

Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicer arietinum*)

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Abbreviations: bgh: Bengal gram husk
FTIR: fourier transform infrared spectroscopy

The potential to remove Cr (VI) from aqueous solutions through biosorption using the husk of Bengal gram (*Cicer arietinum*), was investigated in batch experiments. The results showed removal of 99.9% of chromium in the 10 mg l⁻¹ chromium solution, the biomass required at saturation was 1 g mg⁻¹. Kinetic experiments revealed that the dilute chromium solutions reached equilibrium within 180 min. The biosorptive capacity of the (bgh) was dependent on the pH of the chromium solution, with pH 2 being optimal. The adsorption data fit well with the Langmuir and Freundlich isotherm models. The adsorption capacity calculated from the Langmuir isotherm was 91.64 mg Cr (VI)/g at pH 2. The adsorption capacity increased with increase in agitation speed and an optimum was achieved at 120 rpm. The biosorption of Cr (VI) was studied by Fourier transform infrared spectroscopy (FTIR), which suggested that the presence of Cr (VI) ions in the biomass affects the bands corresponding to hydroxyl and carboxyl groups. Comprehensive

characterisation of parameters indicates bgh to be an excellent material for biosorption of Cr (VI) to treat wastewaters containing low concentration of the metal.

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. The pollutants of serious concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper, nickel, etc. due to pollutants' carcinogenic and mutagenic nature. These toxic materials may be derived from mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives.

The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent

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extraction (Juang and Shiau, 2000; Yan and Viraraghavan, 2001). These techniques apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content

Table 1. Type of Isotherm for various R_L .

R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear

In this context, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous effluents (Volesky and Holan, 1995). The process of heavy metal removal by biological materials is known as biosorption. Biomass viability does not affect the metal uptake. Therefore any active metabolic uptake process is currently considered to be a negligible part of biosorption. Various biosorbents have been tried, which include seaweeds, moulds, yeast, bacteria, crab shells, agricultural products such as wool, rice, straw, coconut husks, peat moss, exhausted coffee (Dakiky et al. 2002), waste tea (Amir et al. 2005), walnut skin, coconut fibre (Espinola et al. 1999), cork biomass (Chubar et al. 2003), seeds of *Ocimum Basilicum* (Melo and d'Souza, 2004), defatted rice bran, rice hulls, soybean hulls and cotton seed hulls (Marshall and Champagne, 1995, Teixeira and Zezzi, 2004), wheat bran, hardwood (*Dalbergia sissoo*) sawdust, pea pod, cotton and mustard seed cakes, (Iqbal et al. 2002, Saeed et al. 2002).

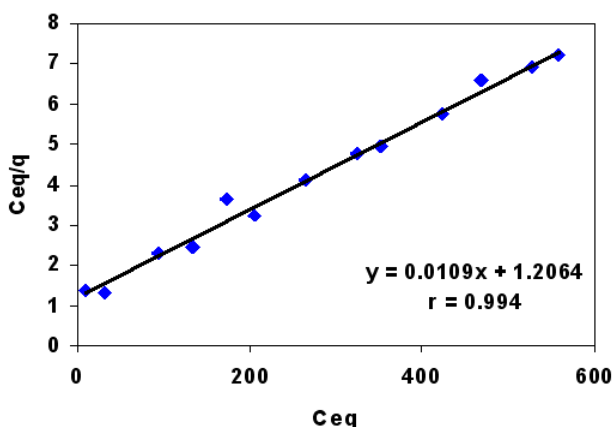


Figure.1. Langmuir adsorption isotherm for Cr (VI) biosorption by bgh at optimum conditions.

Chromium is a toxic metal of widespread use and exists in several oxidation states. The most stable and common forms are the trivalent Cr (III) and the hexavalent Cr (VI)

species, which display quite different chemical properties. Cr (VI) considered to be the most toxic of chromium, is usually associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) ions. The hexavalent form of chromium is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties (Cieslak-Golonka, 1995). Cr (VI) is a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from the textile dyeing, leather tanning, electroplating and metal finishing industries. The untreated effluent from electroplating industry contains approximately 100 mg/l Cr (VI), which is much higher than the permissible limit of 0.05 - 1 mg/l (De Filippis and Pallaghy, 1994).

