Effect of Process Parameters on the Adsorption of Chromium VI on a Packed Bed Column (PBC) using Vetiver (*Vetiveria zizanioides*)

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Abstract

The objective of this study is to evaluate the different process parameters on adsorption of chromium VI on a packed bed column using Vetiver (Vetiveria zizanioides) and to examine the effect of pH, Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) at a constant contact time of 10 minutes at a temperature of 40 ºC under two experimental conditions namely, tannery effluent with and without microwave treatment. The results revealed that microwave heating process had a higher impact on chromium (VI) adsorption than normal heating process. The pH values of microwave treated sample were found to be 6.65±0.65 when compared to normal heated sample where the pH was 4.62±0.72 when compared to the initial pH of effluent found to be 3.47±0.58.

Further, a threefold reduction in BOD and COD values was observed in microwave treated vetiver sample which was around 86.73±1.43 and 107.90±2.82 mg/l respectively when compared to normal heated sample (250±1.45 and 200±2.65 mg/l respectively) and untreated effluent (780±2.53 and 920±3.86 mg/l respectively) which indicated the reduction of chromium VI present in the effluent water. It was also observed that the metal adsorption capacity of the vetiver powder and the adsorption characteristics were positively correlated with the FTIR and SEM analysis which confirmed the presence of chromium (VI) on the surface of vetiver.

Keywords: Adsorption, Packed Bed Column, Tannery Effluent, Chromium VI, FTIR, SEM

Introduction

Adsorption is a favored technique over others because of its easy availability, widely studied mechanism, case of operation, simplicity in design, wider applications and non-formation of bye-products as well as offering the potential for regeneration, recovery and recycling of adsorbent material[1]. Adsorption is a chemical process in which liquid solute usually deposits on the surface of solid or liquid to create an atomic or molecular film layer on the top of adsorbate[2]. This process differs from absorption and mainly sorption refers to process in which both adsorption and absorption take place simultaneously[11]. At molecular level, adsorption is due to interaction between surface and species being adsorbed.

Molecules on surface have been adsorbed in two main types and they are physio sorption and chemisorption. Physical adsorption is a result of intermolecular forces of attraction between molecule of adsorbents and adsorbate[4]. Adsorbate accumulates to surface only through weak intermolecular (Vander walls) set of conditions and it is reversible process. Physical adsorption offers multilayer adsorption and here no activation energy is required and chemical adsorption occurs due to chemical interaction between solid and adsorbed material, which is commonly known as activated adsorption[12].

Usually, the presence of hexavalent chromium i.e. Cr(VI) in the form of industrial pollutants in water can be a major source of carcinogenicity due to its increased solubility and mobility in water and soil respectively[6].Many technologies have been adopted to treat the Cr(VI) contaminants which utilize various aspects such as solidifying or stabilizing process, recycling process or recovery process including various operating parameters by which the industrial polluting wastes are converted into less toxic substances that can be discarded or re-utilised[13].

The most effective method of treating Cr(VI) wastes is to precipitate using Cr(III) hydroxides[8].The limitation of this method is that the huge amount of sludge production requires excessive downstream treatments[9].Various other drawbacks include poor aggregation and settling capacities accompanied by lower precipitation rates that could be a source of soil pollution[10]. Hence natural sources of materials are of great advantage in treating pollutants. In India, *Vetiveria zizanioides* is known as “khus” or “khus - khus”, shown in figure 1.

Figure 1: Roots of Vetiver (*Vetiveria zizanioides*)

Vetiveria zizanioides is used as adsorbent material. *Vetiveria zizanioides* can be cultivated in warm climates and it prevents soil erosion. It is a scented grass with straight and stiff stem usually tall, tufted, perennial with long narrow leaves that is abundant and extensive special characteristics of *Vetiveria zizanioides* like highly tolerant to extreme soil conditions, especially heavy metal contaminant It acts as anti-inflammatory among *V. species*. *Vetiveria zizanioides* is most valuable in terms of economics and its roots can be used for long time in perfumes, medicines and other area of application[3,5,7]. Hence, the main objective is to study the effect of process parameters on the adsorption of chromium VI on a packed bed distillation column using vetiver.

