

# ADSORPTIVE REMOVAL OF Cr (VI) ION FROM AQUEOUS SOLUTION USING LOW COST ADSORBENTS:A COMPARATIVE STUDY

**Suma Bino Thomas**  
Associate Professor,  
Baselius College, Kottayam

**Abstract:** *Cr (VI) is a heavy metal released into the environment by industrial processes such as mining, electroplating, tanning, metallurgical operations, and manufacturing, and it cannot be degraded unlike organic pollutants, which are biodegradable. Over the past decade, the need for safe and economical methods of removing heavy metals from contaminated waters has necessitated research into alternatives to activated carbon, such as coconut shell, sawdust, mango leaves, chitosan, egg shells, and other low-cost adsorbents that possess high adsorption capacities. The purpose of this study was to compare the adsorption efficiency of different low cost adsorbents, namely rice husk, a surplus agricultural byproduct, pea nut shells, passion fruit peels, and egg shells, in removing Cr (VI) from aqueous solutions. Investigation of effect of some experimental parameters such as initial metal ion concentration, contact time and temperature as it relates to adsorption of the metal to the adsorbents was also done.*

**Keywords:** *low cost adsorbents, Cr (VI) ion, rice husk, egg shells, pea nut shells, passion fruit peels*

## INTRODUCTION

Metals are a class of pollutants, often toxic and dangerous, widely present in industrial and household wastewaters. Industrial activities such as mining, electroplating, tanning, metallurgical operation and manufacturing have led to the release of heavy metals into the environment. Unlike the organic pollutants which are bio-degradable, heavy metal like Cr(VI) are not bio-degradable thus, making them a source of great concern. As, Cd, Cr, Cu, Fe, Pb, Ni, Ag, Sn & Zn are some of the toxic elements listed by 'The Agency for Toxic Substances and Disease Registry' (ATSDR). Heavy metals are reported as priority pollutants because of their mobility in natural water ecosystems. The major ill effects caused by metal ions are erythrocyte destruction, dermatitis, inhibition of enzyme activity headache, Wilkinson's disease, dizziness, nausea and vomiting, chest pain, dry cough, shortness of breath, rapid respiration, nephritis, cyanosis & extreme weakness. A wide range of various treatment techniques such as ion exchange, reduction, precipitation, reverse osmosis, dialysis, biodegradation, oxidation, solvent extraction and adsorption have been reported to be used for removal of heavy metal ions from industrial effluents. Adsorption has been universally accepted as one of the most effective pollutant removal process, with low cost, ease in handling, low consumption of reagents, as well as scope for recovery of value added components through desorption and regeneration of adsorbent. Activated carbon is highly porous, amorphous solid containing micro crystallites with a graphite lattice and higher exposed surface area and hence high surface capacity for adsorption. But its drawback is that it reacts with oxygen at moderate temperature (over 300°C) and is very expensive. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives such as coconut shell, sawdust, mango leaves, chitosan, egg shell, and other adsorbents, which have high adsorption capacity and are locally available to commercially available activated carbon.

In this study the removal of Cr (VI) from aqueous solutions by batch adsorption technique using different low cost adsorbents was investigated. Adsorbents such as rice husk a surplus agricultural byproduct, Pea nut shell, peel of Passion fruit and egg shell were used to determine adsorption efficiency. In the environment, Chromium exists in two stable forms which are the + 3 and the + 6 states. While chromium (III) is known to be an essential trace element in plants and animal metabolism, Chromium (VI) is toxic, carcinogenic and mutagenic.

## Objectives of the study

The specific objective of the study is to compare the adsorptive efficiency of four different low cost adsorbents, namely passion fruit peel, rice husk, egg shell and pea nut shell towards chromium (VI).

- Preparation of low cost adsorbents from biomass/agricultural waste.
- Characterization of all the adsorbents using CHNS, FTIR and SEM.
- Investigation of effect of some experimental parameters such as initial metal ion concentration, contact time and temperature as it relates to adsorption of the metal to the adsorbents.
- Comparative study of Cr (VI) removal by four different adsorbents.

