Removal Of Basic Green 4 Dye Using Raw and Surface Modified *Streculia Foetida* Seeds

Manikandan Gandhi (manikandang@svce.ac.in)
Sri Venkateswara College of Engineering
Meyyappan Narayanan
Sri Venkateswara College of Engineering
Pitchai Ramu
B V Raju Institute of Technology, Narsapur

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Abstract

Industrialization and Urbanisation are considered as some of the important problems for the pollution of air, soil, and water system. Among these systems, water is affected to the great extent. The addition of the various pollutants to the water resources is considered as the major threat for the deterioration of water quality and makes it unsuitable for domestic purposes. Out of many water pollutants, dyes are the most hazardous substances for plants, animals, and also humankind. Majorly, malachite green dyes are used in the industries processes like textile industries to produce large quantities of colored effluents that contain organic and inorganic chemical compounds. So, effective and efficient treatment of them is very important for eco-friendly sustainability. In the present study, the Indian or the Wild almonds (Sterculia foetida as its biological name) was used as an adsorbent for the removal of basic green 4 dye from the aqueous solutions in batch mode operations. The basic parameters like initial concentration, pH, contact time, and adsorbent dosage were studied. The experimental result shows that the Sterculia foetida seeds are very good adsorbent for the removal of basic green4 dye from the prepared dye solutions.

1. Introduction

Our Earth is often referred to as the Blue planet because it comprises 70% of water. The earth's water exists in different forms and locations: in the air, on the surface, below the ground, and in the oceans. Also, both saline and freshwater resources are available with 97.5% being saline water and 2.5% being freshwater.[1][2] Now a great pressure lies on the water resources around the world. Human activity and natural sources are the main reason for the rise of pressure over water resources. Water gets polluted to a major extent by the industries like textile, refineries, certain wastewater treatment plants which directly release the untreated hazardous effluents into the land, thereby the groundwater, rivers, lakes, etc. are highly affected[3][4][5][6]. Science and certain practices are widely made to reduce these criteria.

The direct contact of untreated dye effluent in the natural water resources will lead to some toxic effects on the living organisms when they consume that water. Some measures are taken to reduce the discharge of dyes into the environment. The current study focuses on the treatment of Basic green4 dye through Batch studies using the naturally available raw material as an adsorbent.[7][8][9]10]

Basic green4 dye is one of the textile dyes which lies under the kind of base dyes. It is also known as the cationic dye with salts of organic bases.[11][12][13][14] They are used for dyeing wool, silks, and acrylic, and modacrylic fibers. Basic green4 which is also known as the Malachite green dye has some health effects when it is made contact with the water resources.[15] On the whole, the structure of this dye strongly finds the tendency to carcinogenicity on living organisms. Besides, some health effects like organ damage, carcinogenic, mutagenic, and developmental abnormalities in certain mammals.[16][17][18]Thus, the exposure limit should be taken much importance to overcome certain ecological and health-related issues.[19][20]

Several treatment processes are found for the removal of dyes from the untreated dye waste from textile industries.[21][22] It includes coagulation, precipitation, ion exchange process, membrane separation process, and oxidation-reduction, and so on. However, these methods are very expensive. To overcome certain drawbacks, Adsorption is preferred and it is one of the common treatments for the removal of dyes, which is very simple and cost-effective if we prefer naturally available seeds to obtain adsorbent rather than activated charcoal or carbon that is prepared synthetically, which is more expensive. Bio sorption is also a technique that uses biological matters as an adsorbent.[23][24][29]However, the efficiency is not exploded throughout the effective adsorption for the removal of dyes. Our current study focuses on the use of naturally available Indian or Wild almond seeds for the preparation of the adsorbent. Its biological name is Sterculia foetida.

2. Materials And Methods

2.1 Adsorbate:

All chemicals are used in the present examination were analytical grade and utilized all things considered with no extra refinement. Analytical grade of basic green 4 was procured from E.merck Mumbai, India. Its chemical formula is $C_{23}H_{25}ClN_2$. The Stock solution preparation involves the following steps,

Step 1: Take 1 gm of Basic green dye powder.

Step 2: Make up this to 1-liter solution by adding distilled water in the Standard Measuring Flask Step 3: Now, the prepared one was the Stock solution and it has 1000 ppm (parts per million) Concentration.

2.2 Preparation of adsorbents:

The adsorbents preparation involved both physical and chemical treatment processes to obtain Raw and Surface modified ones. In this study, the adsorbents are raw and surface modified Indian almond seeds. *Sterculia foetida* is a large, straight umbrella-shaped spreading deciduous tree belonging to the family Sterculiaceae. It is also called Java olive, Poon tree, Wild almond, Hazel Sterculia, and Sterculia nut. In India, it is known as Jangli badam (Hindhi), Gorapu badam (Tamil). It was first described in the year 1753 by Carolus Linnaeus. The origin of the name *Sterculia* genus comes from the Roman God, Sterquilinus, who is the God of fertilizer or manure. *Sterculia foetida* seeds can be eaten raw or roasted, so their usage is not harmful to humans and other animals. The common names are Java Olive, Peon, Poon tree, Wild Indian Almond, Sterculia nut.Seeds are numerous ovoid-oblong, black with a small yellow rudimentary at the base. It consists of cyclopropene fatty acids such as Sterculic acid and Malvalic acids that show effectiveness against carcinogenic and co-carcinogenic activities.

Oil was recovered from the SF seed found to have the following characteristics:

Specific gravity (400^oC) – 0.9239

Refractive index (400^oC) – 1.4662

Acid value – 5.7

Saponification value – 177.5

Iodine value (wijs) – 74.0

The *Sterculia foetida* seeds were gathered from agro field range from Tiruvannamalai, Tamilnadu, India. The adsorbents preparation involved both physical and chemical treatment processes to obtain Raw and Surface modified ones. It is a common procedure for obtaining Raw and Surface modified adsorbents.

The following steps were involved in the physical treatment,

Step 1: The Indian almond seeds were collected.

Step 2: It is frequently washed by the distilled water for the removal of certain sand and dust deposits over the seeds.

Step 3: After, frequent washing it was allowed to dry for two or three days for removal of excess water, under sunlight.

Step 4: When the sunlight drying is over, it was kept inside the muffle furnace at a temperature of about 350 0C for 2 to 3 hours. It was carried as such, because of the oil present in it

Step 5:It was then, cooled down in the natural atmospheric condition. After that, it was finely powdered and stored in an airtight container. Thus, it was further used as an adsorbent for subsequent studies. Mainly, this kind of treatment was carried after the physical one. It was highly important to obtain the surface-modified seeds, which improved the adsorption efficiency.

The following were the various steps involved in the chemical treatment of the seeds.