Material and Methods

Sample collection: Tannery effluent was collected from a tannery outlet and from a drain near the SBS Leather industry, Erode, Namakkal. Plastic bottles were used for sample collection. Two treatments were finalized for the experiments based on the initial trials

- Sample S1: Tannery effluent with microwave treatment
- Sample S2: Tannery effluent with normal heat treatment

Formulation of the adsorbent: Vetiver was purchased from a local market and it was cleaned, shade dried and powdered. It was further ground and sieved by sieve analyzer. The amount of sieved product taken as an adsorbent in the column was 250g. The adsorbent had an average particle size of D = 0.191± 0.86 mm.

Experimental Procedure: The tannery effluent was circulated through peristaltic pump connected with the packed bed column (Figure 2) and this study was performed in a batch process because of its simplicity. Based on the initial trials of the experiments, the process time of the adsorbent (both the microwave and thermal treatment) was finalized to 10 minutes. The thermal treatment of the adsorbent was carried using a commercial thermostat heater at 40ºC and commercial microwave oven at 2.45 GHz. Samples were collected at different time intervals and analysed based on the process parameters and pH, BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) were measured using standard protocols[16].

Flow cycle of adsorbent: Flow rate of adsorbent and pH was analyzed for both the treated water and effluent by attaining time for every five minutes in first cycle and every two hour in second cycle. By maintaining 10 RPM for first cycle and 20 RPM for second cycle, the cycle was repeated until a clear solution is obtained.

Fourier Transform Infrared Spectroscopy: Samples were also analysed for FTIR spectral analysis to find out the changes in the chemical composition of the effluent water samples as well as treated samples after the adsorption using vetiver[14]. The analyses were carried out initially as well as after 30 minutes of treatment. All experiments were conducted with duplicate sets and analyses of samples were run in triplicate and averaged. The samples (10 mg) were ground with 200 mg of KBr (spectroscopic grade) in a mortar before pressing into 10mm diameter disks under 6 tons of pressure. FTIR spectra were obtained on a Shimadzu™ IR Tracer – 100 spectrophotometer. The analysis conditions used were 16 scans at a resolution of 4 cm^{-1} measured between 400 – 4000 cm^{-1}.

Scanning Electron Microscopic (SEM) analysis: SEM analysis was carried out using a Sigma: Zeiss Atlas 5 and pre-treatment filters were prepared for ESEM by attachment to a stainless steel SEM stub by copper tape. ESEM imaging was conducted by a FEI Nova NanoSEM 600 with a Schottky field emitter source at 5 kV accelerating voltage using a 30 µm aperture at a working distance of 3–6 mm with a secondary electron detector at high-vacuum or an immersion lens secondary electron detector at low vacuum (water vapor pressure of 0.38 mTorr). The vetiver samples before and after effluent treatment for 30 minutes were analysed by SEM[15].

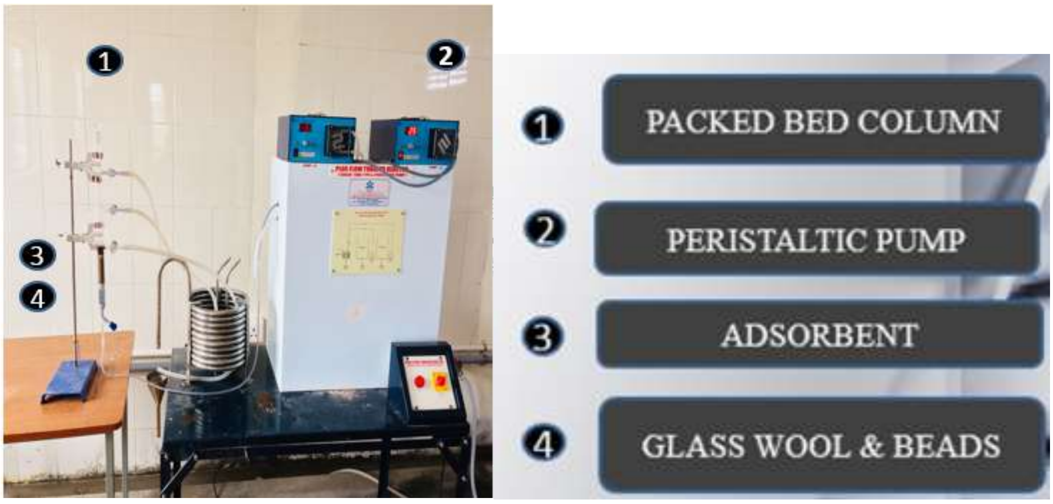


Figure 2: Designed and Fabricated Packed Bed Column with powdered roots of Vetiver (*Vetiveria zizanioides*) as adsorbent