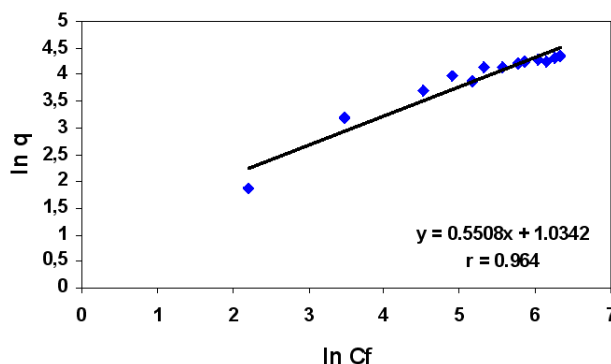


Figure 2. Freundlich adsorption isotherm for Cr (VI) biosorption by bgh at optimum conditions.

In the present study, Bengal gram husk (bgh) (*Cicer arietinum*), which is a milling agrowaste available in plenty in a tropical country like India is used for the removal of Cr (VI) ions from aqueous solutions.

MATERIALS AND METHODS

Biosorbent material

Bengal gram husk (bgh), seed coat of *Cicer arietinum* was collected from a legume seed-splitting mill. The bgh was washed extensively in running tap water to remove dirt and other particulate matter. Washing and boiling in distilled water repeatedly to remove colour followed this. The washed and boiled bgh was oven dried at 105°C for 24 hrs, stored in dessicator and used for biosorption studies in the original piece size.

Preparation of stock solution

An aqueous stock solution (1000 mg/l) of Cr (VI) ions was prepared using $K_2Cr_2O_7$ salt. pH of the solution was adjusted using 0.1 N HCl or NaOH. Fresh dilutions were used for each study.

Biosorption studies

The biosorption capacity of bgh was determined by

contacting various concentrations (10 - 100 mgL⁻¹) of 100 ml Cr solution in 250 ml conical flasks, with 1 gram of bgh. The mixture was shaken in a rotary shaker at 120 rpm followed by filtration using Whatman filter paper (No. 1). The filtrate containing the residual concentration of Cr was determined spectrophotometrically at 540 nm after complexation with 1,5 diphenylcarbazide (Eaton et al. 1995). For the determination of rate of metal biosorption by bgh from 100 ml (at 10, 20, 50, 100 mgL⁻¹), the supernatant was analysed for residual Cr after the contact period of 15, 30, 60, 120, 180, 240 and 300 min. The effect of pH on Cr sorption by bgh was determined at pH values of 2, 3, 4, 5, 6 and 7. The effect of different doses of bgh ranging from 1 to 40 g/l at varied Cr (VI) concentrations was determined. Adsorption isotherm studies were carried out with thirteen different initial concentrations ranging from 20 to 600 mg/l of Cr (VI) while maintaining the adsorbent dosage at 1g/100ml. Langmuir and Freundlich models were applied to the adsorption isotherm and different constants were generated. The Langmuir and Freundlich adsorption parameters and correlation coefficient were also calculated from the adsorption isotherm data.

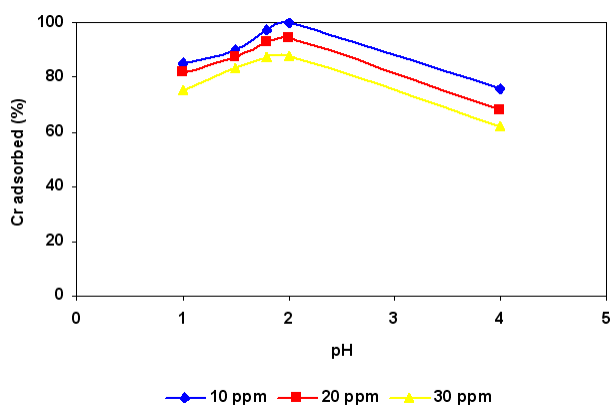


Figure 3. Effect of pH on the biosorption of Cr (VI) at different concentrations, by 10 gL⁻¹ at 120 rpm with equilibrium time of 200 min.

