Removal of Chromium (VI) from Industrial Effluent using pumpkin peel powder as adsorbent

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Abstract
Adsorption efficiency of prepared biomass of pumpkin peel powder (PPP) as low-cost adsorbent material for efficient removal of Cr (VI) ions from electroplating industrial effluent was carried out. The effects of pH, initial concentration, biosorbent dosage and contact time were studied using batch equilibrium method. Experimental data showed approximately 45% of Cr (VI) ions removal at highly acidic medium (pH-2) within 60 min by PPP biomass on experimental conditions.

The removal mechanism of Cr (VI) was studied using adsorption isotherm of biomass materials by fitting experimental data into Langmuir and Freundlich equations. Experimental results suggest that PPP, an agro waste material is efficient biosorbent for removal of Chromium (VI) from industrial effluent.

Keywords*:* Peel powder, biosorbent, adsorption isotherm, metal salt.

Introduction

Improper disposal of industrial effluent containing heavy metals as well as various anthropogenic activities containing a wide range of potential contaminants pollutes water bodies' results into toxicity to both human and aquatic life. Amongst the heavy metals, chromium is an essential metal which exists in nine different oxidation state ranging from Cr (-II) up to Cr (+VI) from which Cr (III) and Cr (VI) are the two commonly available forms.[1] Out of which Cr (VI) is more hazardous metal ion, causes skin irradiation resulting in ulcer formation and its over exposure leads to liver damage, pulmonary congestion and oedema.[2]

In addition, Cr (VI) is toxic and a suspected carcinogen material is quite soluble in the aqueous phase almost over the entire pH range and is mobile in the natural environment.[3] In last few decades various methods for the removal of chromium oxy anion from wastewater such as precipitation, electrochemical reduction, ion exchange, filtration, membrane technology, reverse osmosis and adsorption are used.[4]

Literature survey revealed that use of biomaterials as low-cost adsorbent for metal recovery from industrial effluent is of great importance as it is reusable.[5-8] The presence of various functional groups and fine particle size of biomaterials are responsible for their excellent adsorption property.[9] In present work, the efficiency of pumpkin peel powder has been studied as biomasses onto chromium removal efficiency from electroplating industrial effluent.

Material and Methods

Sample and Adsorbent Collection: Area nearby Vithal Udyog Nagar, Anand was selected for the study. Water effluent was collected from electro plating industry near GIDC, Vitthal Udyog Nagar, Anand, Gujarat, India. In present study, pumpkin peel powder was used as an adsorbent for removal of chromium (VI) from industrial effluent and was obtained from local market.

Batch Adsorption Experiment: Water effluent was collected from electro plating industry. It was yellow in color. pH of industrial effluent was 4.00 and initial concentration of chromium in effluent was 170.12 mg/L. In order to study the efficiency of the pumpkin peel powder, the effluent was digested with concentrated acid and then filtered through Whatmann No. 41 filter paper. Batch adsorption experiments were carried out in 250 ml Erlenmeyar flasks containing 25 ml industrial effluent to determine the effect of pH, contact time and adsorbent dose on metal removal.

Preparation of Solution: The stock solution of Cr (VI) using potassium dichromate, $K_2Cr_2O_7$, concentration of 1000 mg/l was prepared by dissolving appropriate amount of $K_2Cr_2O_7$ of analytical grade in 1000 ml of deionized water. The stock solution was further diluted with distilled water to desired concentration of test solution.

Preparation of Adsorbent: Pumpkin peel powder was used as an adsorbent. Pumpkin waste was obtained from local market of Vitthal Udyog Nagar. Prior to experiment, peels of pumpkin were cut into small pieces (<5 mm), washed two to three times with distill water to remove external dirt and then dried in sunlight for a week. Dried pumpkin peel was ground into powder using kitchen grinder, sieved using 250 μ (micron) sieve size and kept in air tied bottle prior to the experiment. Dried peel powder were yellow in color. After drying, physical, chemical and Infrared spectroscopy analysis were carried out.