Step 1: After the physical treatment, the powdered ones were taken and allowed to react with 40% conc. H_2SO_4 in the ratio of 1:4.Thus, one part of the powder was allowed to submerge in 4 parts of conc. H_2SO_4.

Step 2: It was kept undisturbed for nearly 20 hours.

Step 3: It was then frequently washed with distilled water to remove excess acid content and until a constant pH was achieved.

Step 4: The obtained content was kept inside the oven for nearly an hour under the temperature of 1000 C.

Step 5: The surface-modified powder was obtained and stored in an airtight container and used as an adsorbent for batch studies.

2.3 Batch experimental procedure

Adsorption was one of the important mass transfer operations, mainly used in the wastewater treatment process. For all the wastewater treatment processes, this type is a quite simple and familiar one. Batch adsorption studies were done to bring a conclusion of the way of treatment involved for the removal of a toxic textile dye from the industrial effluent. The experiment was carried out at room temperature only. The Batch adsorption experiments were carried out by varying parameters Such as solution initial Basic 4 green dye concentration, pH, adsorbent dose, contact time, to study the Percentage removal of basic green dye from its aqueous solution. The Experimental studies were conducted by taking 50 mL of BG4dye solution of desired concentration in a 250 mL flask. The initial solution pH was adjusted by adding 0.1M NaOH to get the desired pH. An optimum quantity of SMSF was added to each of the experimental solutions and the mixture was allowed in the photochemical reactor. The experimental contact time was varied from 10 to 90min. At various time intervals, the flasks were withdrawn from the photochemical reactor, and then the mixture was filtered to separate the adsorbent and supernatant. Using UV–Vis Spectrophotometer the residual dye concentration in the supernatant was measured. The percentage removal of BG4dye was calculated using the following equation:

$$\% \text{ Removal of BG dye} = (Ci - Cf) \div Ci$$

where Ci and Cf are the initial and final BG4 dye concentration in the solution, respectively. The following parameters Effect of pH, Effect of initial concentration, Effect of contact time, Effect of adsorbent dosage were considered for this Batch studies.

3. Results And Discussion

3.1 Characterization studies

3.1.1 SEM Analysis

SEM images of raw sterculia foetida seeds (RSF) and surface-modified sterculia foetida seeds (SMSF) are shown in Figs. 1, 2, 3, and 4 respectively. The figures show that SMSF is more porous than RSF, indicating that SMSF seeds have better morphology for the adsorption of BG4 dye molecules.

3.1.2FTIR Analysis

The FT-IR spectrum of RSF and SMSF seeds is shown in Fig. 5and 6. The FT -IR analysis is defined as the Fourier transform infrared and it is used to determine the presence of various functional groups based on its wavelength obtained in the graph. Here, fig indicates the FT- IR analysis for RSF and fig represents the FT-IR graph for SMSF. In the fig various narrow and broad peaks exist. The peak observed at 3411cm^{-1} ascribed the presence of N- H bond stretch which was the amines groups. The peak 3019 cm^{-1} indicated the presence of O-H groups. The vibrational stretch at 2852 cm^{-1} ascribed the presence of C-H bonds. The stretching vibration at 2797 cm^{-1} was further confirmed the hydrogen bonding in the carboxylic acids. The narrow curve at 1743 cm^{-1} and 1703 cm^{-1} confirmed the C = O vibrational stretches. Also the vibrational stretches at 1591 cm^{-1} was due to the presence of alkenes. The curve at 1374 cm^{-1} and at 1105 cm^{-1} indicated the vibrational stretches were due to C- F. The peaks at 790 cm^{-1} and 733 cm^{-1} showed the presence of chloroalkanes. Also the curves lied at 578 cm^{-1}, 563 cm^{-1} and 517 cm^{-1} strongly indicated the existence of bromoalkanes along with iodoalkanes. Thus, the presence of these functional groups proved that the RST was a good adsorbent for the removal of malachite green dye from the aquoeos solutions.

Fig showed the FT-IR analysis for the surface modification by the addition of sulphuric acid to the RST. The peak at 3789 cm^{-1} indicated the presence of the N-H functional groups. Then the peak at 3399 cm^{-1} was ascribed to O-H vibrational stretches. The presence of C-H functional groups was indicated at the peaks 2924 cm^{-1} and 2833 cm^{-1}. The functional groups like C = O was present at 1744 cm^{-1} and 1709 cm^{-1} .The presence of alkenes was showed in the vibrational stretch at 1627 cm^{-1}. Also the peak at 1377 cm^{-1} was ascribed by the esters and ethers functional groups. The curve at 1051 cm^{-1} indicated the availability of both esters and fluoroalkanes. The peak at 722 cm^{-1} showed the presence of chloroalkanes and at 580 cm^{-1} indicated the existence of bromoalkanes. Thus, the presence of chlorolkanes, fluroalkanes, bromoalkanes, ethers, esters and some of the alkane, akynes functional groups strongly confirms the existence of carbon. The carbon content in this SMST is more compared to the RSF because of the treatment with the concentrated sulphuric acid. Thus, the FT- IR results strongly confirmed the presence of carbon content in both RSF and SMSF. Hence, the FT-IR studies described the various different functional groups that were present in the RST and SMST seeds, which can be used as a natural and good adsorbent for the removal of malachite green dye from the prepared dye solutions.

3.2 Parameter Analysis

3.2.1 Effect of initial concentration:

The effect of initial BG4 dye concentrations (500-1000ppm) on the removal of BG4 dye by the adsorbent (RSF and SMSF) is shown in Table:1,2, Figs. 7 and 8. From these figures, it shows that the removal of BG4 dye decreases with the increase in BG4 dye concentration. At the lowest concentrations, the adsorbent rate is high. A defined quantity of adsorbent dose was utilized for the present study, so it can able to remove only a particular quantity of BG4 dye molecules from its aqueous solution.

Table 1
Effect of initial dye concentration using RSF

Time (min)	% Removal of BG4 dye using RSF		
	500 ppm	**750 ppm**	**1000 ppm**
10	73.9	62	62
20	78	63	63
30	78.15	63.8	63
40	78.16	72.05	63
50	78.9	73.18	63
60	79.6	73.9	63
70	79.7	74	64
80	80	75	64.4

Table:2Effect Of Initial Concentration For SMSF

Time (min)	% Removal of BG4 dye using SMSF		
	500 ppm	**750 ppm**	**1000 ppm**
10	84.8	79.45	83.5
20	87.7	82.7	84.5
30	88.46	82.8	84.7
40	89	83.3	86.04
50	89.4	83.7	86.47
60	89.8	83.8	86.7
70	89.9	83.9	86.8
80	90.5	90.5	87.67

3.2.2 Effect of pH

The percentage removal of BG4 dye by RSF over the pH Range 4–8 was investigated and the experimental results are adsorbent sites increases. At higher pH value, the negatively charged adsorbent sites increase, which in turn enhances the adsorption of positively charged BG4 dye because of the electrostatic forces of attraction. But the SMSF-BG4 dye system has only slight changes in the percentage ofBG4 dye removal when the pH was within the range of 4–8, which indicates that the electrostatic attraction or repulsion mechanism was not only the adsorption mechanism for the removal of BG4 dye in the present system. The percentage removal of BG4Dye molecules was also affected by the chemical reaction between the SMSF adsorbent and the MB dye molecules. These various adsorption rate changes with various pH are shown in Table 3,4 and Figs. 9,10.