## MATERIALS AND METHODS

### 1) Adsorbent

Passion fruit peel (PF), Rice husk (RH), Pea nut shells (PN) and Egg shells (ES) were collected, washed with distilled water and dried in the sun. Then it was grounded and sieved to 200 $\mu$ m particle size. It was then dried to remove moisture and stored in a closed bottle for later use in adsorption studies. The adsorbent was characterized by IR spectroscopy SEM and CHNS.

### 2) Preparation of Cr (VI) solutions

All the chemicals used are of analytical grade. A stock solution of 1000 mg/L of Cr (VI) was prepared by dissolving 2.8287 g of potassium dichromate ( $K_2Cr_2O_7$ ) in 1000 ml of distilled water. This solution is diluted as required to obtain standard solutions containing 100 -1000 mg/l of Cr (VI).

#### 3. Effect of operating parameters

##### 1) Batch experiments

The batch experiments were carried out in 50 ml reaction bottles. 0.2g of the adsorbent is added to each reaction bottle and 10 ml of the Cr (VI) solution whose concentration ranging from 100-700ppm were added, and then stirred for 1 hour in water bath cum-mechanical shaker.

##### 2) Effect of time

The influence of time on Cr (VI) adsorption is studied at 30°C with initial Cr (VI) concentration which have the maximum absorbance value for that adsorbent. The absorbance values were noted at every 10 minutes.

##### 3) Effect of temperature

The effect of temperature on Cr (VI) solution is studied at different temperatures ranging from 30°C-80°C with 0.2 g of the adsorbent and 10ml of the Cr(VI) solutions for 1 hour. Afterwards the resultant solutions were filtered through filter paper.

##### 4) Measurement of Cr (VI) concentration in aqueous solutions

The concentration of the free Cr (VI) ions in the effluent is determined colorimetrically by developing a brown colour with 1,5-diphenyl carbazide in acidic solution as a complexing agent. The absorbance of the brown coloured solution was read at 540 nm.

## RESULT AND DISCUSSION

### 1. Characterisation of the adsorbent

#### 1.a. FT-IR spectroscopy

The IR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of heavy metal ions. The IR spectrum of ground nut shell was recorded to obtain the information regarding the stretching vibrations of the functional groups which are involved in the adsorption of the adsorbate molecules.

#### i. Egg Shell

The IR spectrum of egg shell before and after metal ion adsorption is shown in the figure 1. The IR spectral analysis of egg shell shows distinct peak at 712.27, 873.61, 1216.97, 1416, 1047.54, 1738.5 and 2335.08 $cm^{-1}$ .

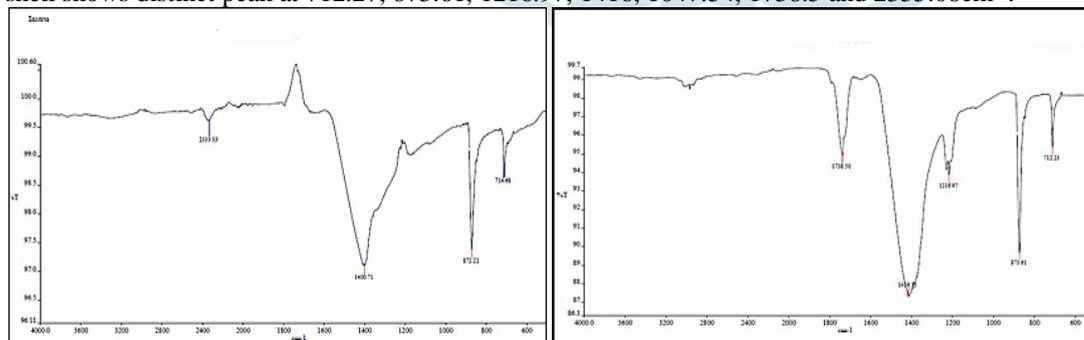


Fig.1. IR Spectrum of ES & Cr adsorbed ES

The peak observed at 712.27 and 873.61 may be assigned to the presence of  $CaCO_3$ . The peak observed at 1738.5 $cm^{-1}$  confirms the presence of carbonyl group. The peak at 2335.08 $cm^{-1}$  reveals OH stretching vibration. The sharp peak at 1738.5 disappears in the spectrum of Cr adsorbed egg shell. Peak at 1416.2 become broad and slight change in the positions of other peaks can be noticed.