Sorption Experiment: Batch adsorption experiments were carried out in 250 ml Erlenmeyar flasks containing 25 ml industrial effluent to determine the effect of pH, contact time and adsorbent dose on metal removal. The pH of sample solutions was adjusted using 0.1N NaOH and 0.1N HCl. Addition of biomass in different quantity was added batch wise. Flasks were agitated for 60 minutes at 400 rpm to ensure equilibrium was reached and filtered using Whatmann filter paper no. 1. 2 ml sample was withdrawn at different time intervals for the determination of residual metal ion concentration by using UV Visible spectrophotometer. Sorption study was carried out using 250 µ sieved size particles.

Study of pH: The effect of pH for Cr (VI) adsorption onto biomaterial was investigated. A set of six flasks (a batch) with 25 ml water effluent were taken and varying pH (1 to 8), was adjusted using 0.01N NaOH and 0.01N HCl. Preset amount of biomass was then added to each flask. Mixture was agitated for half an hour at 400 rpm at room temperature and then filtered. Absorbance of solution was measured at 540 nm using Spectrophotometer.

Study of contact time: The effect of contact time on adsorption of Cr (VI) was investigated batch wise with time interval of 0 to 180 minutes in 25 ml effluent containing 4 gm of adsorbent in each flask. Mixture was agitated for 180 min at 400 rpm at room temperature and samples were withdrawn at fixed time intervals, filtered and absorbance was measured at 540 nm using Spectrophotometer.

Study of adsorbent dose: The study of adsorbent dose on Cr (VI) removal was investigated with biomaterial peel powder (0.05 to 6 gm) in 25 ml of effluent in each flask. Two batch sets were prepared for a fixed quantity biomass. Absorbance was measured at 540 nm using Spectrophotometer.

Characterization of Adsorbent: Prepared biomaterials were characterized using FTIR (Fourier transformer infrared) as it is a technique used to identify functional group taking part in metal sequestering. Energy dispersive X-ray analysis (EDX) referred to as EDS or EDAX was used to identify the elemental composition of materials.

Results and Discussion

The data of the performed experimental sets has been summarized in table 1.

Table 1
Percentage removal at different dose, pH and Time.

Dose gm/25 ml	Removal efficiency (%)	pH	Removal efficiency (%)	Time in minute at 400 rpm	Removal efficiency (%)
0.5	20.82	1	26.54	**30**	**52.92**
1	21.22	**2**	**48.15**	60	49.12
2	23.93	3	19.54	90	48.62
3	25.21	4	16.44	120	48.42
4	**26.06**	5	14.73	150	45.22
5	23.73	6	4.81	180	42.02
6	22.54	7	3.11	--	--
--	--	8	2.69	--	--

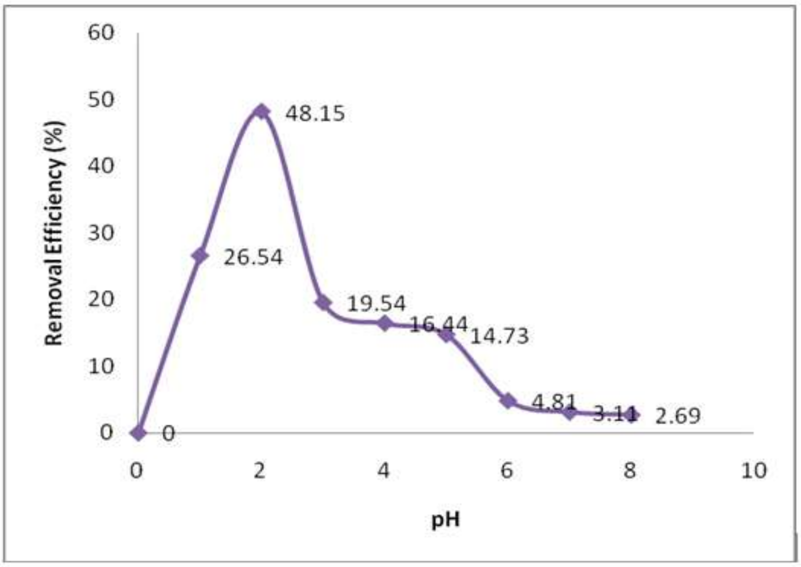

Figure 1: Effect of pH on adsorption at fix dose i.e. 4 gm/ 25 ml at 400 rpm.

