of gypsum in a representative wetland sediment that was aerated. It was found that the differences between dissolved sulphate in untreated control and the other treatments with $CaCl_2$ amendments can be attributed to the precipitation of gypsum. $CaCl_2$ treatment should be used in the sites that do not contain elevated amounts of these metals[10,13,14].

In the present study, an attempt has been made to establish the role of composite material made up of raw coir pith and bagasse waste, to provide a medium for Sulphate removal. To carry out the study, raw materials are collected from various agricultural units present nearby and are mixed in a desired proportion to prepare composite matrix which could protect the and purify the contaminated water sources from toxic nutrients and pollutants.

Material and Methods

In the present study both the raw materials were collected from the local areas and were subjected to Physico-chemical analysis. The data are represented in table 1 and table 2. These two agro-based waste materials are mixed in different ratio to prepare ten different types of composite matrix consisting of coir pith and bagasse waste dusts. The details are represented in table 3. In order to prepare an efficient absorbent for sulphate removal, both the raw materials are added in different combinations so as to synthesise a good quality absorbent, represented in the flow sheet as in figure 1.

After activation of the materials, they are subsequently mixed by addition of an organic binder an admixture. The matrix is prepared using a mechanical mold. The specific parameters for individual matrix is represented in figures 2 to 4. The study revealed that among all the combinations, matrix composite of type- 5 (CM - 5), prepared with the combination of CP and BW (Ratio 6:4) is found to have good compressive strength of 2.24 MPa, tensile strength of 1.521 MPa and density of 398.74 kg/m^3. These matrices are employed to treat the contaminated water to remove sulphate.

Table 1
Physical Parameters of the Raw Material

Physical Properties	Coir Pith	Bagasse waste from Corn
C:N ratio	112.1	86.4
PH Value	5.8	8.9
Bulk Density	230 Kg/m^3	388Kg/m^3
Maximum water holding capacity	624	514

Table 2
Chemical Composition of Raw Material

Composition	Coir Pith	Bagasse waste from Corn
SiO_2	36.00	88.2
K_2O	26.50	1.3
CaO	24.00	0.6
P_2O_5	0.30	0.4
MgO	0.01	0.4
Al_2O_3	0.78	2.3
Fe_2O_3	0.40	5.1
Na_2O	0.36	0.1
SO_3	0.07	<0.1
TiO_2	12.50	0.05
ZnO	7.50	0.08