#### ii. Passion fruit peel

The IR spectrum of passion fruit peel shows peaks at 3319.21 and 2918.09  $cm^{-1}$  which refers to (-OH) and identical alkyl group(-CH<sub>2</sub>-) respectively. Also, the spectrum shows bands at 1736.71 and 1013.07  $cm^{-1}$  were to be the presence of (C-O) and (-OH), respectively. The band at 3319.21 $cm^{-1}$  was attributed to the surface hydroxyl groups and chemisorbed water.

An examination of the adsorbent before and after sorption reaction possibly provides information regarding the surface. Some peaks become more intense and sharp after adsorption. It was found that the spectra of treated sorbents differ significantly from the spectrum of the “parent” (untreated) material, suggesting that the treatment procedures change the peel structure substantially.

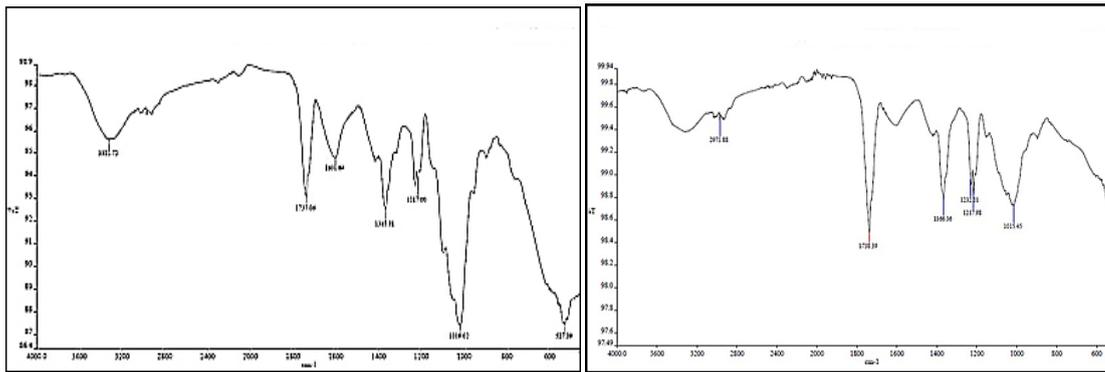


Fig.2. IR Spectrum of PF peel & Cr adsorbed PF peel

### iii) Rice Husk

In the IR spectrum of rice husk strong peaks were found at 3293.17, 1737.70, 1365.58, 1216.81 and 1049.21  $\text{cm}^{-1}$ . The peaks corresponds to -OH, C=O group, Nitro group and C-X groups respectively.

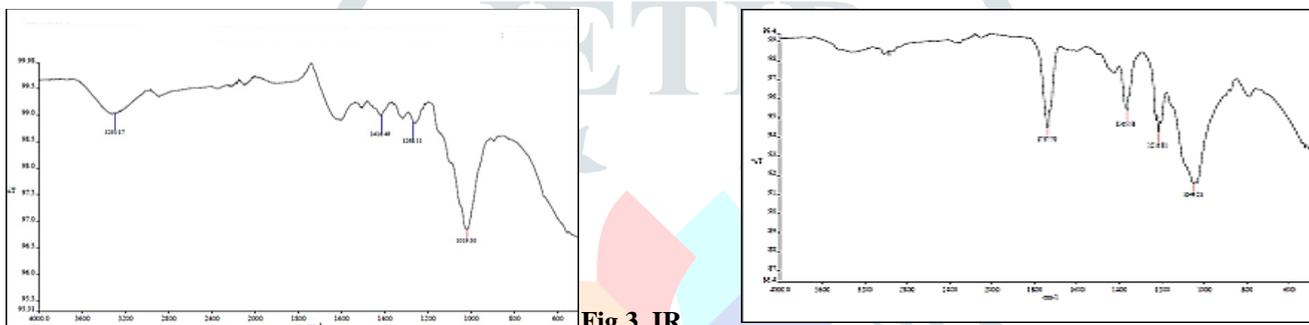


Fig.3. IR Spectrum of RH & Cr adsorbed RH

It also shows that after adsorbing metal ion, the peak at  $3293.17\text{cm}^{-1}$  almost disappears indicating the involvement of -OH group in metal adsorption. Other peaks also show slight variation in their positions. This fact indicated the surface functional groups of rice husk could combine with metal ion intensively. These groups had been reported to enhance metal ions adsorption. It also shows that after adsorbing metal ion, the peak at  $3293.17\text{cm}^{-1}$  almost disappears indicating the involvement of -OH group in metal adsorption. Other peaks also show slight variation in their positions. This fact indicated the surface functional groups of rice husk could combine with metal ion intensively. These groups had been reported to enhance metal ions adsorption.