Infrared spectra analysis

In order to determine the functional groups responsible for metal uptake, an un-reacted bgh sample and bgh pre-treated with 100 mg/l chromium solution were analysed using a Fourier transform infrared spectrometer (FTIR). FTIR technique is used mainly to identify functional groups (like carboxyl, hydroxyl, etc.) that are capable of adsorbing metal ions.

All the experiments were carried out in triplicate and the mean values with standard deviation are presented. The maximum deviation was 2.0% (standard deviation ± 2%).

RESULTS AND DISCUSSION

Sorption equilibria studies

The chromium uptake capacity of the bgh was evaluated

using the Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm:

$$q = \frac{q_{max} b C_{eq}}{1 + b C_{eq}}$$

where q is milligrams of metal accumulated per gram of the biosorbent material; C_{eq} is the metal residual concentration in solution; q_{max} is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates (Chong and Volesky, 1995). The Langmuir isotherm is based on these assumptions (Langmuir, 1918).

- metal ions are chemically adsorbed at a fixed number of well defined sites;
- each site can hold only one ion;
- all sites are energetically equivalent and;
- there is no interaction between the ions.

When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation.

$$C_{eq}/q = 1/q_{max} \cdot b + C_{eq}/q_{max}$$

The linear plots of C_{eq}/q vs C_{eq} show that adsorption follows the Langmuir adsorption model (Figure 1) The correlation coefficient is 0.9948 (regression coefficient 0.9896). q_{max} and b were determined from the slope and intercept of the plot and were found to be 91.64 mg/g and 0.009 l/mg respectively.

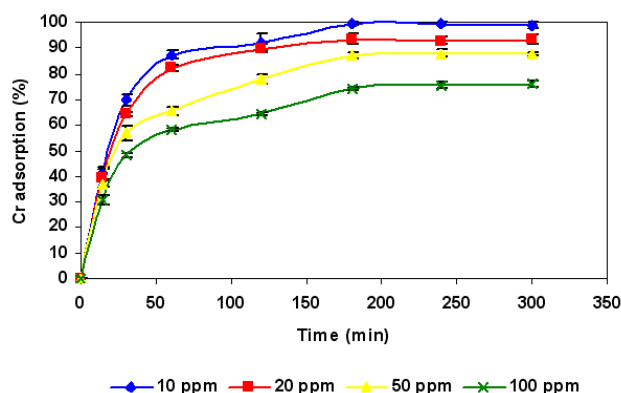


Figure 4. Percentage biosorption of Cr (VI) from solution of different concentration, pH 2.0, by 10 gL⁻¹ bgh as related to the time of contact at 120 rpm.

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as:

$$R_L = 1/(1+bC_0)$$

Where b is the Langmuir constant and C₀ is the initial concentration of Cr (VI). The R_L value indicates the shape of isotherm as given in Table 1.

According to McKay et al. (1982), R_L values between 0 and 1 indicate favourable adsorption. The R_L were found to be 0.8475 to 0.15625 for concentrations of 20-600 mg/l Cr (VI).

The Freundlich isotherm is represented by the equation (Freundlich, 1907):

$$q = K_f C_{eq}^{1/n}$$

where C_{eq} is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The linearised forms of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\ln q = \ln K_f + 1/n \ln C_{eq}$$

K_f and n were calculated from the slopes of the Freundlich plots (Figure 2) The constants were found to be K_f = 2.815 and n = 1.814. According to Kadirvelu and Namasivayam (2000), n values between 1 and 10 represent beneficial adsorption.

The comparison of Freundlich constants with adsorption capacity for Cr (VI) with other adsorbents is given in Table 2.