Table 3
Effect of pH for RSF

Time (min)	% Removal of BG4 dye using RSF		
	pH 6.5	pH 5.0	pH 4.5
10	34.15	44.2	55.9
20	96	62	92.26
30	97.8	90.8	86.57
40	97	90	88

Table 4
Effect of pH for SMSF

Time (min)	% Removal of BG4 dye using SMSF		
	pH 6.5	**pH 5.0**	**pH 4.5**
10	54	74	76
20	97	90	86
30	97.6	92	88
40	98	92	89
50	98	92.4	89.6

3.2.3.Effect Of Contact Time

The effect of contact time on the percentage of BG4 dye removal by the RSF and SMSF was investigated to study the rate of BG4 dye removal and the results are shown in Table 5,6 and Fig. 11,12.The results revealed that the percentage of BG4dye removal increases with an increase in contact time and equilibrium was reached at 50 min for RSF and 40 min for SMSF for 3 different initial BG4 dye concentrations. A further increase in the contact time has a negligible effect on the percentage of BG4 dye removal. Initially, the percentage of BG4dye removal is higher due to the larger surface area of the RSF and SMSF being available for BG4 dye adsorption. As the adsorbed BG4 dye forms a monolayer, the capacity of the SMSF And RSF gets exhausted and then the uptake rate is controlled by the rate at which the BG4 dye are transported from the exterior to the interior sites of the RSF and SMSF particles As SMSF has more activated sites than RSF,the equilibrium time was reached earlier for SMSF.

Table 5
Effect of contact time for RSF

Time (min)	% Removal of BG4 dye using RSF		
	500 ppm	750 ppm	1000 ppm
10	73.9	62	62
20	78	63	63
30	78.15	63.8	63
40	78.16	72.05	63
50	78.9	73.18	63
60	79.6	73.9	63
70	79.7	74	64
80	80	75	64.4

Table 6
Effect of contact time for SMSF

Time (min)	% Removal of BG4 dye using SMSF		
	500 ppm	**750 ppm**	**1000 ppm**
10	84.8	79.45	83.5
20	87.7	82.7	84.5
30	88.46	82.8	84.7
40	89	83.3	86.04
50	89.4	83.7	86.47
60	89.8	83.8	86.7
70	89.9	83.9	86.8
80	90.5	90.5	87.67

3.2.4.Effect of adsorbent dosage

The effect of adsorbent dose (for RSF and SMSF) on the Removal of BG4 dye was investigated by the use of Different adsorbent doses between 0.5 and 1 g at a BG4 dye concentration of 500ppm and the result is Shown table 7,8 and in Fig. 13,14. From Fig. 13,14, it was observed that the Removal of BG4 dye molecules increases with the increase in adsorbent dose and then reached a saturation value. This may be due to the increase active sites available for the adsorption of BG4 dye molecules with the increase in adsorbent dose. The maximum removal of BG4 dye was observed at an optimum dose of 1 g per 100mL for RSF and 0.5 g per 100mL for SMSF.

Table:7 Effect of adsorbent dosage for RSF

Time (min)	% Removal of BG4 dye using RSF		
	0.5 gram	**0.75 gram**	**1 gram**
10	34	36	32
20	55	60	67
30	61	68	72
40	66	73	77
50	75	82	86
60	75.2	82	86

Table:8 Effect of adsorbent dosage for SMSF

Time (min)	% Removal of BG4 dye using SMSF		
	0.5gram	**0.75gram**	**1gram**
10	61	68	72
20	66	73	77
30	75	82	86
40	90	95	96
50	96	95	96
60	96	95	96

Conclusion

This investigation showed that surface-modified sterculia foetida seeds are effective adsorbent for removal of BG 4 dye from aqueous solutions. Results obtained from SEM analysis showed that surface-modified sterculia foetida seeds can be used as an adsorbent for the removal of BG4 dye. Adsorption of dye by surface-modified sterculia foetida seeds was affected by solution pH, initial dye solution concentration, and adsorbent dosage. The experimental study showed that the best results were obtained by use of a 6.5 solution pH, and initial BG4 dye concentration of 500ppm, and adsorbent dosage of 1g/100ml.

Declarations

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Conflicts of interest/Competing interests: No Conflict of interest.

Ethics approval: The manuscript in part or in full has not been submitted or published anywhere. Not used previously published materials.

Consent to participate: No informed consent used in our research.

Consent for publication (include appropriate statements): All authors interested to publish our work in Applied Biochemistry and Biotechnology.

Availability of data and material (data transparency): Available with us. After submitting our report to University only possible to deposit the data.

Code availability: Available with us. After submitting our report to University only possible to deposit the code.