Results and Discussion

pH reduction in the treated samples: The adsorbent-adsorbate solutions prepared in the adsorption process for the removal of hexavalent chromium VI have been estimated for effect of contact time. The adsorbent dosage having 7g/l and concentrations of chromium maintained with different time intervals for samples (S1, S2) were evaluated. An equilibrium was attained for the sample which had same initial concentration when the percentage of hexavalent chromium removal has increased with time. On analyzing further, there was a huge difference in pH values in both the samples S1 and S2 when compared with the untreated effluent. The pH value (Figure 3) was significantly less acidic in the sample S1 when compared to S2 which predominantly signifies the adsorption of heavy metal in the packed bed during the adsorption process.

A similar kind of inference was evident from the studies of Maji et al[18], where the removal of chromium was very much evident with the change in the pH value due to the usage of polyaniline synthesized on jute fiber in which the pH variation was used as a key indicator in the chromium removal process. Similarly, the change in pH was a key indicator component for checking out the removal of metal from the effluent water[17,18].

BOD and COD reduction in treated samples: The COD and BOD study were conducted by having constant adsorbent dosage of having 7g/l and using different time intervals for the samples (S1, S2) where it was clearly evident that there was a threefold reduction in the BOD and COD values respectively in both the samples S1 and S2 which clearly indicates that the chromium VI has been adsorbed in the packaging material (Vetiver powder). There was a significant difference between the BOD and COD values of samples S1 and S2 when compared to untreated sample (Table 2). The S1 sample had a higher reduction in BOD and COD values than S2 as depicted in table 1 which is due to the treatment of adsorbent sample with microwaves prior to adsorption.

The intermolecular adsorption could have happened due to increase in the pore size (cavity) of the adsorbent due to microwave treatment. The reduction in the BOD and COD values was also evident in the studies conducted by Nag et al[19] and Namasivayam et al[20] which clearly suggested that due to the increase in the porosity of adsorbent materials, the rate of adsorption is comparatively higher. The use of microwave radiation to treat the adsorbent bed could have aided in increasing the surface area and porosity of the vetiver powder which is used as an adsorbent in this study.

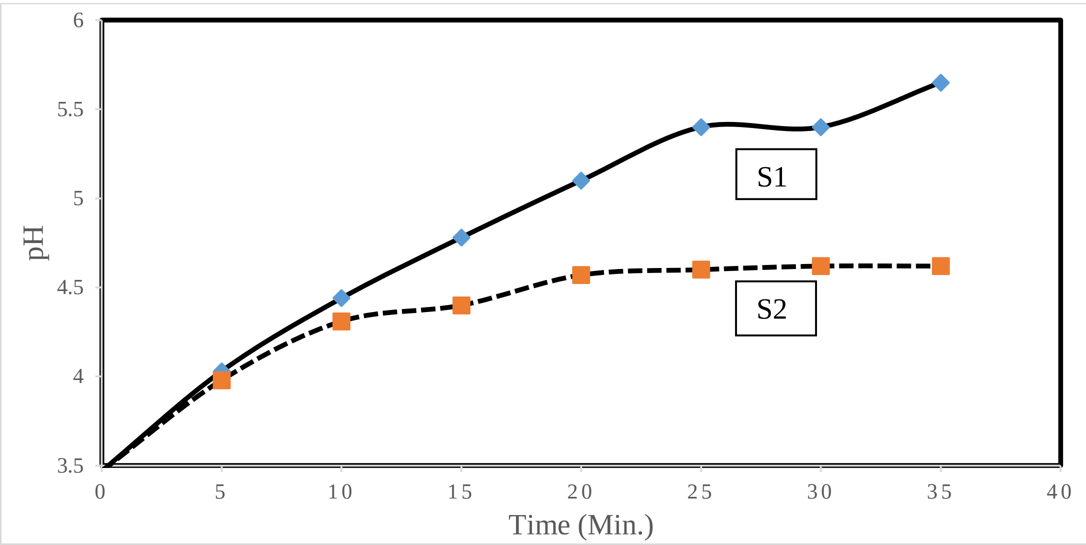
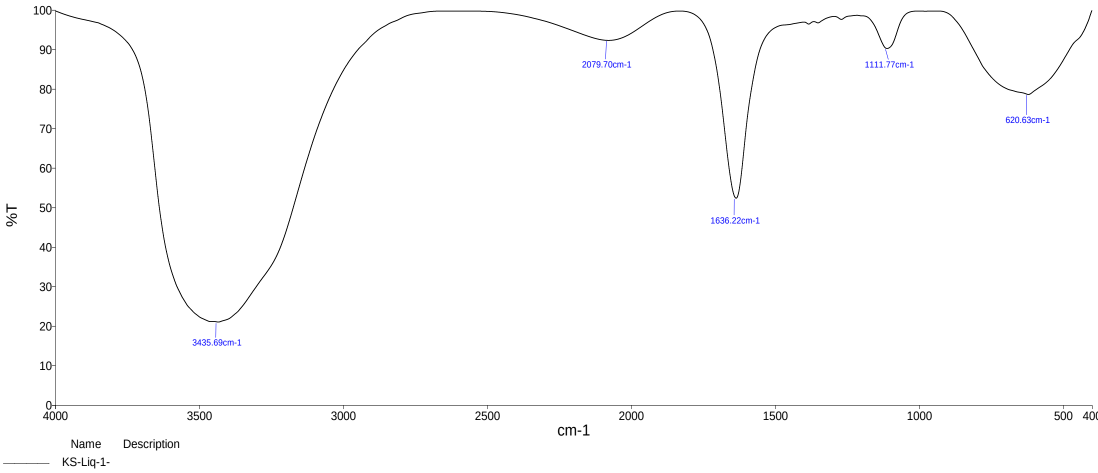