### iii. Peanut Shell

The IR spectral analysis of ground nut shell shows distinct peak at 558.27, 1047.54, 1738.35 and  $3335.08\text{cm}^{-1}$ . The peak observed at 558.2 and 1047.54 may be assigned to the presence of vinyl compound ester group respectively. The peak observed at  $1738.35\text{cm}^{-1}$  confirms the presence of carbonyl group. The peak at  $3335.08\text{cm}^{-1}$  reveals OH stretching vibration. It can be seen from the spectra that upon adsorption of metal ions by ground nut shell, the broad OH and NH bands at  $3395\text{cm}^{-1}$  was shifted to  $3285\text{cm}^{-1}$ . This is indicative of the binding of metals with hydroxyl and amino groups. There is a shift in the C=O of ester from 1035 to  $1031\text{cm}^{-1}$ . This indicates that carboxyl groups are likely to be the main group to be involved in binding with metals.

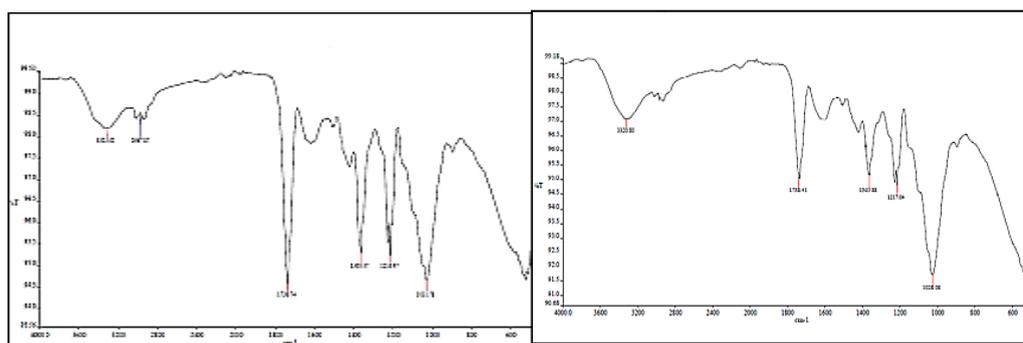


Fig.4. IR Spectrum of PN shell & Cr adsorbed PN shell

## 1.b. Scanning Electron Microscopy

The Scanning electron microscopy photographs before and after adsorption clearly reveal the morphology and different level of porosity of the adsorbents. It is found that after the adsorption of the metal ion to the adsorbent the surface of the adsorbent become rough. The porous and irregular surface structure of the adsorbent can be clearly observed in SEM images shown in Fig.5-. It clearly reveals the porous surface textures which endorse the adsorbent with increased surface area and high adsorption capacity.