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Figures

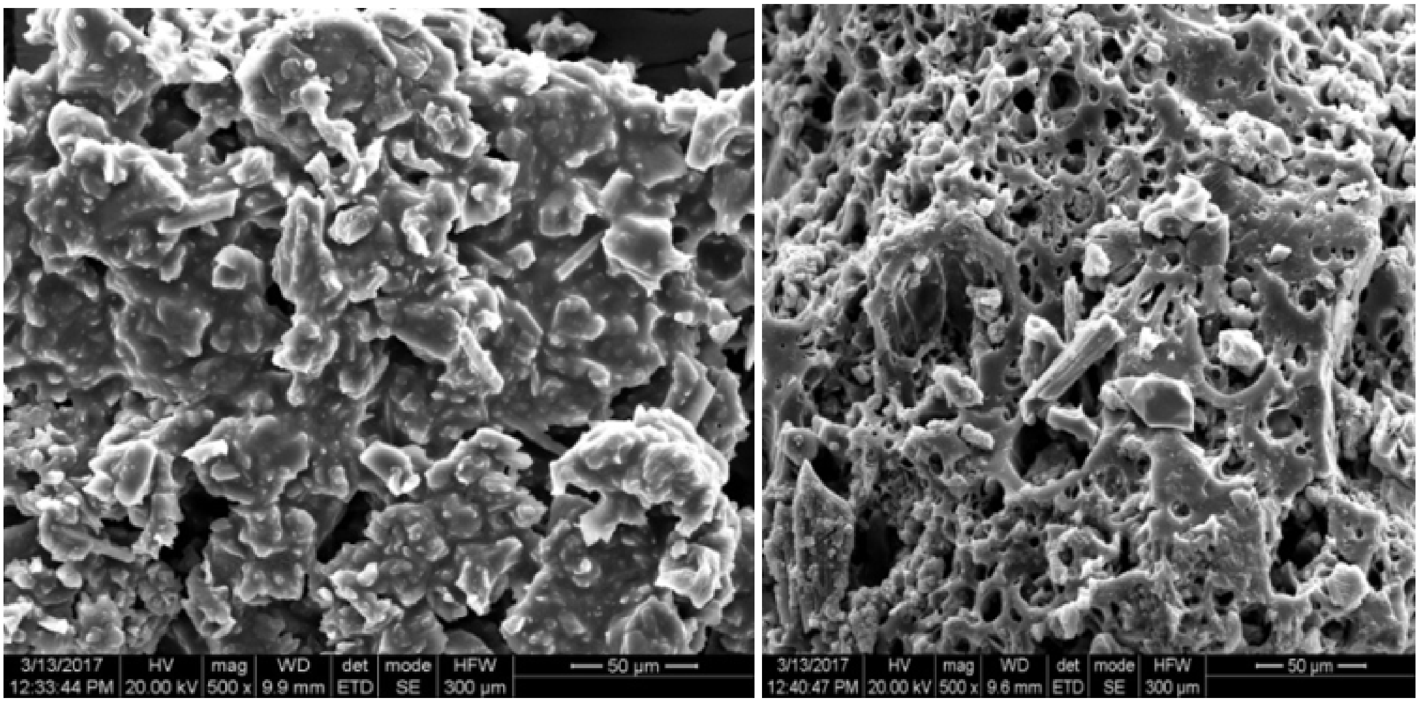

Figure 1

SEM image for RSF and SMSF at 500* magnification

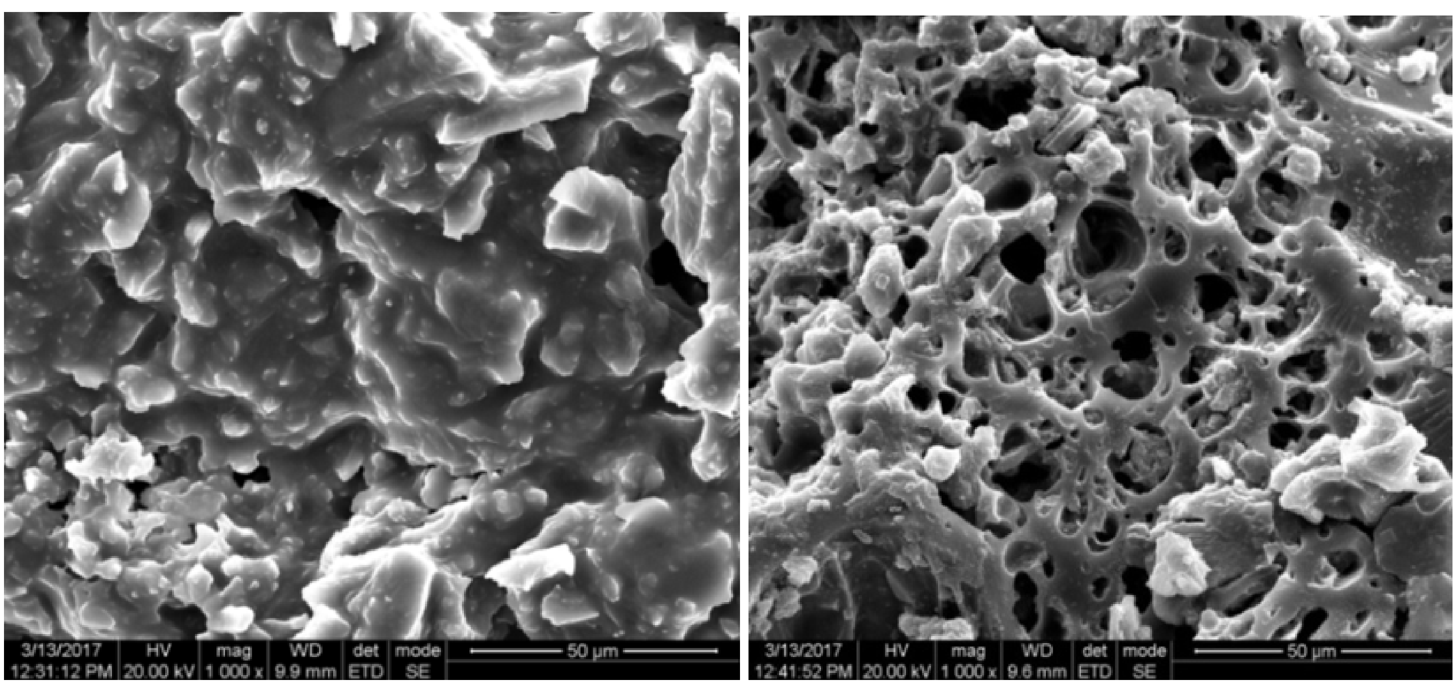

Figure 2