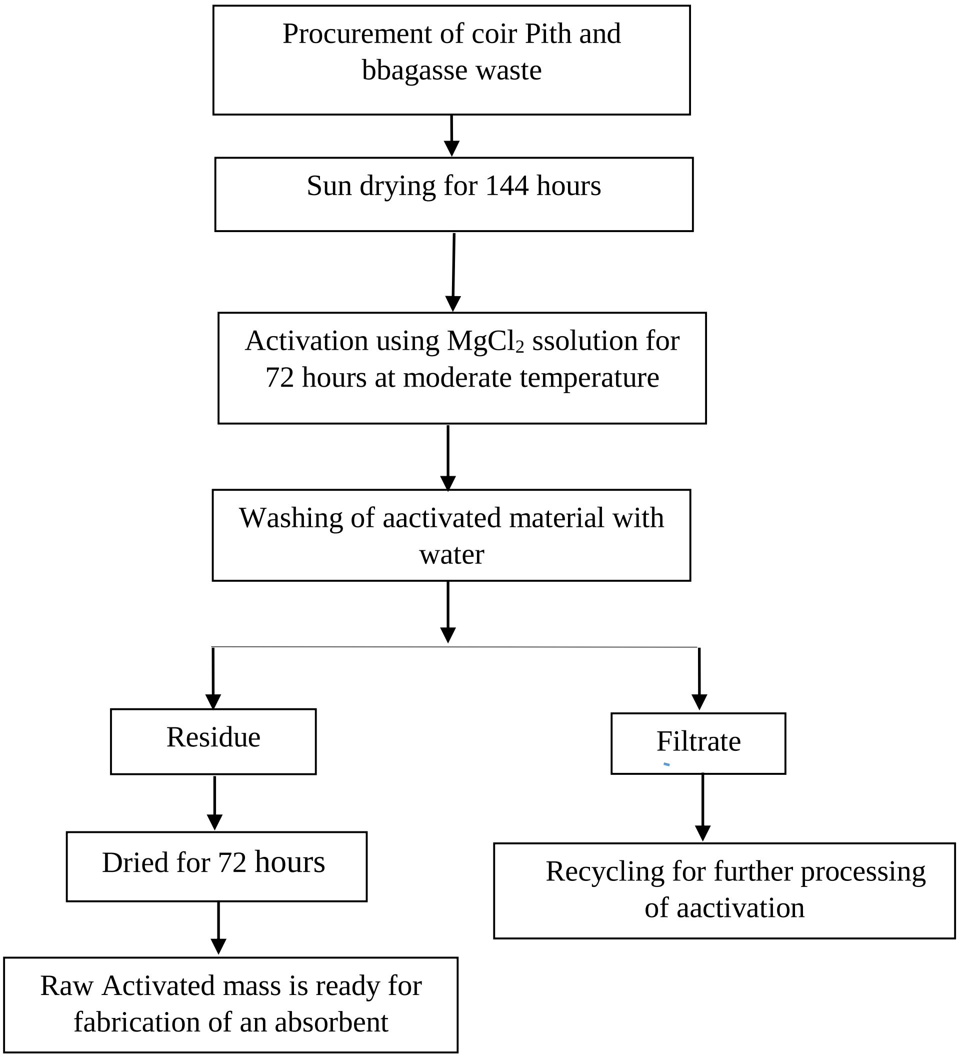

Figure 1: Process flow sheet for sulphate absorption material preparation

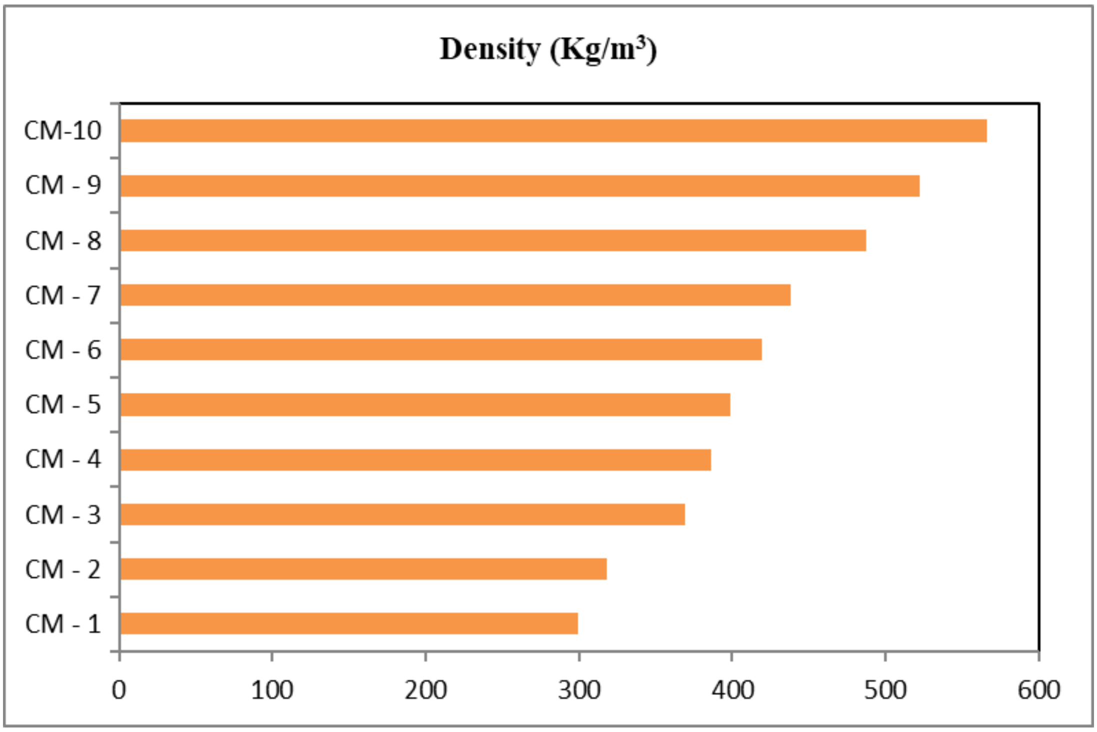

Figure 2: Comparative density of different composite matrix

https://doi.org/10.25303/296rjce075083

Table 3
The ratio for addition of Coir Pith to Bagasse waste

S.N.	Coir Pith (g)	Bagasse waste (g)	Ratio (CP:BW)
S - 1	95	05	9.5:1
S - 2	90	10	9:1
S - 3	80	20	8:2
S - 4	70	30	7:3
S - 5	60	40	6:4
S - 6	50	50	5:5
S - 7	40	60	4:6
S - 8	30	70	3:7
S - 9	20	80	2:8
S-10	10	90	1:9