Effect of pH: Metal adsorption is highly depended on pH of the medium. In order to study effect of pH on chromium (VI) adsorption onto pumpkin peel powder, the batch adsorption study at various pH values (1 to 8) was carried out and result is shown in table 1. It suggests, significant adsorption of Cr (VI) at pH 2. Decrease in adsorption at higher value of pH of medium might be due to formation of water soluble hydroxyl complexes resulting in the decreased adsorption of Cr (VI). The effect of pH on Cr (VI) is important parameter because it affects the solubility of adsorbent and concentration of the ions on the functional group of the adsorbent.

Adsorption study was carried out at various pH value (1 to 8) while the other operational parameters such as adsorbent dose (4 g), contact time (30 min) with agitation speed of 400 rpm were kept constant. Removal efficiency of pumpkin peel powder was observed maximum at pH 2 with approximately 48.15% chromium removal.

Effect of Time: Time of contact and agitation rate on biosorption experiment were carried out at pH 2.0. The agitation speed was 400 rpm on mechanical shaker. Results obtained show that contact time and speed affect adsorption of metal ion. As per figure 2, it depicts that as time increases, the adsorption value decreases, indicating the adsorption on function group has occurred in initial 30 minutes, further agitation leads to loss of metal ions from the surface.

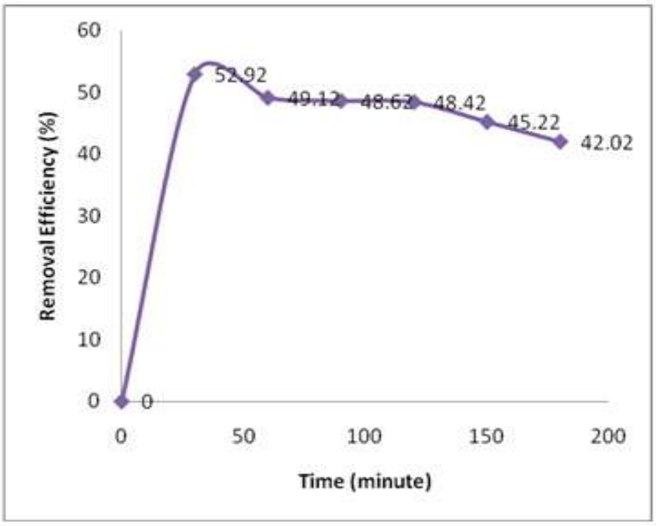

Figure 2: Effect of time on adsorption at fix dose i.e. 4gm/25ml and 400rpm

Effect of adsorbent dosage: Adsorbent dose also affects the adsorption of chromium metal ion because it determines the availability of binding site on the surface of adsorbate. In present study adsorbed dose was varied from 0.5 g /25 ml to 6 gm /25 ml. Results obtained show that adsorption increases approximately 20 to 30% with increased adsorbent dose. As shown in figure 3, the maximum removal of Cr (VI) ion has occurred with 4 gm of adsorbent dose with 26.06% removal efficiency. However, it decreases and becomes constant after sometime.

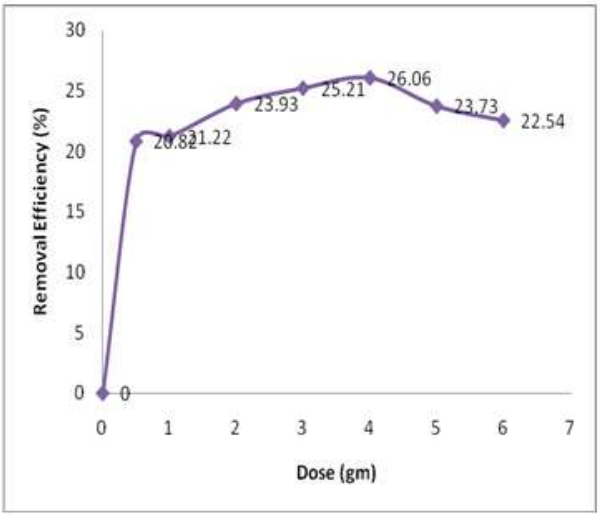

Figure 3: Effect of dose on adsorption at 400 rpm.