Figure 3: pH variation in Sample (S1) Microwave heating at 2.45 GHz at T = 40ºC for 10 minutes treated adsorbent and Sample (S2) with normal heating T = 40ºC for 10 minutes

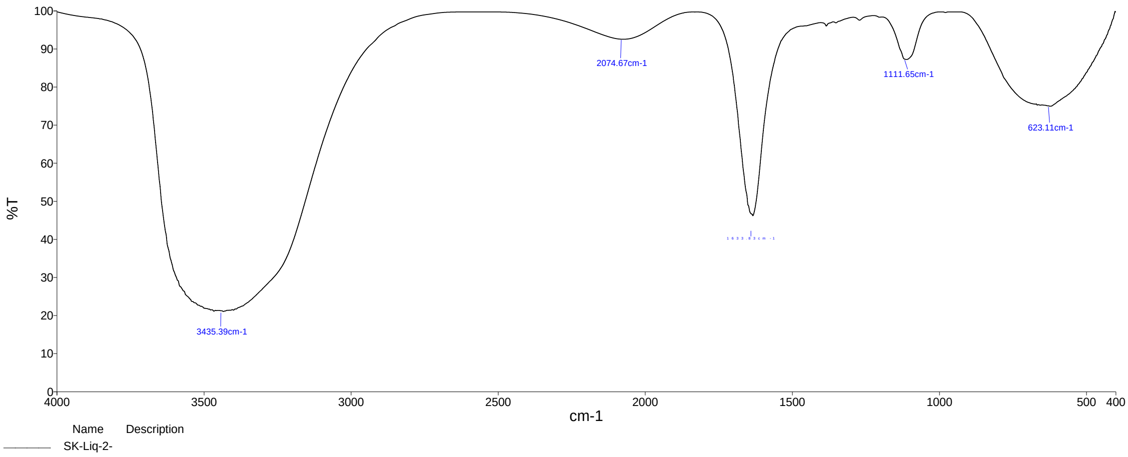
Table 1
Therapeutic uses of Vetiver plant in different parts of India[22,24]

Region	Part of the plant	Medicinal uses
Madhya Pradesh and Maharashtra	Whole plant	Anthelmintic for children, Tonic for weakness
West Bengal	Root (paste)	Headache, Rheumatism and Sprain
	Stem (decoction)	Urinary tract infection, Rheumatism lumbago and Sprain
Madhya Pradesh	Leaf (juice)	Anthelmintic
Bihar (Varanasi)	Root (vapour)	Malarial Fever
Jharkhand, West Bengal, Odisha and Chhattisgarh (Oraon tribes)	Root (ash)	Acidity

FTIR Analysis: Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the adsorption of various infrared light wavelengths by the material of interest. These infrared adsorption bands identify specific molecular functional groups and structures. FTIR spectra obtained are presented in the subsequent results. FT-IR studies identified the groups responsible for adsorption and also the nature of adsorption. The adsorptive properties of activated carbon are determined not only by its porous structure but also by its chemical composition.