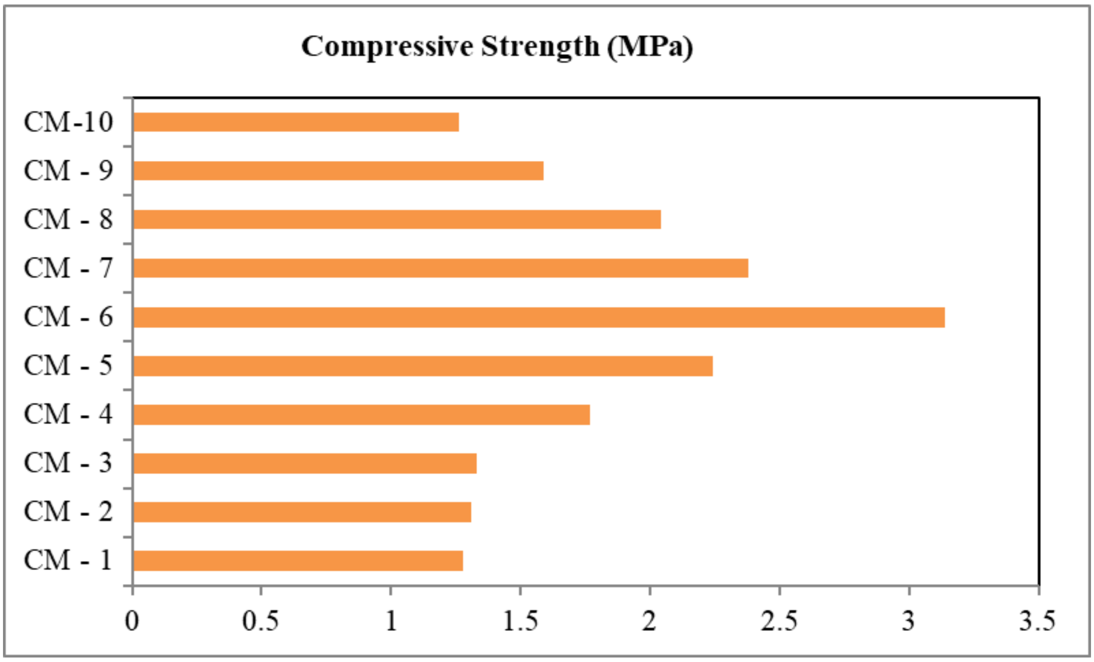

Figure 3: Comparative Compressive strength of different composite matrix

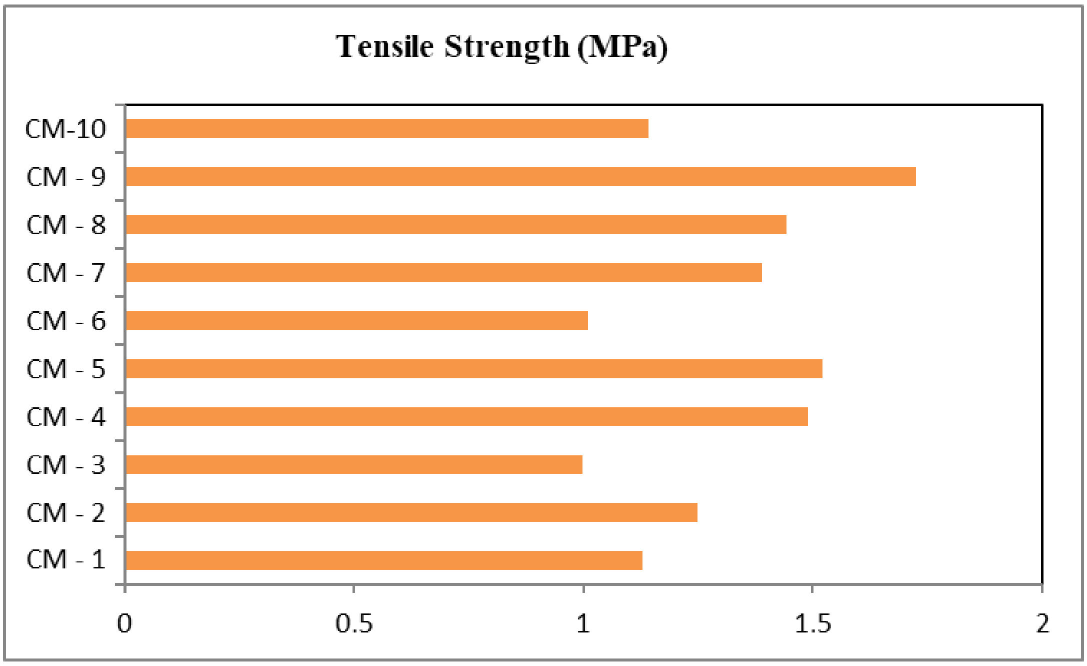

Figure 4: Comparative tensile strength of different composite matrix

Results and Discussion

The best efficient composite matrix molds prepared from a suitable combination of CP and BW are subjected to various studies in order to optimize the process parameters. The impact of various physical and chemical parameters on removal of Sulphate from contaminated water sources is revealed as follows:

Role of pH on Sulphate Removal: In order to study the role of pH in sulphate removal, water is collected from various points of river Rushikulya and is subjected to treatment. The data represented in figure 5 revealed that sulphate removal is strongly pH dependant.

It has been observed that with the increase in pH, there is gradual increase in sulphate removal from contaminated water bodies till pH range of 5 after which there is fall in the recovery. When the composite matrix is added to the water sources, due to the acidic nature of the material there is gradual increase in pH of the medium. The result obtained showed that at a pH range of 4.5 - 5.4, there is removal of 95% (or) above amount of sulphate.

The optimum pH in found to be 5, where maximum of 97.8% of sulphate could be removed from the water source. With the further increase in pH, there is gradual decrease in removal of sulphate. The decrease in removal of sulphate with increase in pH may be attributed to the fact that presence of K_2O and CaO might be reacting with sulphate at an elevated temperature and definite pH to form calcium sulphate and potassium sulphate, which might get coagulated in the water medium leading to decrease in sulphate removal. Thus, in order to get a maximum removal of sulphate from the contaminated water sources, the water medium should be buffered at a pH of 5. Table 4 represents sulphate removal % at different conditions of pH and different doses of CM-4(70:30). It is found that about 80% sulphate removal is possible at an acidic medium and with moderate dose of CM-5.