Characterizations of adsorbent by Fourier Transform Infrared Spectroscopy (FT-IR): FTIR analysis of pumpkin peel powder unloaded and loaded with Cr (VI) had been carried out. Figure 4 shows the FTIR spectrum of pumpkin peel powder before adsorption. For pumpkin peel powder, the strong and broad peak at 3429.07 cm^{-1} was attributed to the stretching vibration of O-H group due to inter- and intra-molecular hydrogen bonding of polymeric compound such as alcohol or phenols. The strong and banded peaks observed at 2919.64 cm^{-1} and 2851.02 cm^{-1} were associated with the stretching vibration of C-H bond of methyl, methylene and methoxy group.

The peak detected around 1652.36 cm^{-1} showed a C=C stretching, which might be attributed to the presence of alkenes and aromatic bond. The peak observed at 1736.40 cm^{-1} showed the presence of the C=O carbonyl group. The intense peak appearing at 1067.76 cm^{-1}, 1101.36 cm^{-1}, 1156.16 cm^{-1}, 1243.68 cm^{-1} indicated the C-O stretching of acids, anhydrides and alcohols for pumpkin peel.

The peaks were appearing at 3429.07 cm^{-1}, 2919.64 cm^{-1}, 2851.02 cm^{-1}, 1736.40 cm^{-1}, 1652.36 cm^{-1}, 1243.68 cm^{-1}, 1156.16 cm^{-1}, 1101.36 cm^{-1}, 1067.76 cm^{-1} before loaded with chromium ions. But the adsorption of Cr (VI) ions on pumpkin peel later shifted the IR band at 3440.00 cm^{-1}, 2922.16 cm^{-1}, 2852.75 cm^{-1}, 1736.98 cm^{-1}, 1635.51 cm^{-1}, 1247.42 cm^{-1}, 1156.16 cm^{-1}, 1101.36 cm^{-1}, 1068.70 cm^{-1} as shown in figure 5.

Characterization of adsorbent by (SEM) Sem Electron Microscopy and (EDX) Energy Dispersive X-ray analysis: The SEM and EDX images of the native and Cr (VI) loaded biosorbent are given in figure 6-7 and figure 8-9 respectively. In SEM image the native biosorbent has an amorphous structure with no definable surface. Uneven and rough surface morphology of Cr (VI) loaded adsorbent in comparison with native biosorbent suggests that chromium ions may have deposited as aggregates.

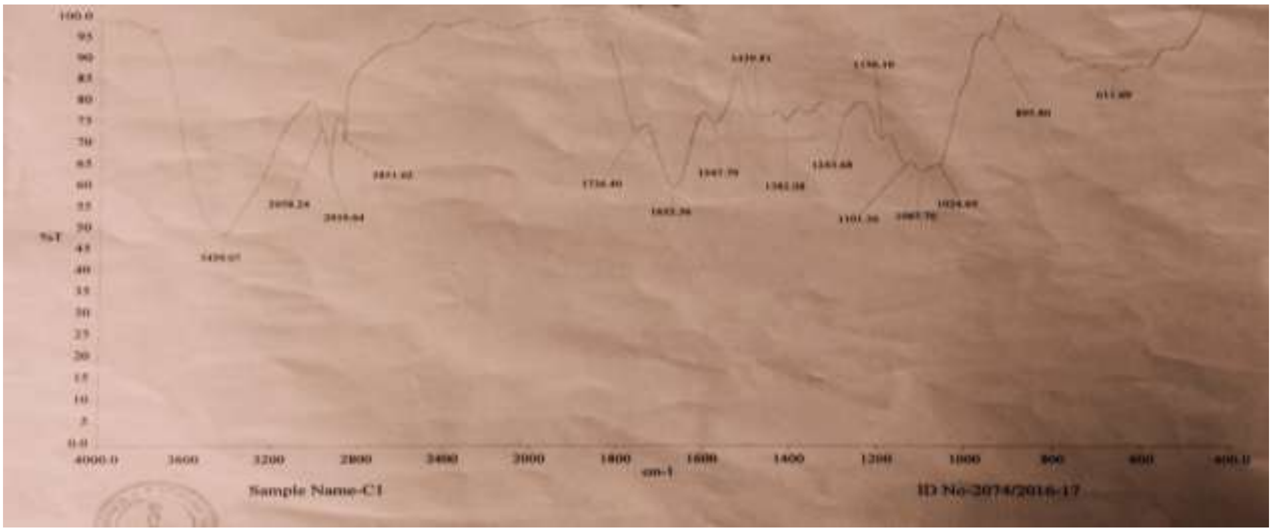

Figure 4: FTIR spectrum of pumpkin peel before adsorption.