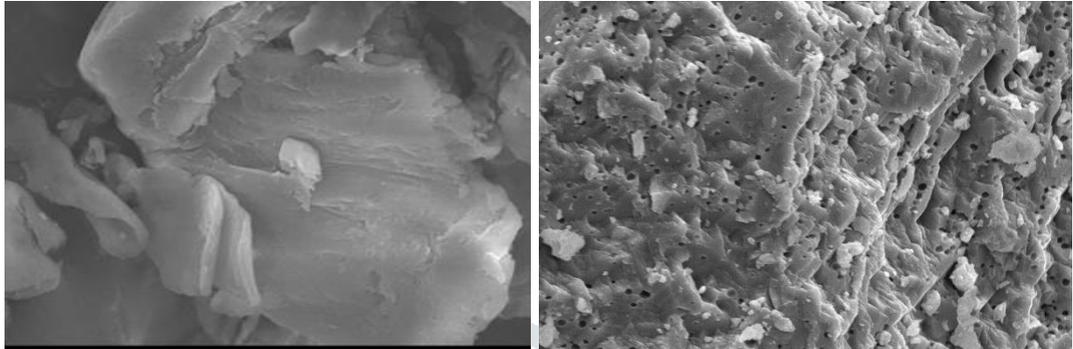


Fig.5. SEM of ES & Cr adsorbed ES

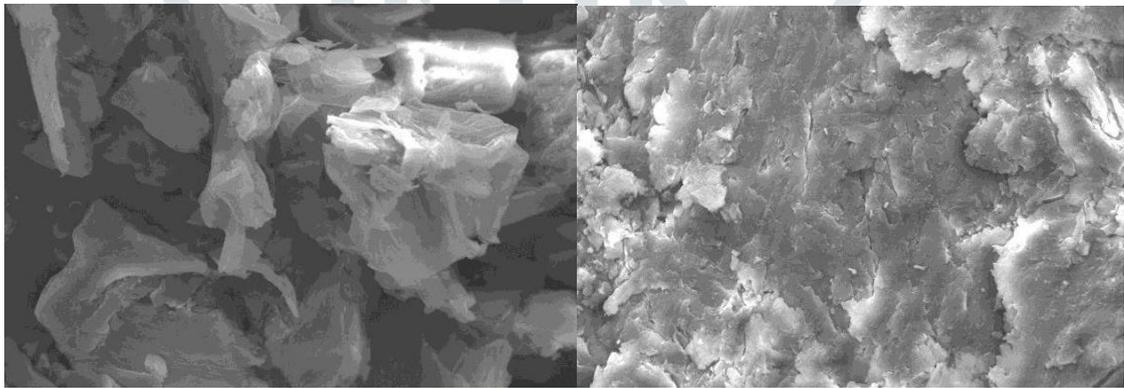


Fig.6. SEM of PF peel & Cr adsorbed PF peel

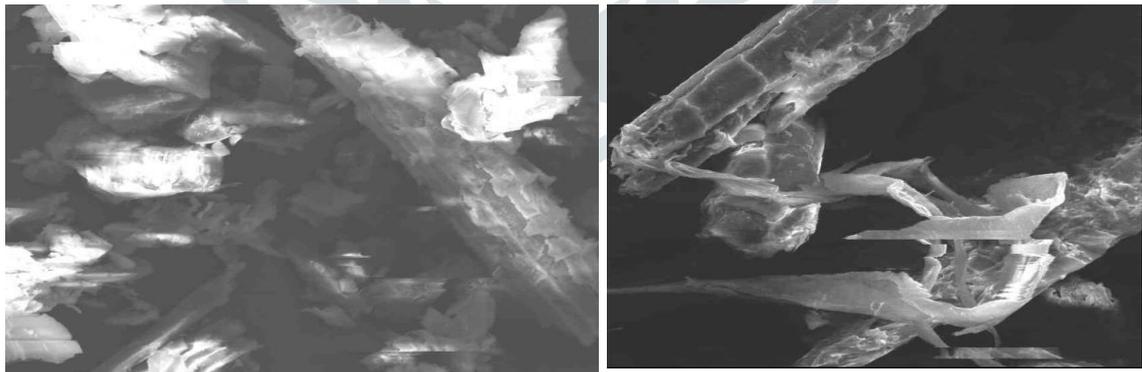
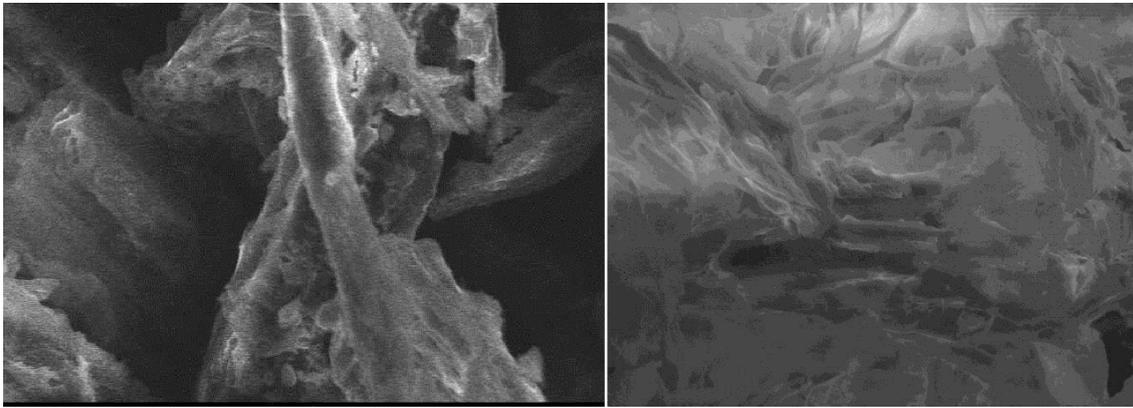