Scanning electron microscopic studies on the Composite Matrix samples: The Scanning electronic microscopic studies are carried out to investigate the role of pH on sulphate removal. The sulphate absorptivity on composite matrix is studied. In this context, the SEM of a composite matrix (CM-5) is taken into consideration and the texture is found to be quite uniform throughout. The texture shows a uniform mixing of both bagasse waste and coir pith dust particle forming a porous composite matrix for sulphate absorption as represented in the figure 6.

In order to study the effect of various pH containing waste water on the textural changes of the matrix, acidic, neutral and alkaline mediums of waste water are added to the composite medium to study the rate of absorption and textural variations. When an alkaline medium is passed through the composite material, it has been observed that there is minimal textural variation attributed by alkaline water sources.

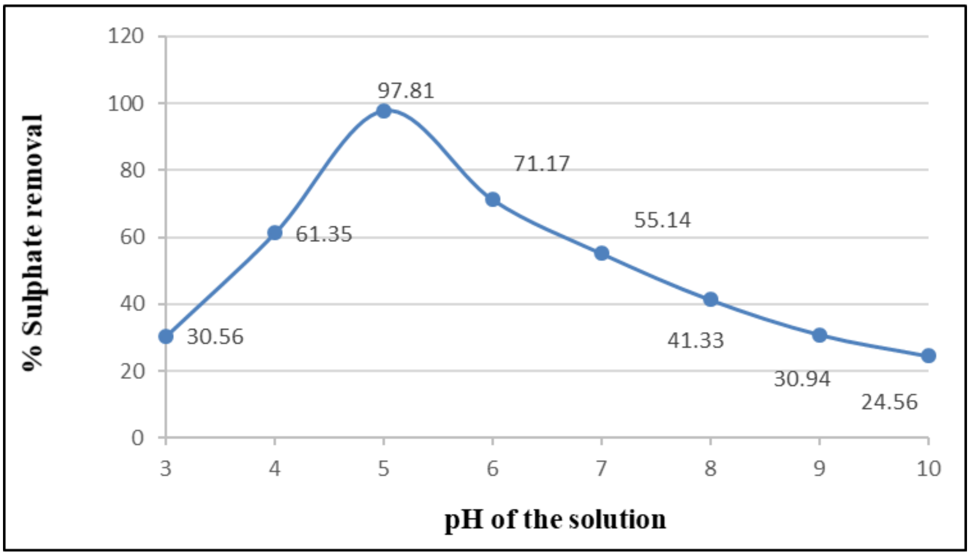

Figure 5: Impact of acidic and alkaline pH on Sulphate adsorption

Table 4
Site selected for sample collection and subsequently removal of Sulphate

S.N.	pH of Water	% Addition of CM (g/L)	% Sulphate removed
Site - I	4.1	5.8	65.10
Site - II	4.9	6.2	70.22
Site - III	5.3	5.9	70.87
Site - IV	5.8	5.5	74.05
Site - V	6.2	5.1	80.44

https://doi.org/10.25303/296rjce075083

After passing the alkaline water, there is not much variation in the texture of the material. Figure 7 represents the SEM for the treated material, which is approximately 25% distorted. When an acidic medium is passed through the composite material, it has been observed that there is considerable textural variation attributed by acidic water sources. After passing the acidic water, there is remarkable variation in the texture of the material. Figure 8 represents the SEM for the treated material, which is completely disturbed.

With the gradual increase in acidity of the medium, there is complete distortion in the matrix texture attributed to the high reactivity of sulphate in presence of acidic pH. Figure 9 represents the SEM for the treated material which is completely distorted. Thus, it is concluded that 97% sulphate can be removed away from the contaminated water sources.