(a)



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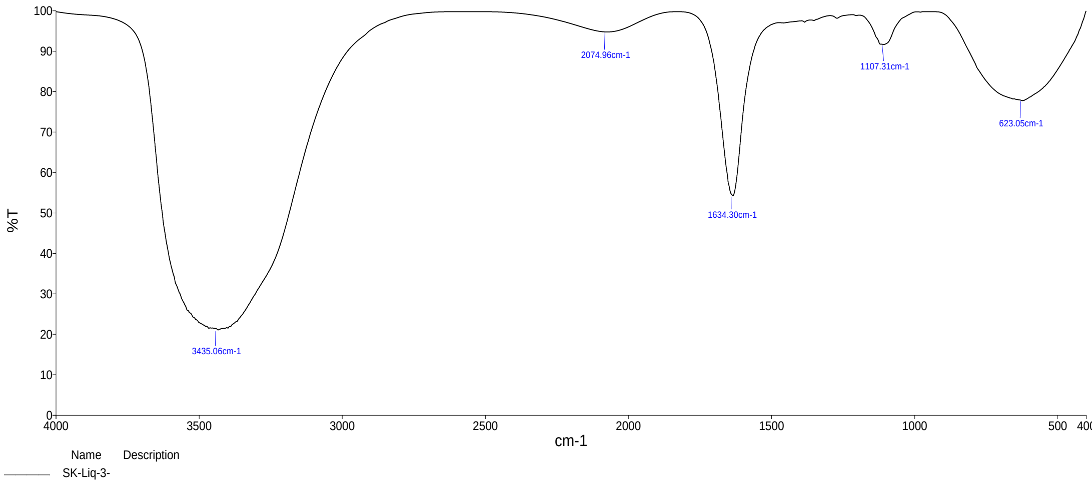

(c)

Figure 4: FTIR Analysis of (a) Effluent, (b) Sample S1: Microwave Treated and (c) Sample S2: Normal Heating

FTIR (Fourier Transform Infrared Spectroscopy) analysis is used to identify the presence of certain functional groups present in the bio adsorbent[21].The FTIR spectrum of *Vetiver zizanoides* treated samples S1 and S2 and effluent sample as a control is depicted in figures 4 to 6 with various range of wavelengths. It contain certain functional groups with peak around 3435.69cm^{-1}. Functional groups present in each surface can peak around 3435.69 cm^{-1} which indicates that free O-H group is present in the surface of the adsorbent and also it predicts the presence of alcohols[20,23]. The spectrum having 1636.22 cm^{-1} band indicates the presence of C=C of aromatic. The band having the range 1111.77 cm^{-1} indicates the presence of C=F of alkyl halide and a shift is seen in sample S2 which can be due to the influence of microwave treatment. The band appeared in the range of 620.63 cm^{-1} indicating the presence of C-Cl having alkyl halide group[19,25].

Table 2
Parameters tested for effluent (as reference) and samples

Parameters Tested	Effluent	Sample S1	Sample S2
pH	3.47±0.58	6.65±0.65	4.62±0.72
BOD mg/l	780±2.53	86.73±1.43	250±1.45
COD mg/l	920±3.86	107.90±2.82	200±2.65