Fig.7. SEM of RH & Cr adsorbed RH



**Fig.8. SEM of PN shell & Cr adsorbed PN shell**

The heterogeneous pores and cavities provided a larger exposed surface area for the adsorption of dye molecules. On adsorption of the dyes, the porous structure disappears and surface becomes rough.

### 1.c. CHNS analysis

CHNS elemental analysis provide a means for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials.

Sample No	Sample Name	N%	C%	H%	S%
1	ES	0.8	13.6	0.52	0.1
2	PF peel	1.17	34.76	5.14	0.27
3	RH	0.76	36.42	5.04	0.19
4	PN Shell	1.45	46.68	5.73	0.36

**Table.1. CHNS Analysis data of adsorbent**

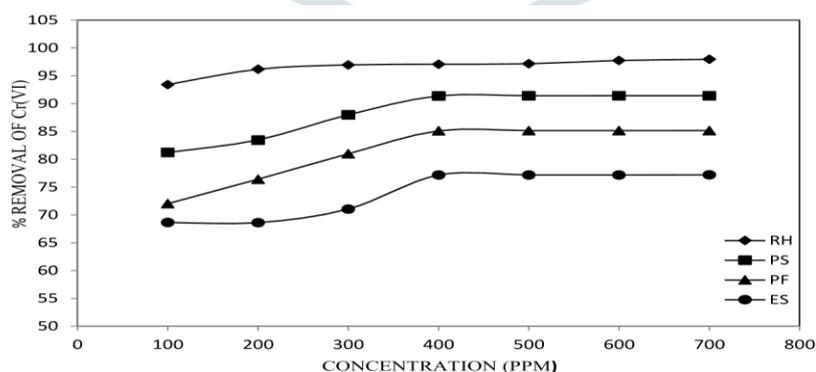
Elemental analysis on carbon, hydrogen and nitrogen is the most essential and in many cases the only investigation performed to characterize and/or prove the elemental composition of an organic sample. Numerous compounds include no additional elements besides C, H and N except oxygen, which is seldom determined separately.

## 2.OPTIMIZATION OF OPERATIONAL VARIABLES

### Effect of initial concentration

Initial metal ion concentration is one of the effective factors in removal efficiency. Fig.9. depicts the effect of increase in initial metal ion concentration of Cr (VI) on the adsorption of the various adsorbents.

With an increase in the metal ion concentration the % removal is found to be increasing. This is due to the adsorption of the metal ions to the vacant sites on the surface of the adsorbent.



**Fig.9. Effect of initial concentration**

After 600 ppm the % removal is found to be unaffected even with an increase in concentration. This may be due to the saturation attained on the surface of the adsorbent.

### Effect of Time

To establish an appropriate contact time between the ground nutshell and metallic ion solution, adsorption capacities of metal ion were measured as a function of time (Fig.10).