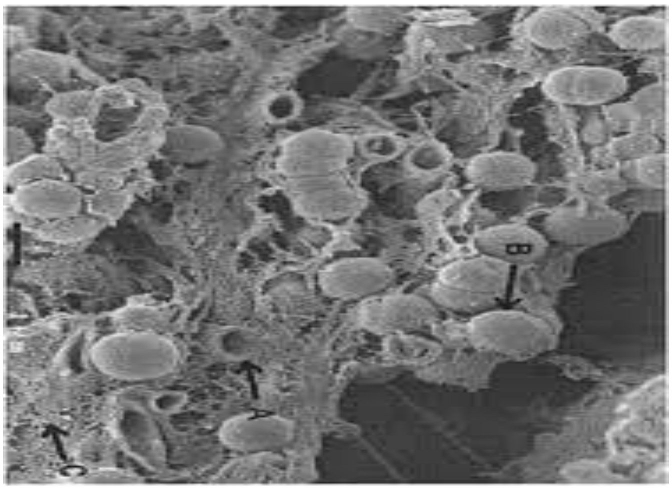

Figure 6: SEM of the composite matrix before treatment

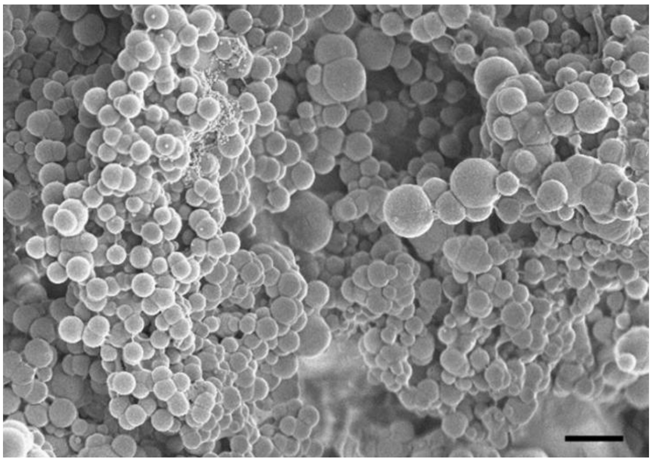

Figure 7: SEM of the composite matrix after treatment of an alkaline waste water

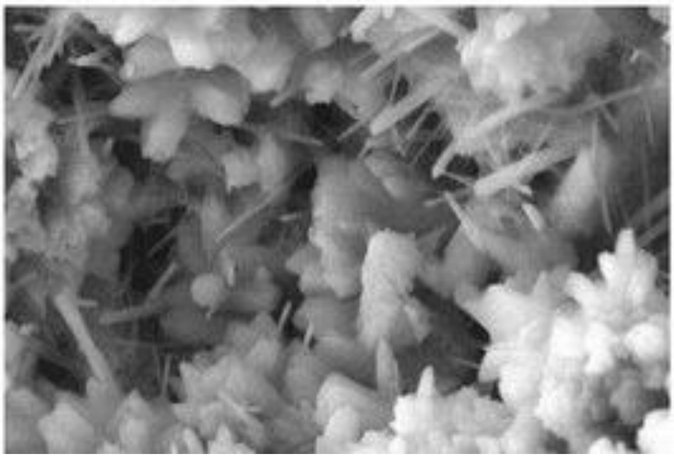

Figure 8: SEM of the composite matrix after treatment of an acidic waste water

Effect of dosage of CM on Sulphate Removal: The impact of dosage on sulphate removal is being studied by adding the composite matrix of variable wt. % to the contaminated water sources. The data revealed that the composite matrix added at different dosages is capable of removing sulphate effectively from the contaminated water. Among all the given dosage, 60 mg/L addition of composite matrix provide best efficiency for sulphate removal. It has been observed that with rise in concentration of dosages to the contaminated water, there is gradual decrease in sulphate adsorption, which may be attributed to the fact that due to addition of more quantity of activated composite matrix, there may be destabilization of the colloidal suspension. The result is represented in table 5. The pH of the solution, with addition of more quantity of dosages is recorded and it has been found that sulphate removal is partially based on pH of the solution.