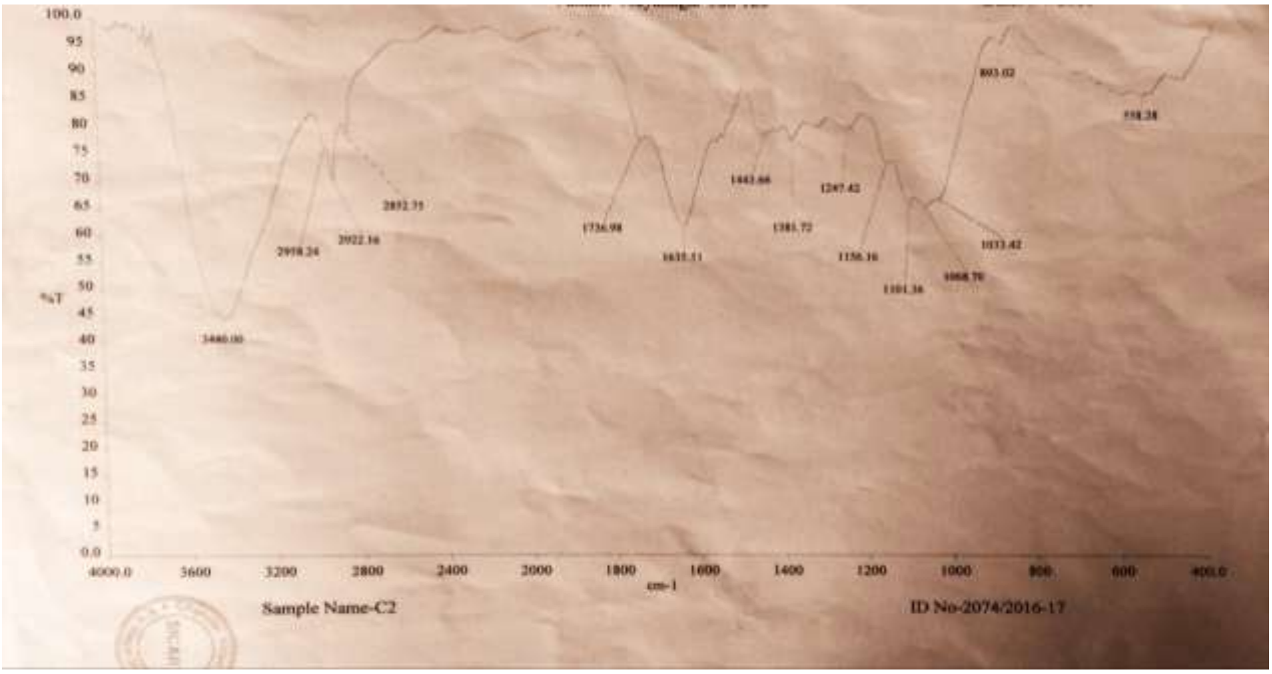

Figure 5: FTIR spectrum of pumpkin peel after adsorption

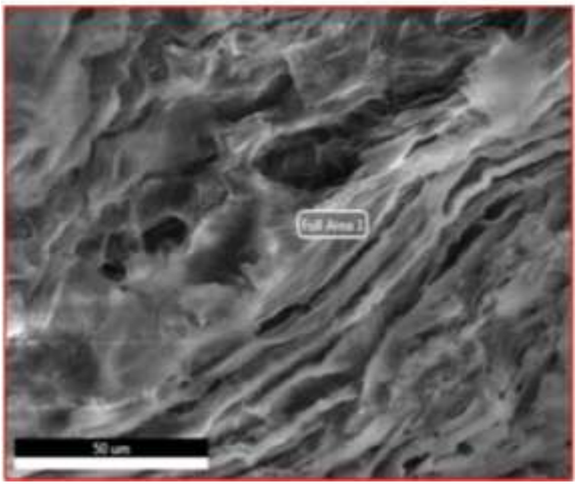

Figure 6: SEM of unloaded pumpkin peel

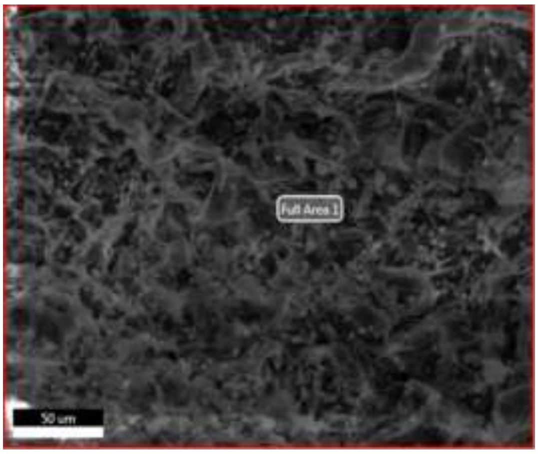

Figure 7: SEM of Cr (VI) loaded pumpkin peel

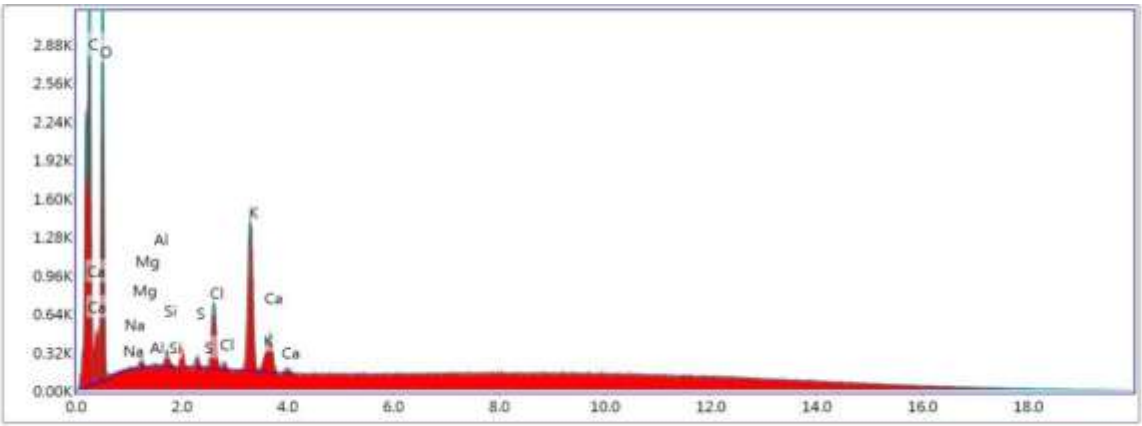

Figure 8: EDX of unloaded pumpkin peel

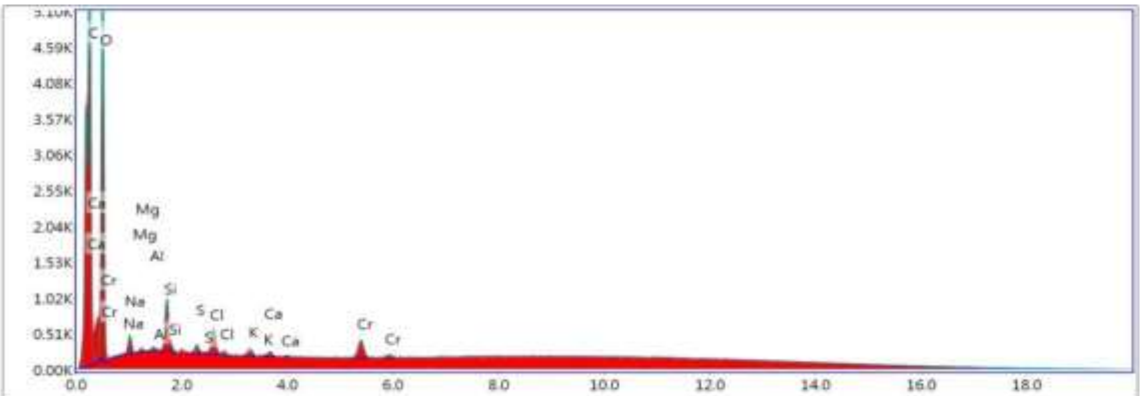

Figure 9: EDX of Cr (VI) loaded pumpkin peel

EDX graph shown in figure 8 shows that the peaks of carbon, calcium and oxygen indicate the presence of –OH and –COOH functional groups in pure lingo cellulosic biomass, having no traces of a chromium peak whereas the EDX data shown in figure 9 shows reduction in calcium peaks and the appearance of chromium ion peak, which indicates the binding of Cr (VI) on the biosorbent.[10]

Adsorption Isotherm: Langmuir and Freundlich models represent the adsorption of metal ion on the solid surfaces. Langmuir model applies to monolayer adsorption and is given by:

$$Ce/Qe = 1/Qo\ K + Ce/Qo$$

where Ce is equilibrium concentration (mg /L) Qe + amount of metal adsorbed (mg/g), Qo and K are Langmuir constant. The plot between Ce/qe and Co is shown in figure 10. The linear plot is obtained which shows that adsorption process obeys Langmuir equation.