SEM image for RSF and SMSF at 1000* magnification

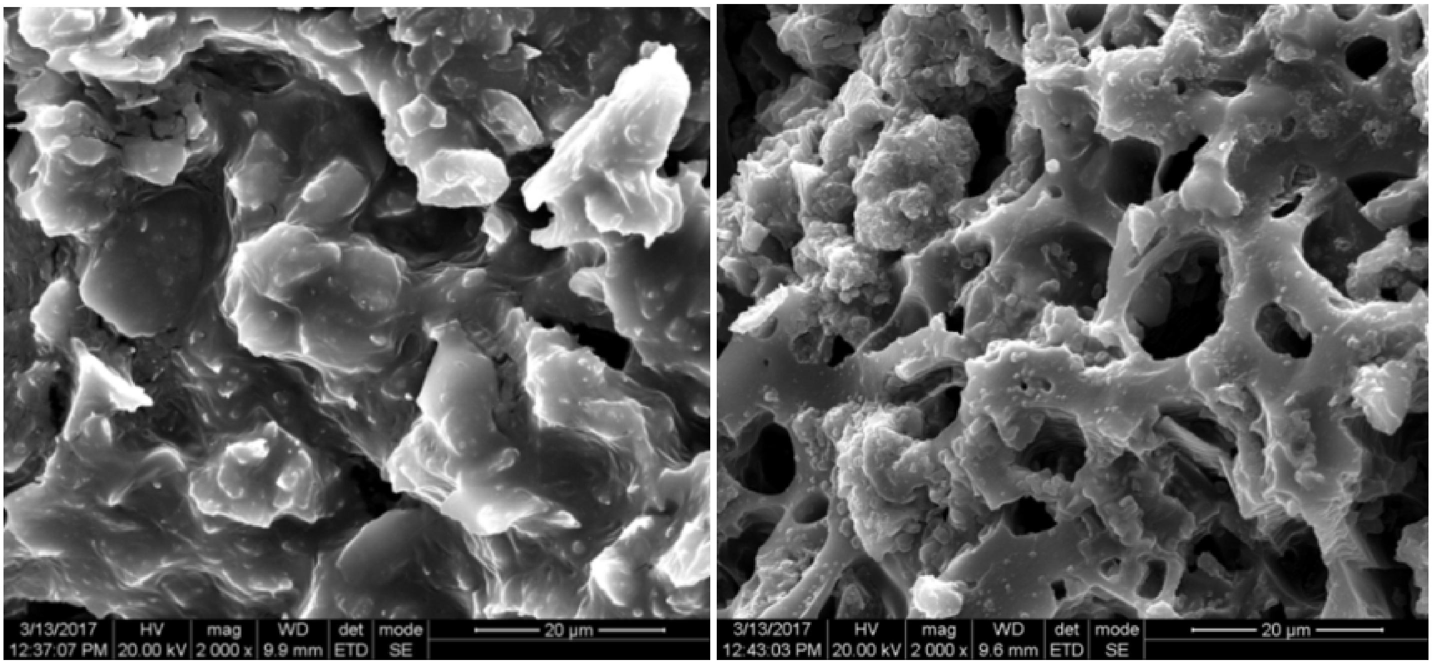

Figure 3

SEM image for RSF and SMSF at 2000* magnification

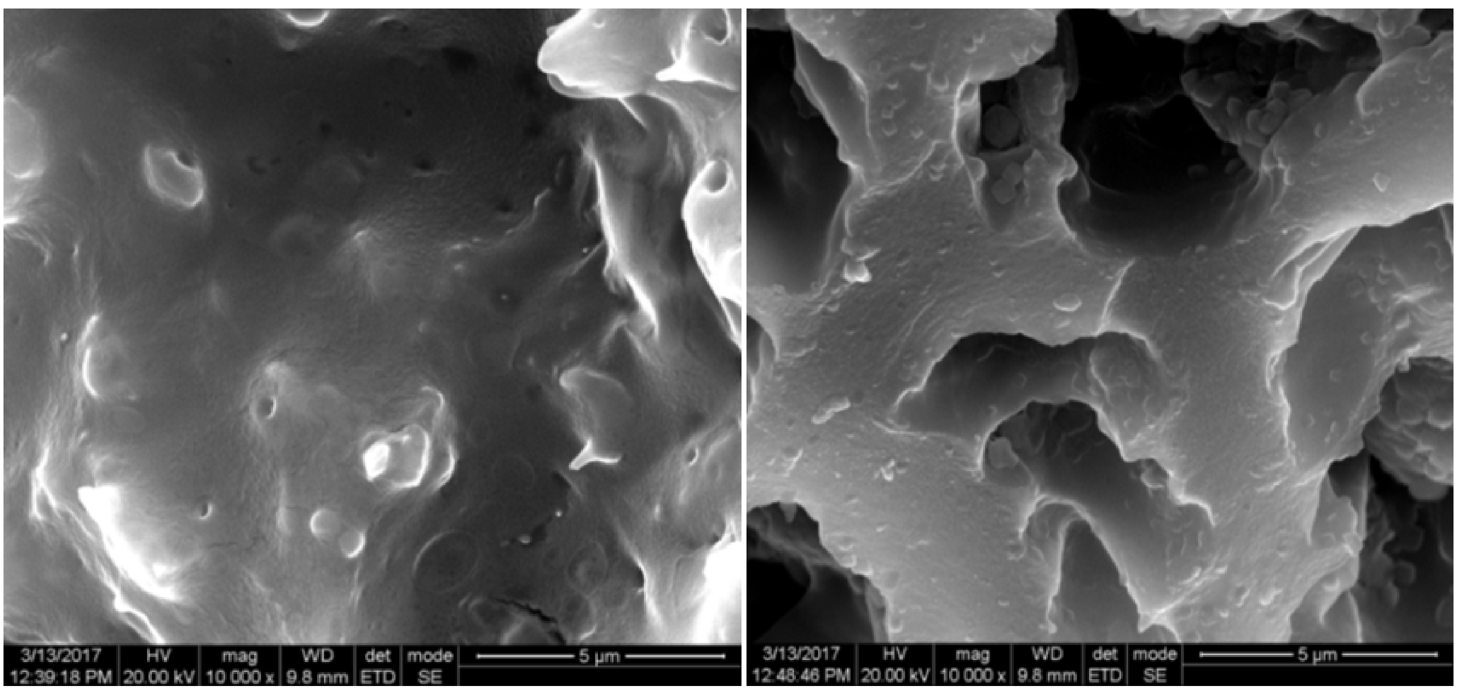

Figure 4

SEM image for RSF and SMSF at 10000* magnification.