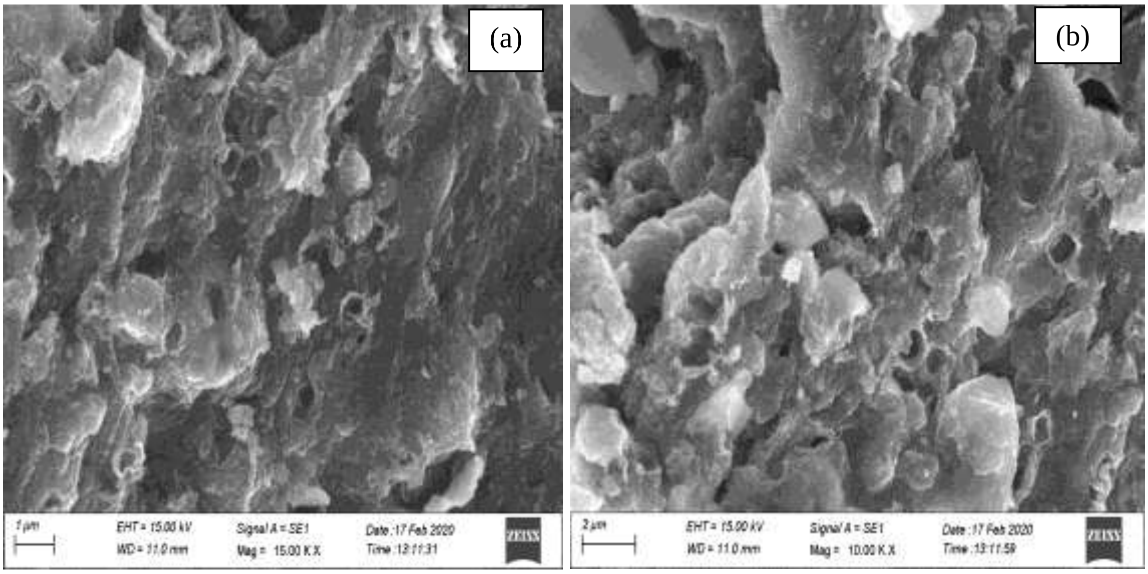

Figure 5 (a) and (b): SEM analysis of *Vetiveria zizanioides* powder before adsorption of Cr (VI)

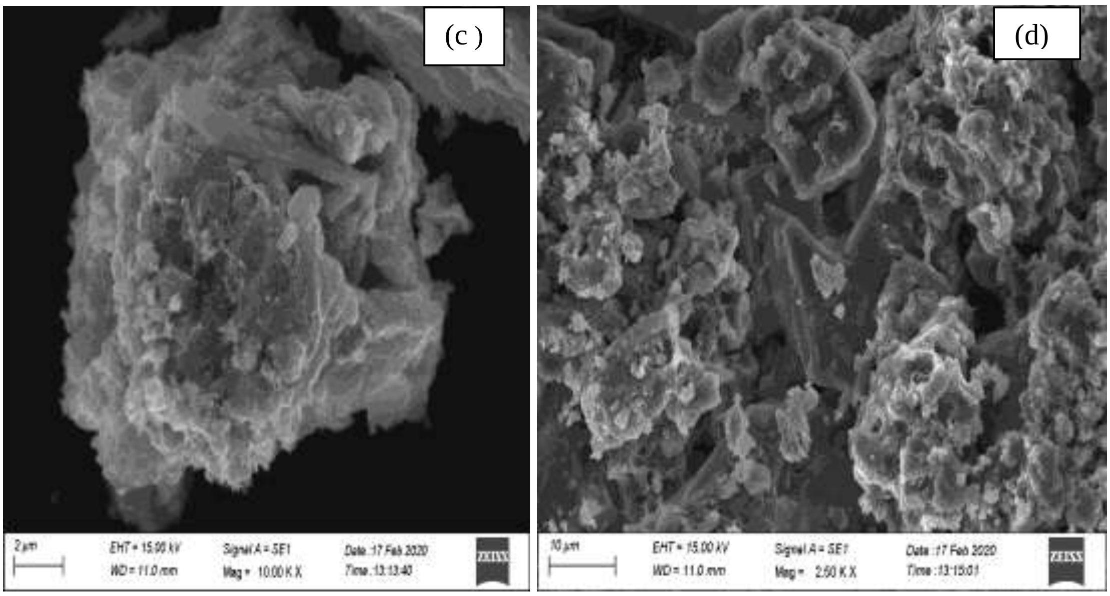

Figure 5 (c) and (d): SEM analysis of *Vetiveria zizanioides* powder after adsorption of Cr (VI)

SEM Analysis: The morphology and porous structure of *Vetiveria zizanioides* were characterized by SEM analysis before and after Cr (VI) adsorption. The structure of *Vetiveria zizanioides* samples before analysis was irregular with uneven and rough surface containing macro and micro pores of various size and shapes, showing effective adsorption sites and after Cr (VI) adsorption, the adsorbent surface showed an agglomerated morphology and pores were covered by Cr (VI) which was correlated with previous studies on chromium adsorption[26,27].

Conclusion

The use of low cost adsorbent such as vetiver powder in adsorption of heavy metals such as chromium VI can be a significantly useful technology in abetting environmental pollution due to heavy contaminants. The current study has investigated the effect of usage of vetiver powder using two different treatment conditions in which it was evident that microwave treated adsorbent had better adsorption levels when compared to a normal heating activated adsorbent. Thus pH, BOD and COD can be key indicators in analyzing the removal of metal contaminants in adsorption experiments.

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