Role of COD on Sulphate removal: The role of COD in water sample restricts to determine the organic matter present in any water medium. COD is a specific parameter to determine the degree of pollution during sewage treatment. The result of the study for COD is represented in figure 10. The maximum limitation of COD should be below 100. In case of the water sample under study, the COD concentration is found to be 8 to 10 times higher than the acceptable limit. The impact of rise in concentration of COD in water sample is determined. The optimum COD range is determined and the data is plotted in figure 11.

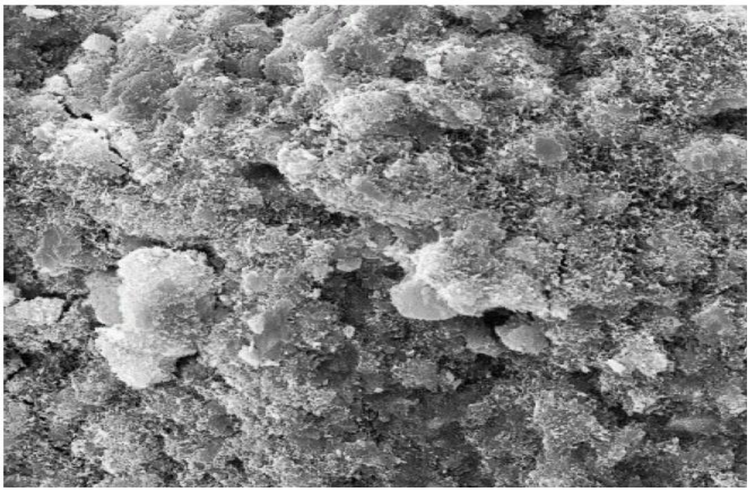

Figure 9: SEM of the composite matrix after treatment of neutral waste water

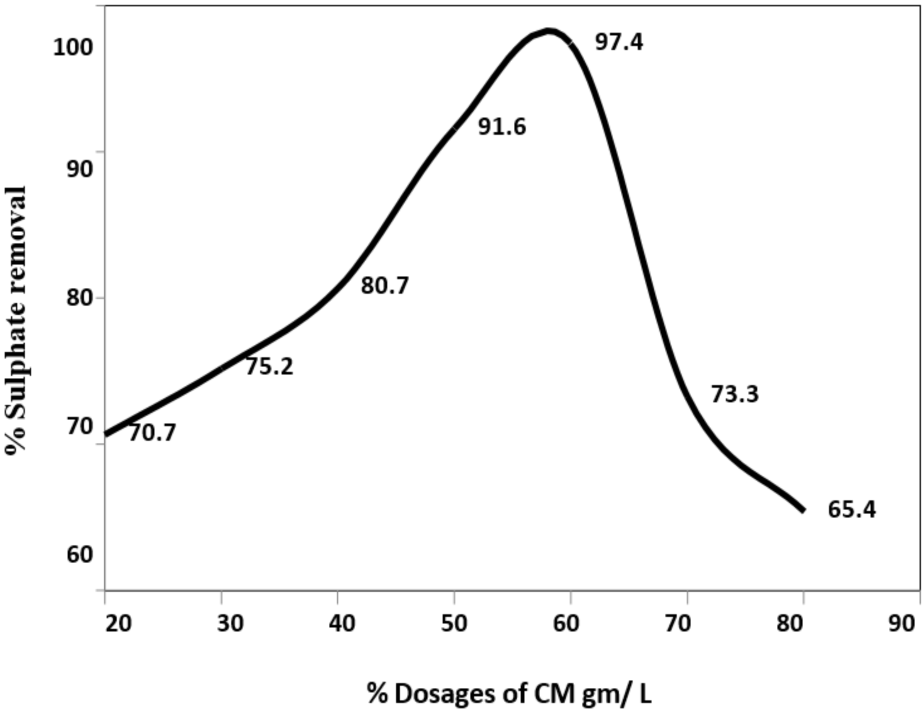

Figure 10: Impact of CM dosages on Sulphate adsorption

Table 5
Impact of composite matrix dosages variation on Sulphate removal
Conditions: pH = 11.2, Sulphate Content = 100mg/L., Room Temperature (30°C)