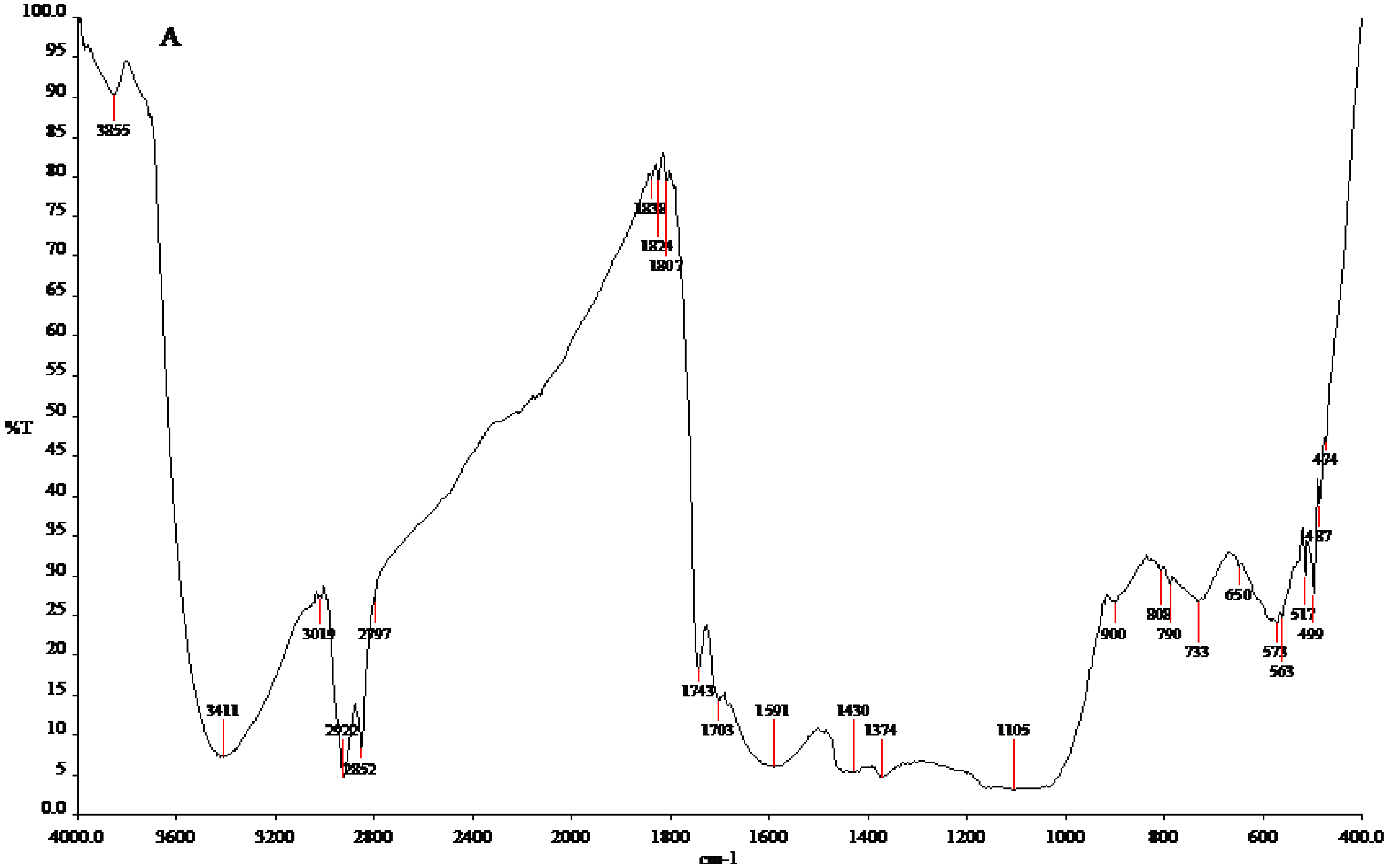

Figure 5

FTIR of surface modified sterculia foetida seeds

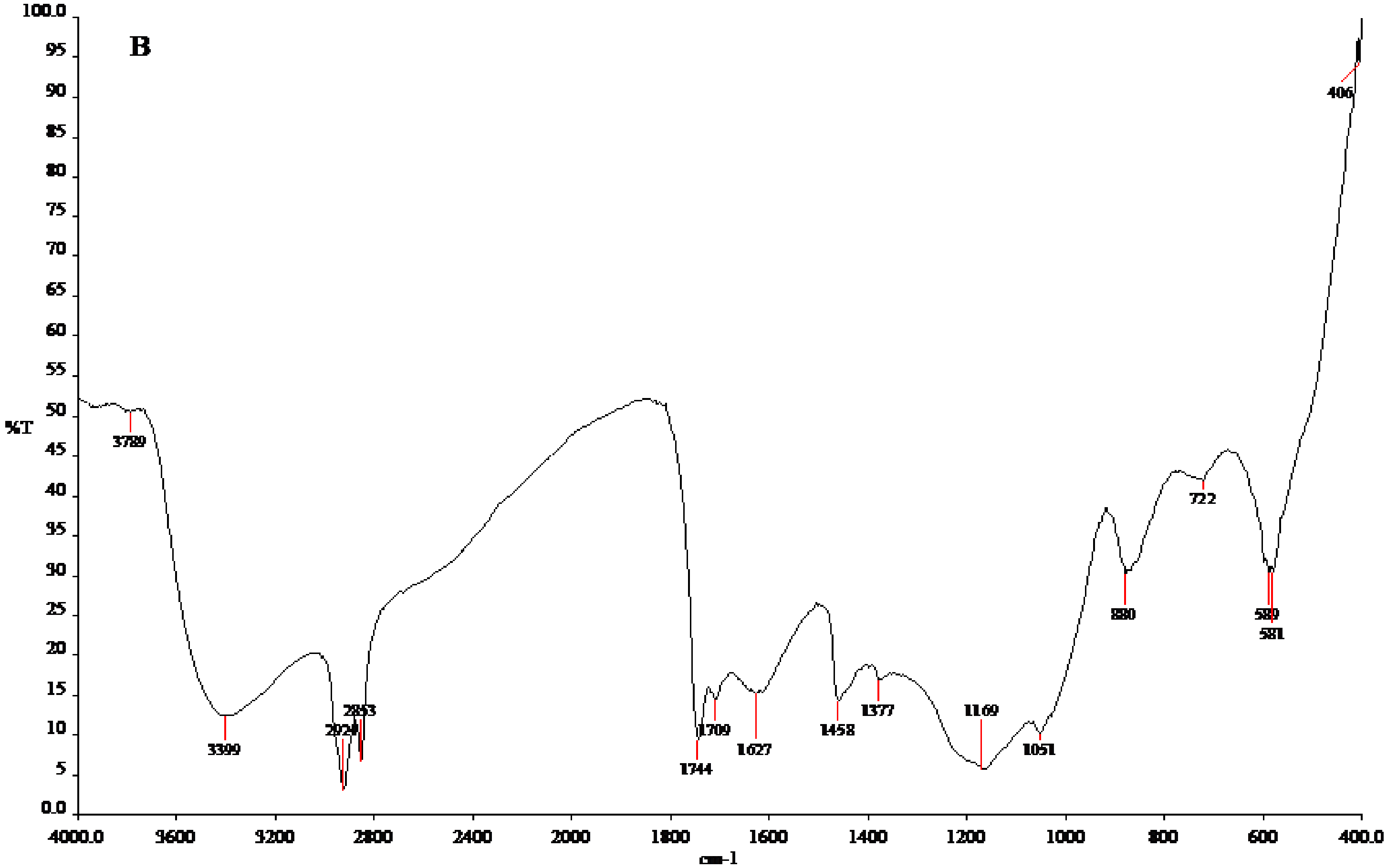

Figure 6

FTIR of surface modified sterculia foetida seeds

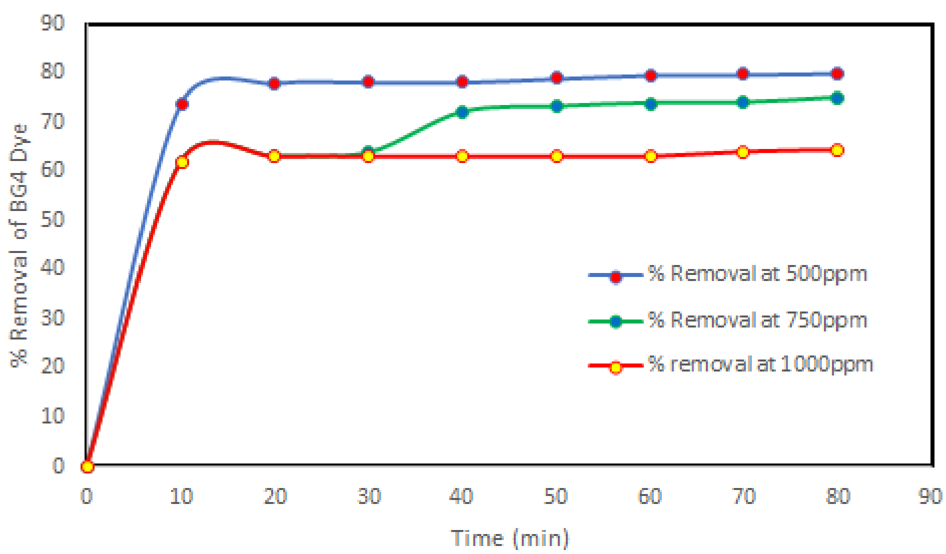

Figure 7

Effect of initial concentration of BG4 for RSF

