ABSTRACT:
Due to increase in population coupled with mining, extraction and use of various metals as different industrial and household materials, the load of toxic metal pollution in the environment is increasing. The waste from metallurgical/mining sectors, in general, creates destabilization in the ecosystem, as most of the heavy metal ions are toxic to the living organisms. The demand of chromium has been increasing globally because of its extensive use in various metallurgical, chemical and leather tanning industries due to its various physico-chemical properties. A new low cost, easily available and environment friendly adsorbent was used for removal of hexavalent chromium Cr(VI). The studies on adsorption were conducted by varying various parameters such as contact time, pH, amount of adsorbent, concentration of adsorbate and temperature. Langmuir adsorption isotherm was employed in order to evaluate the optimum adsorption capacity of the adsorbent. The adsorption capacity was found to be pH dependant.

Keywords: Adsorption, Hexavalent Chromium Cr(VI), Effect of pH, Adsorption Isotherm.

1. INTRODUCTION
Water of high quality is essential to human life and water of acceptable quality is essential for agriculture, industrial, domestic and commercial uses. All these activities are also responsible for polluting the water. Billions of gallons of waste from all these sources are thrown to freshwater bodies everyday. The requirement for water is increasing while slowly all the water resources are becoming unfit for use due to improper waste disposal. The task of providing proper treatment facility for all polluting sources is difficult and also expensive, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient. The extensive use of chromium in leather tanning, metallurgy, electroplating and other industries has resulted in higher chromium concentrations in aquatic systems. Chromium and its salts have many industrial uses such as electroplating, alloying, leather tanning, corrosion protection, etc. [1]; therefore, their demand is increasing with time. The waste and effluent streams of chromite mining and processing units contain chromium in two oxidation states, i.e. Cr(VI) and Cr(III), in aqueous solution. As Cr(VI) species is mobile, its oxidizing character is regarded as potentially carcinogenic [2]. On the other hand, Cr(III) hydroxide has limited solubility in the aqueous phase and is thus regarded as a non-dangerous pollutant. As a consequence, these metals are found well above the tolerance limit many a times in aquatic environment. The Cr(VI) is of particular concern because of its toxicity. The recommended limit of Cr(VI) in potable water is only 0.05 mg/ lit [3]. But the industrial and mining effluents contain much higher concentrations compared to the permissible limit. Thus, treatment of the effluent to reduce/remove the pollutant before discharging into the environment becomes important.

Abatement of pollution due to Cr(VI) mainly consists of two main processes: reduction of Cr(VI) to Cr(III) to render it harmless, and removal of Cr(VI) as such. The reduction followed by precipitation technique is widely used for the treatment of wastewater containing Cr(VI), although the process suffers from several drawbacks such as solid–liquid separation and disposal of sludge. Alternate methods are now being developed to treat Cr(VI) contaminated wastewater using various techniques such as
USE OF NATURALLY AVAILABLE LOW COST ADSORBENTS FOR REMOVAL

adsorption, ion exchange, and membrane separation. The membrane system has problems like scaling, fouling, and blocking. The ion-exchange system is uneconomic due to the cost of commercial ion exchange resins. The adsorption technique is economically favorable and technically easy to separate as the requirement of the control system is minimum. In recent years, a number of low-cost non-conventional adsorbents have been used to treat Cr(VI) contaminated wastewater [4–8].

2. EXPERIMENTAL

Adsorption experiments were conducted by varying contact time, adsorbent dose and adsorbate concentration. The experiments were carried out in 100 ml conical flasks and the total volume of the reaction mixture was kept at 50 ml. The pH of Cr(VI) was the highest among them. The percentage adsorption increased with increase in adsorbent dose. The contact time between adsorbate and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of adsorbate and establishment of equilibrium in a short period signify the efficiency of that adsorbate for its use in wastewater treatment.

2.1. Preparation and Characterization of adsorbent

The lemon, orange and sweet lime skin to prepare adsorbent in the form of powder. These adsorbent for removal of hexavalent chromium from the solution. These are collected from various fruit juice centers where it was treated as waste. Collected skin of these fruits and kept it for drying for more than 3 weeks by checking the moisture content of the all skins alternate days. Skin covered with a plastic paper to prevent its contamination. Since these all are citric fruit, the skin of fruit is spongy somewhat. When all the skins get dry, next processes such as grinding, screening took place. After grinding, screening is done by using the last screen 315 micron. This prepared powder is used as adsorbent for the removal of chromium(VI) from the solution.[9]

3. ADSORPTION KINETICS

The kinetics of removal of Cr(VI) is explained in the literature using pseudo first-order kinetics. In order to define the adsorption kinetics of heavy metal ions, the kinetics parameters for the adsorption process were studied for contact times ranging from 1 to 360 minute monitoring the removal percentage of the Cr(VI).