Figure 1 and Figure 2 conforms with the Langmuir and Freundlich models. The Langmuir capacity or q_{max} is used to compare the efficiency of bgh with other materials, which have been tested as biosorbents for Cr (VI). Table 2 shows that, for Cr (VI), the bgh has a greater capacity than some of the materials. The magnitude of K_f and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity. The value of n, which is related to the distribution of bonded ions on the sorbent surface, is found to be greater than unity for bgh, indicating that adsorption of Cr (VI) is favourable.

Effect of Ph

Chromium exhibits different types of pH dependent equilibria in aqueous solutions. As the pH is shifted, the equilibrium will also shift; in the pH range 2-6, HCrO₄⁻,

and Cr₂O₇²⁻, ions are in equilibrium. At lower pH (pH <2.0) values, Cr₃O₁₀⁻ and Cr₄O₁₃²⁻ species are formed. The optimum initial pH for biosorption of hexavalent chromium on to bgh (husk of *Cicer arietinum*) was observed at pH 2.0. This indicates the formation of more polymerized chromium oxide species with decreased pH.

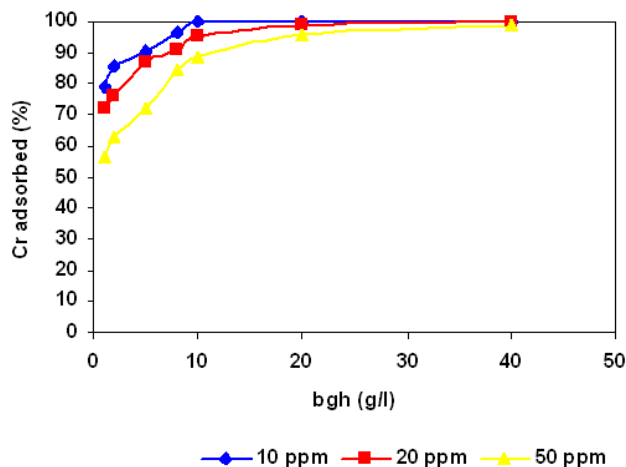


Figure 5. Effect of quantity of bgh biomass on biosorption of Cr (VI) from solutions of different concentrations, pH 2.0 for contact time 200 min at 120 rpm.

As illustrated in Figure 3, 99.6% of Cr ions was adsorbed from a solution of 10 mg/l at pH 2.0, whereas a 23% reduction in biosorption was determined as the pH shifted from 2.0 to 4.0. The percentage of Cr ions adsorbed at pH 2.0 decreased with increasing metal concentration. The adsorption of metal ions depends on solution pH, which influences electrostatic binding of ions to corresponding metal groups. At the optimum sorption pH 2.0, the dominant species of Cr ions in solution are HCrO₄⁻, Cr₂O₇²⁻, Cr₄O₁₃²⁻ and Cr₃O₁₀²⁻. These chromate anions interact strongly with the negatively charged ions of the bgh matrix.

Biosorption Kinetics and effect of biomass quantity on chromium uptake by bgh

The concentration of both the metal ions and the biosorbent is a significant factor to be considered for effective biosorption. It determines the sorbent/sorbate equilibrium of the system. The rate of adsorption is a function of the initial concentration of ions. The kinetic profiles of the chromium biosorption at various concentrations are shown in Figure 4. The system attained equilibrium, although not

Table 2. Comparison of adsorption capacity and Freundlich isotherm constants for Cr (VI) with other adsorbents.

Adsorbent	K _f	1/n	q _{max}	Reference
<i>Rhizopus arrhizus</i>	10.99	0.18	23.88	Prakasham et al. 1999
<i>Rhizopus nigrificans</i>	12.06	3.24	99.00	Bai and Abraham, 2001
<i>Chlorella vulgaris</i>	0.48	1.26	33.80	Cetinkaya et al. 1999
<i>Scenedesmus obliquus</i>	0.68	1.42	30.20	Cetinkaya et al. 1999
<i>Synechocystis</i> sp.	1.54	1.40	39.00	Cetinkaya et al. 1999
Cone biomass	38.38	0.35	201.81	Ucun et al. 2002
Bengal gram husk	2.815	1.814	91.64	This study

as fast as reported in other concentrations.