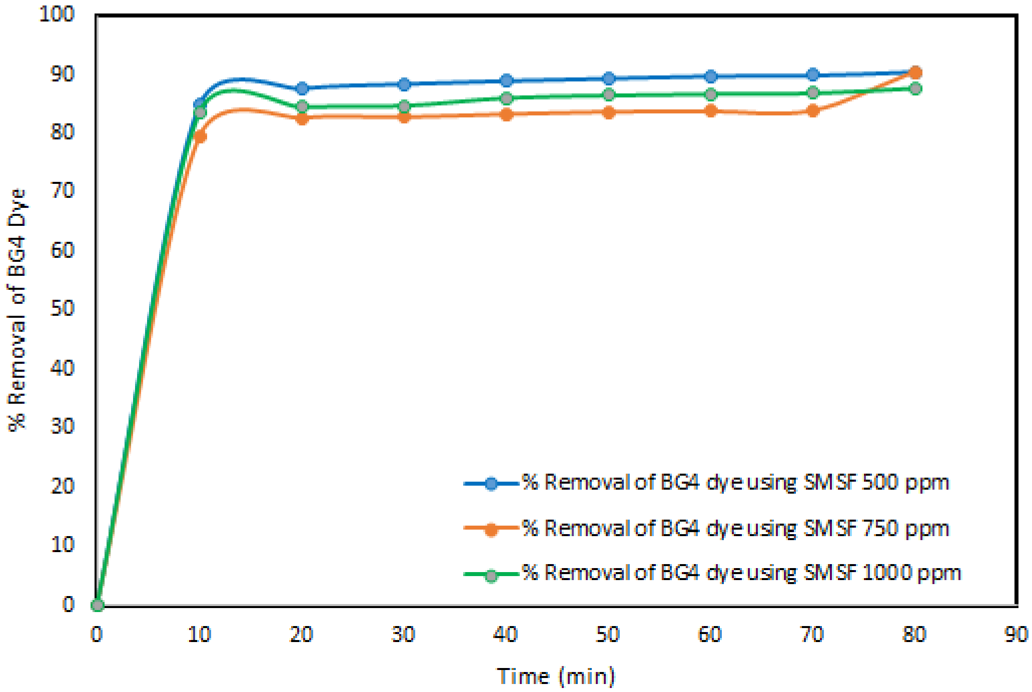

Figure 8

Effect of initial concentration of BG4 for SMSF

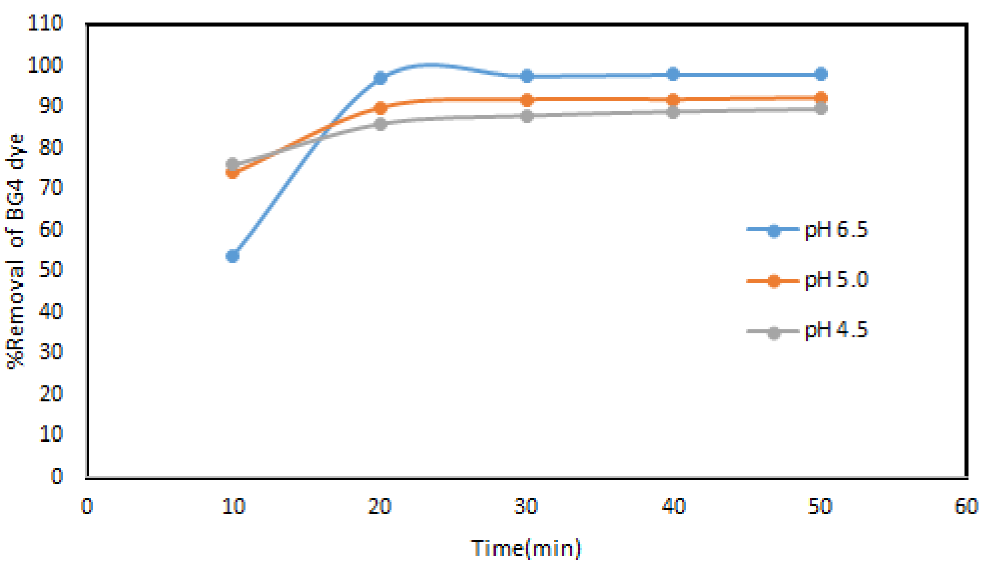

Figure 9

Effect of pH for RSF

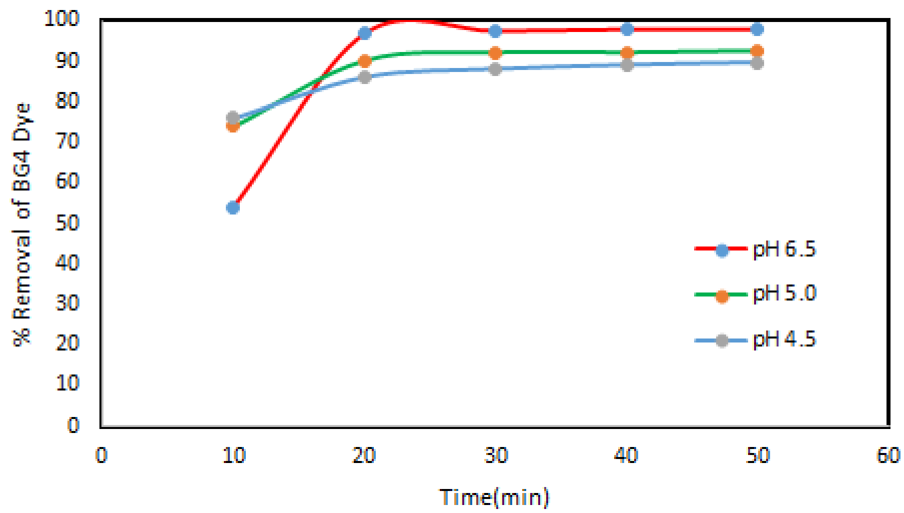

Figure 10

Effect of pH for SMSF

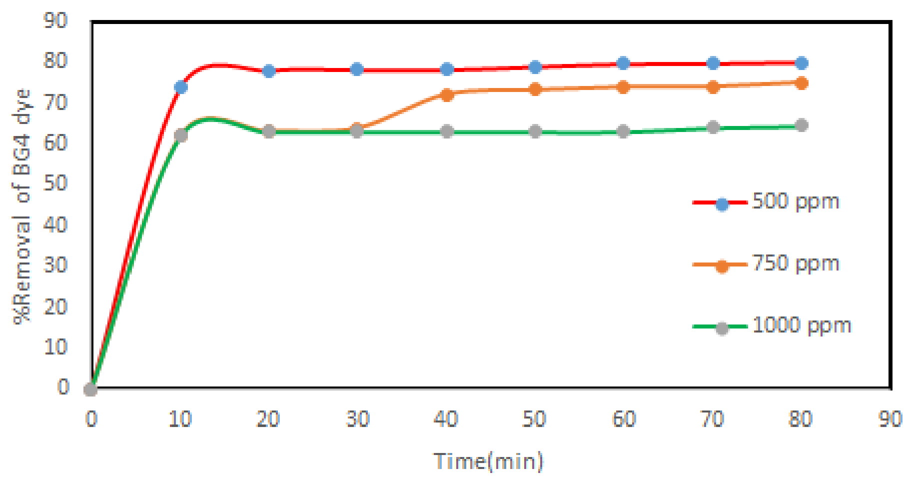