Fig.1 Adsorption kinetics for lemon powder.

Fig.2 Adsorption kinetics for orange powder.

Fig.3 Adsorption kinetics for sweet lime powder.
4. RESULT AND DISCUSSION
Analysis of percentage adsorption versus initial concentration were studied at varying contact time. It was found that the percentage adsorption decreased with increase in initial concentration of the adsorbate. But the uptake capacity increased with increase in initial concentration, which may be due to the availability of more number of Cr(VI) ions in solution for sorption. Moreover, higher initial adsorbate concentration provided higher driving force to overcome all mass transfer resistances of the metal ions from the aqueous to the solid phase resulting in higher probability of collision between Cr(VI) ions and the active sites. This also resulted in higher uptake of Cr(VI) for the given amount of treated adsorbents.[9]

4.1. Effect of contact time on Chromium adsorption (% chromium removal)
Three different adsorbents such as lemon, orange and sweet lime skin powder were taken to compare the efficiency of the treated adsorbent with respect to the each other.

4.2. Effect of chromium concentration on adsorption process
The equilibrium of sorption process is one of the important physico-chemical aspects for the evaluation of sorption process as unit operation. The sorption isotherm is conducted by varying the initial concentration of Cr(VI) only.

4.2.1 Langmuir isotherm for adsorption for lemon powder.

![Fig.5 Langmuir Isotherm for adsorption for lemon powder.](image)

4.2.2 Langmuir isotherm for adsorption for sweet lime powder.

![Fig.6 Langmuir Isotherm for adsorption for sweet lime powder.](image)

4.2.3 Langmuir isotherm for adsorption for orange powder.

![Fig.7 Langmuir Isotherm for adsorption for orange powder.](image)
4.3. Effect of contact time
A plot of percentage adsorption versus adsorption time is shown fig 4 for lemon, adsorption increases linearly with time. At the end of 1 hr, percentage Chromium(VI) removal is 44.45, then there is again decrease in the Chromium removal due to continuous adsorption and desorption process. At the end of 3 to 4 hr there is no significance reduction in chromium concentration. From fig 4, it is seen that the adsorption of chromium(VI) from the solution is maximum for orange powder, then for sweet lime and it is maximum for lemon. All the curves obtained were smooth indicating formation of monolayer on the surface of the adsorbent. In the initial stage, the slope of the plot was one and it decreased with time. It revealed that the rate of uptake was rapid in the early stages but gradually decreased and became constant when equilibrium was reached.

4.4. Effect of Temperature
Temperature has an important effect on the process of adsorption. The percentage of Cr(VI) adsorption was studied as a function of temperature. The decrease in percentage of adsorption with rise in temperature may be due to the desorption caused by an increase in the available thermal energy. Higher temperature induces higher mobility of the adsorbate causing desorption. (HCrO$_4^-$), chromate (CrO$_4^{2-}$), dichromate (Cr$_2$O$_7^{2-}$) and other Cr oxyanions. From the stability diagram of Cr(VI)–H$_2$O System, it was evident that at low pH, acid chromate ions (HCrO$_4^-$) are the dominant species.

4.5. Effect of pH
As the pH increased, there was little increase in the percentage of adsorption and it was maximum at pH 4.5. When the pH is further increased, a sharp decrease in percentage of adsorption was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately lead to the reduction in sorption capacity. When the pH was increased beyond 6.0, a gradual decrease in the percentage adsorption was observed. This might be due to the competition between (OH$^-$) and chromate ions (CrO$_4^{2-}$).[9]. The net positive surface potential of the sorbent decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately led to the lowering of sorption capacity.

5. CONCLUSION
Treated lemon, orange and sweet lime skin powder naturally available adsorbents has been shown in this paper to be an effective for removal of Cr(VI) from aqueous solutions. The equilibrium time is 3 h for the adsorbent having concentration of 30 mg/lit. The maximum adsorption takes place in the pH range of 4.5–6. Decrease in percentage of adsorption with increase in temperature indicates that the process is exothermic in nature and so low temperatures favor the adsorption process. Due to easy availability and high efficiency for removal of Cr(VI), the treated lemon, orange and sweet lime skin powder is an ideal adsorbent for removal of Cr(VI) from aqueous solutions.

**NOMENCLATURE**
X = Amount adsorbed by adsorbent.
$C_e$ = Equilibrium concentration.
$q_e$ = Amount of Cr(VI) adsorbed.

**REFERENCES**