The time taken to attain equilibrium for 10, 20, 50 and 100 mg/l chromium solution were 180 min. But as the chromium concentration increased, the percentage of chromium biosorption progressively decreased from 99.65% in 10mg/l to 75% in 100mg/l solution, even though the sorption equilibrium was achieved during the same period of 180 min. This appears to be due to the increase in the number of ions competing for the available binding sites in the biomass and also due to the lack of binding sites for the complexation of Cr ions at higher concentration levels. At lower concentrations, all metal ions present in the solution would interact with the binding sites and thus facilitated 100% adsorption. At higher concentrations, more Cr ions are left unadsorbed in solution due to the saturation of binding sites. The agitation time was fixed at 200 min for the rest of the experiments.

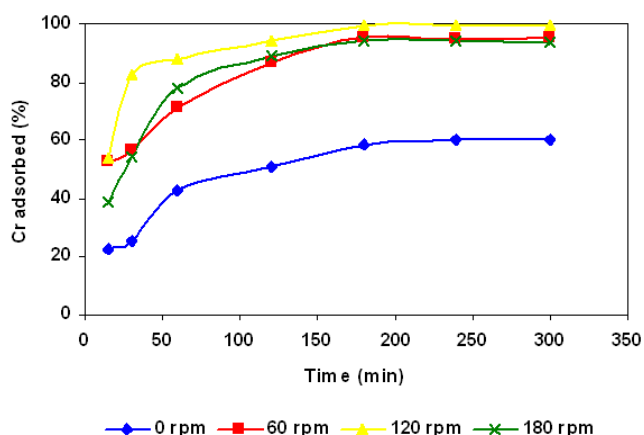


Figure 6. Effect of agitation speed on Cr (VI) adsorption, Cr concentration = 50 mg/l⁻¹, pH = 2.0, bgh dose = 10g/l⁻¹.

For the confirmation of this decline to be due to the saturation of the sorption sites, bgh biomass was varied from 1 to 40 g/l and brought in contact with chromium solutions of different concentrations. For 99% removal of chromium from 10, 20 and 50 mg/l metal solutions, the bgh biomass required was 10, 20 and 40g/l at approximate ratio of 1:1000. The rate of increase of chromium removal was not proportionate to the increase in bgh biomass, (Figure 5). This could be attributed to interference between binding sites at higher concentrations (Puranik and Paknikar, 1999). Higher chromium sorption at lower levels of bgh biomass could be due to the higher metal to biosorbent ratio, which decreases as the biomass quantity is increased (Puranik and Paknikar, 1999).

Effect of agitation speed

The effect of the agitation of the sorbent/sorbate system in Cr adsorption was monitored at low, medium and high speed of agitation using a non-agitated system as the control.

All agitation speeds were found to have a positive impact

over the non-agitated system as shown in Figure 6. A 30 - 40% increase in adsorption was observed in agitated samples during 120 min of biosorption. This is because agitation facilitates proper contact between the metal ions in solution and the biomass binding sites and thereby promotes effective transfer of sorbate ions to the sorbent sites. At 60 and 180 rpm, the adsorption rates monitored were found to be slightly lower than that at 120 rpm. These results indicate that the contact between solid and liquid is more effective at moderate agitation (120 rpm). This observation agrees with the previously reported biosorptive removal of Cr (VI) by *Rhizopus arrhizus* (Niyogi et al. 1998) and *Rhizopus nigricans* (Bai and Abraham, 2003), where 100 and 120 rpm respectively were found to be the optimum speed.

Table 3. IR absorption bands and corresponding possible groups.