Figure 11

Effect of contact time for RSF

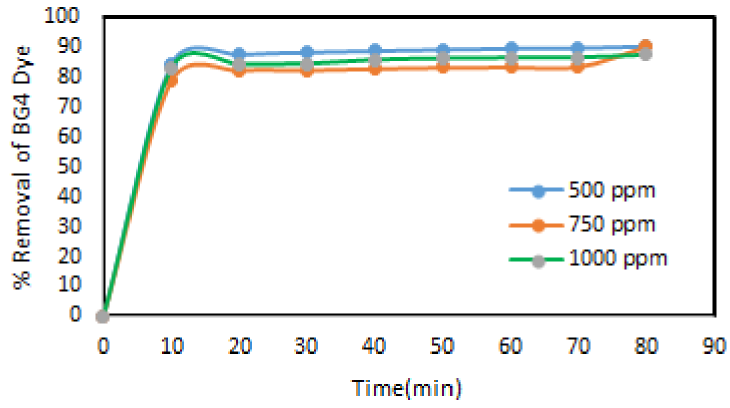

Figure 12

Effect of contact time for SMSF

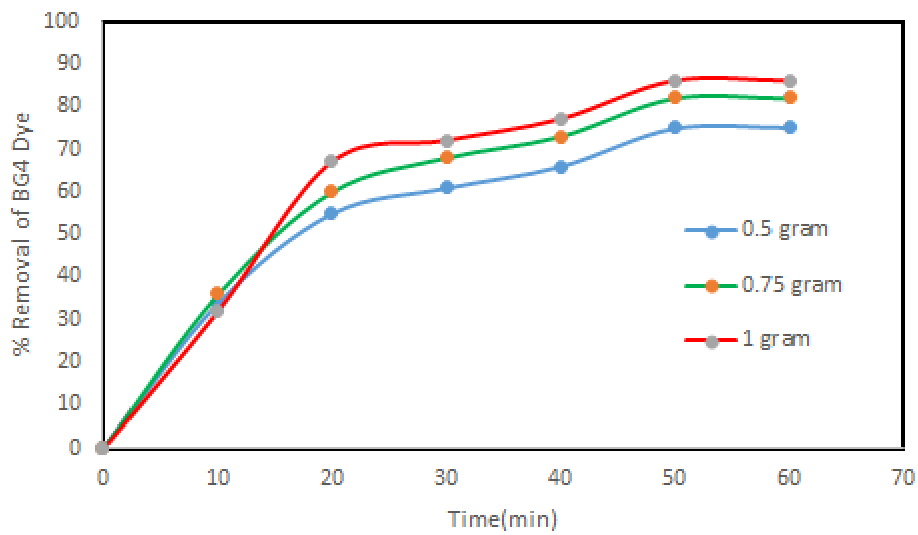

Figure 13

Effect of adsorbent dosage for RSF

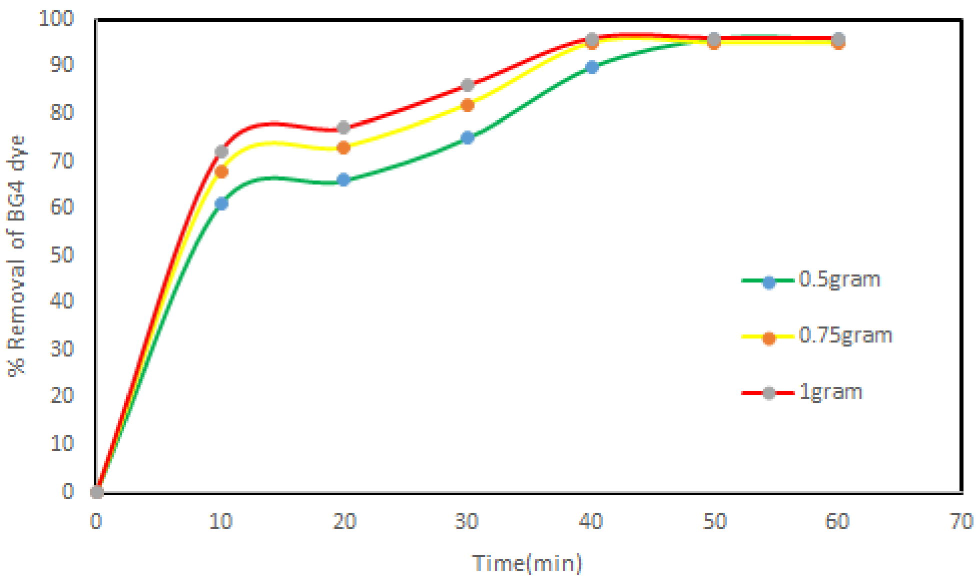

Figure 14

Effect of adsorbent dosage for SMSF