S.N.	Residual Sulphate (mg/L.)	Dosages of CM (mg/L.)	Sulphate Absorbed
1	29.3	20	70.7
2	24.8	30	75.2
3	19.3	40	80.7
4	8.4	50	91.6
5	2.6	60	97.4
6	26.7	70	73.3
7	34.6	80	65.4

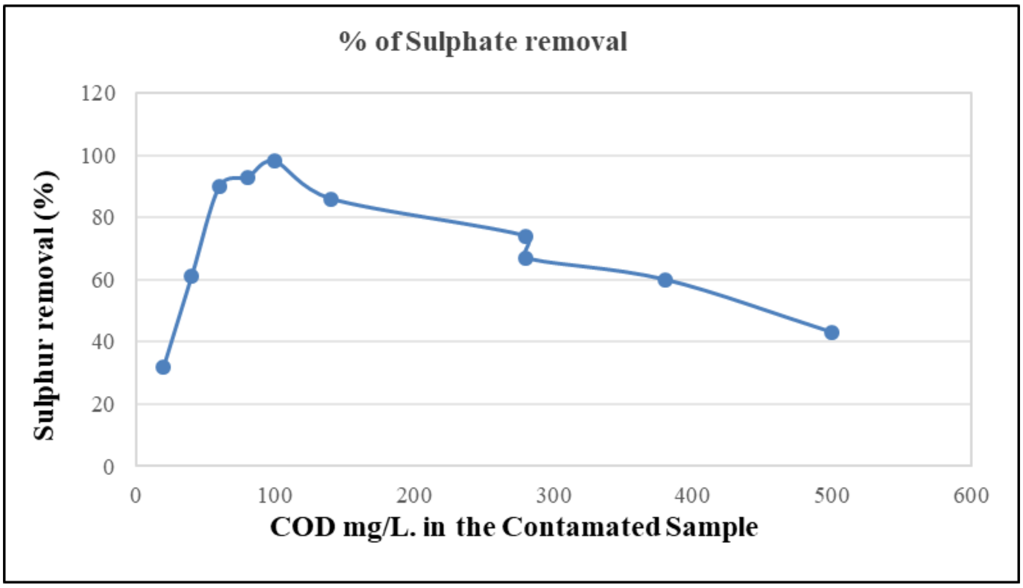

Figure 11: Impact of COD of the sample on Sulphate adsorption

It revealed that sulphate removal directly depends on the COD increases more than 100, after which the removal becomes moderate. This is attributed to the fact that rise in waste content of water medium regulates the pH of the water medium which in turn impacts the sulphate removal. When the COD of the water medium reaches 20, the sulphate adsorption decreases to 32% approximately. Thus, while studying the sulphate removal, adequate measures are to be takes to maintain the COD within 80 to 100 for efficient removal of sulphate. The data revealed that chemical contamination in water medium might be leading to the formation of different metal and chemical sulphates which in turn would have decreased the free Sulphate availability in the medium.

Conclusion

Sulphate concentration in polluted water depends directly on three major parameters i.e. pH of the waste water, COD of the waste water and dosages of the composite matrix present in the system as adsorbent. The data revealed that sulphate absorption is pH dependant and at about pH 6, maximum sulphate could be removed from the contaminated water, keeping a fixed dose of composite matrix and COD of the solution. Similarly, the COD of the waste water in the range between 80 to 100 showed that maximum amount of sulphate in an average of 97% could be removed from contaminated water medium.

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(Received 29th July 2024, accepted 03rd October 2024)