Frequency (cm ⁻¹)	Functional group
3437.38	-OH, -NH
2918.89	-CH
2844.78	-CH
1634.34	-COO ⁻ , -C=O
1115.57	-C-O, C-N
893.25	-CH

Infra red spectral analysis

An un-reacted bgh sample and bgh pre-treated with 100 mg/l Cr (VI) solution were analysed using FTIR, and the percentage transmission for various wave numbers are presented in Figure 7 and Figure 8 respectively. The absorption bands identified in the spectra and their assignment to the corresponding functional groups in the bgh are listed in Table 3.

Wave number of 3000 and 3750 cm⁻¹ for bgh indicates the presence of OH groups on the husk surface. The trough that is observed at 2918.18 cm⁻¹ and 893.25 cm⁻¹ indicates the presence of C-H groups. The 1634.34 cm⁻¹ band is a result of CO stretching mode, conjugated to a NH deformation mode and is indicative of amide I band. The trough at 1115.57 cm⁻¹ is due to CO or CN groups. This reveals the presence of several functional groups for binding Cr (VI) ions on bgh surface.

CONCLUDING REMARKS

Biosorption observations on the ability of bgh to remove Cr (VI) indicate the biomass of having potential of application to sequester heavy metals from low concentration waste waters. Containing approximately 52% crude fibre composed of cellulose, hemicellulose and lignin, the bgh biomatrix indicates the presence of many - OH and - COOH groups in the linocellulosic moieties. Hydrogen of these groups is capable of ion exchange with metal cations.

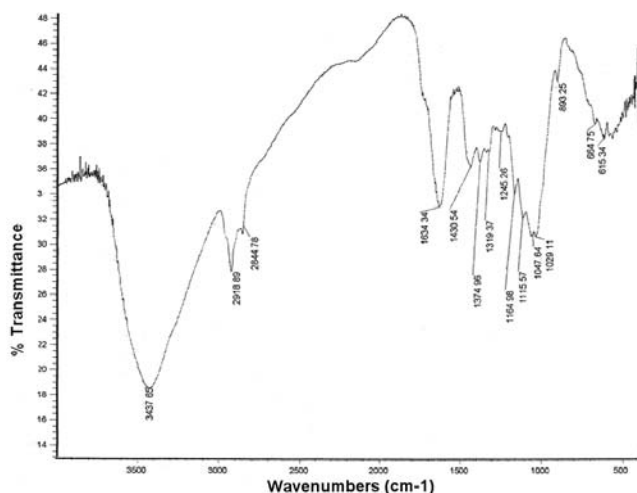


Figure 7. Infrared spectra of untreated bgh.

Protein content in bgh is less than 5%, which is advantageous over the protein rich algal and fungal biomass projected as metal biosorbents, since proteinous materials are likely to putrefy under moist conditions. Further, most metal sorption reported in literature is based on algal and fungal biomass, which must be cultured, collected from their natural habitats and pre-processed, if available as discards and transported under special conditions, thus introducing the factor of additional costs. In contrast, bgh as an agro-industrial waste has negligible cost and has also proved to be an efficient biosorbent for the removal of Cr (VI) ions.

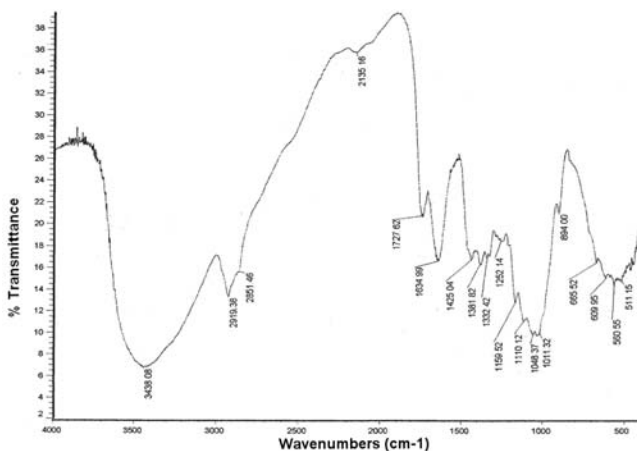


Figure 8. Infrared spectra of bgh reacted with 100 mg/l Cr (VI) solution.

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