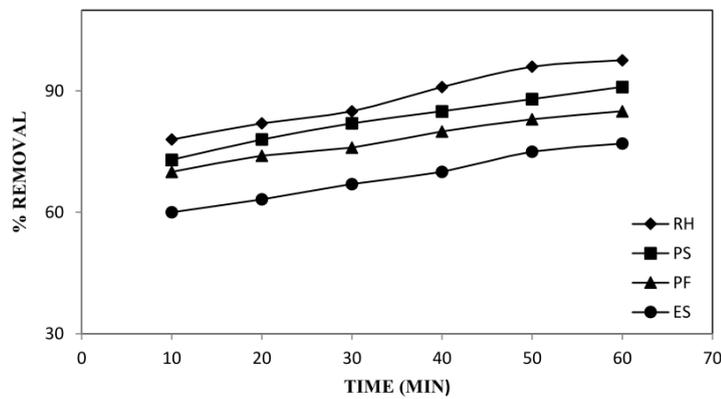


Fig 10.Effect of time

It is clear that the extent of adsorption is rapid in the initial stages and the adsorption increases with increasing contact time and becomes slow till saturation is reached. This shows that time required to attain the equilibrium is 60 min. It is due to saturation of active sites which do not allow further adsorption to take place. The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. In the initial stage of adsorption of Cr(VI), the concentration gradient between the film and the available pore sites is large, and hence the rate of adsorption of Cr(VI) is faster. The rate of adsorption decreases in later stage of the Cr(VI) adsorption probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent.

### Effect of Temperature

Temperature is an important parameter that determines the thermodynamic of adsorption process. As the percentage removal of Cr(VI) slightly increases with an increase of temperature till 60°C and then decreases when the other conditions were kept constant.

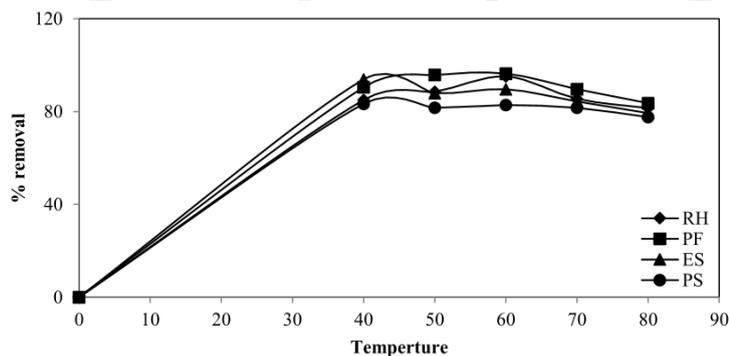


Fig. 11. Effect of temperature

The enhancement in the adsorption efficiencies for some range of temperature may be due to the chemical interaction between adsorbate and adsorbents, creation of some new adsorption sites or the increased rate of intraparticle diffusion of Cr(VI) ions into the pores of the adsorbents. The decrease in percentage of adsorption at temperatures higher than 60°C may be due to desorption caused by an increase of the thermal energy that may induce higher mobility of the adsorbate causing desorption.

## CONCLUSION

The use of four different highly efficient low cost and abundant materials for removal of toxic Cr(VI) ions from contaminated aqueous solution was studied. The rapid uptake and high capacity of rice husk, peanut shell and passion fruit peel indicated that it could be a better alternative for the removal of Cr(VI) from real wastewater by sorption process. The prepared four different sorbents were characterized by FTIR, CHNS and SEM. Adsorption of Cr was evidenced by change in the IR peaks and morphological analysis using SEM.

The metal ion sorption performances are strongly affected by parameters such as: contact time, temperature and initial metal ion concentration. The amount of metal ions sorbed by the four adsorbents increased with time, reached a maximum and remained constant. The extent of adsorption increased with temperature up to 60°C and then decreased with further increase in temperature. The rate of adsorption increases with increase in initial metal ion concentration.

The results of equilibrium experiments indicated that removal efficiencies of the tested adsorbents were in the following order; Rice husk > Peanut shell > Passion fruit peel > Egg shell. Rice husk was found to be most effective, for which the removal reached 97.96% Cr(VI) at 30°C. Based on the experimental conditions, it is found that the removal of Cr ion from their aqueous solution could attain 100%. This shows a new trend or using agricultural wastes as a mean for wastes disposal for the benefit of environmental pollution control. Removal of Cr(VI) from aqueous solution was possible using several abundantly available low-cost adsorbents.

The biosorbents prepared from agricultural waste like rice husk, peanut shell, passion fruit peel and egg shell are inexpensive and use of the same provides an effective solution for treatment of effluents containing hexavalent chromium. Hence the use of low cost adsorbents prepared and used as an adsorbent for Cr (VI) removal in this study is of practical importance and is expected to be economical.

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