Freundlich isotherm model empirical equation can be applied to multilayer adsorption. Freundlich equation is used for non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Freundlich model is given by equation:

$qe = kf\ C_e^n$

where qe is the amount of metal ion sorbed at equilibrium / g of adsorbent (mg /g) Ce is equilibrium concentration (mg /L) and K_f, n are constant.

As shown in figure 11, it was observed that experimental processes are more fitted to Langmuir Model compared to Freundlich. The experimental data of metal ion adsorption as linear regression coefficient values with $R^2 = 0.960$ is for Langmuir model and $R^2 = 0.732$ is for Freundlich model.

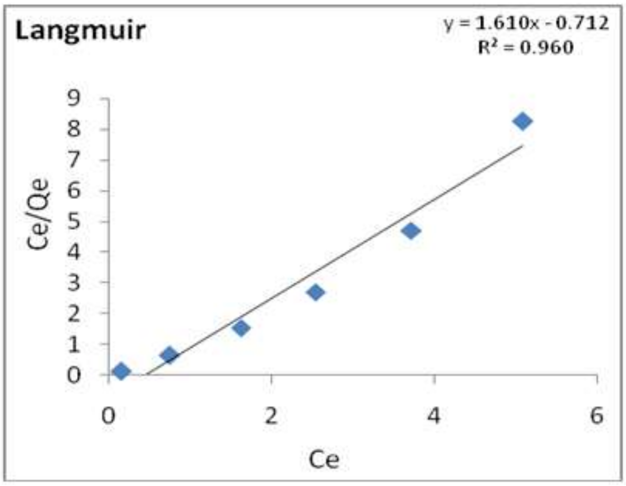

Figure 10: Langmuir Isotherm graph

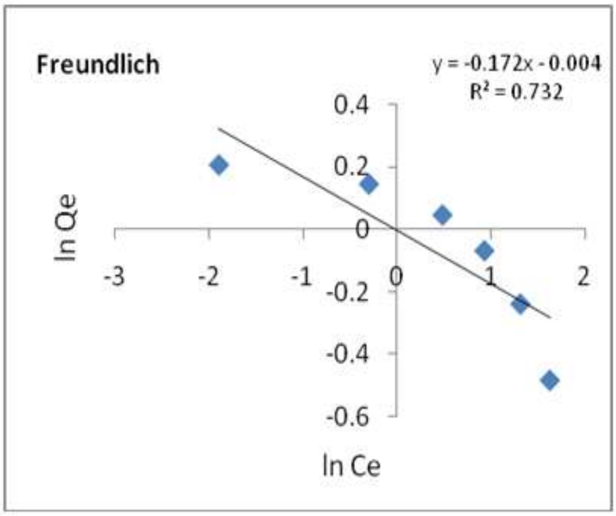

Figure 11: Freundlich Isotherm graph

Conclusion

The removal of heavy metal ion study by pumpkin peel powder a household waste, had been carried out using different parameters like pH, contact time, dose effect and agitation factor and adsorption isotherm kinetics. The data shows that the most effective pH for the removal of Cr (VI) is pH 2.0 with 48.15% removal efficiency whereas maximum adsorption was found in initial 30 minutes of experimentation with 4 gm of biomass and 400 rpm agitation speed.

Langmuir model is in agreement with experimental data of metal ion adsorption with linear regression coefficient value $R^2 = 0.960$ and $R^2 = 0.732$ for Freundlich model showing that the biomass is capable for monolayer adsorption. We can also reuse the material for further adsorption by certain purification process. This biomass is easy to procure as it is a household waste and can be used to remove heavy metals at a cheaper cost in those regions where polluted drinking water is a problem.

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