



## Study on reduction of hexavalent chromium in aqueous solution using GT-Fe<sup>0</sup> nanoparticles

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### ABSTRACT

Cr(VI) is a contaminant in various resources that is used by man in daily life, for e.g. soil ground water, river water, vegetables grown in such soil etc. it is a heavy metal, consumption of which might cause fatality to the consumer. It is seen that iron nanoparticles are able to reduce this Cr(VI) to its trivalent ion Cr(III) which is much less harmful. This article deals with the use of Iron Nanoparticles biosynthesized from green tea (GT) for its possible application in reducing toxicity and pollution caused by Cr(VI). The method used is a batch method where we get a number of similarly proceeding reaction which do not interfere with each other. The decrease in concentration of the standard solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> on addition of iron nanoparticles is used as an indicator of reduction of Cr(VI) to Cr(III). It is seen that the GT Fe-NPs remove Cr(VI) from the solution with good efficiency and may have good future prospects as an antipollution measure.

**Keywords:** iron nanoparticles, hexavalent chromium, reduction, Cr(VI), Cr(III)

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### INTRODUCTION

Hexavalent chromium, Cr(VI), refers to chemical compounds that contain the element chromium in the +6 oxidation state [1]. It is very toxic and mutagenic when inhaled. Cr(VI) has not been established as a carcinogen when in solution, although it may cause Allergic Contact Dermatitis (ACD) [2, 3]. The two environmentally stable oxidation states of chromium, Cr(VI) and Cr(III), exhibit very different toxicities and mobility's. Cr(VI) and Cr(III) compounds differ in their health and environmental effects, with Cr(VI) being far more dangerous. Ingesting small to moderate amounts of Cr(III) is essential to human metabolism, and there is no current evidence that Cr(III) is carcinogenic. In contrast, exposure to Cr(VI) is known to be a serious human health risk [4, 5].

Cr(VI) does not readily precipitate or become bound to components of soil, therefore, Cr(VI) can move throughout aquifers to contaminate groundwater and other sources of drinking water [6,7]. On the other hand, Cr(III) is relatively insoluble in aqueous systems, much less toxic and even essential in human and animal nutrition. The World Health Organization (WHO), the International Agency for Research on Cancer (IARC), and the Environmental Protection Agency (EPA) have determined that Cr(VI) compounds are known human carcinogens.

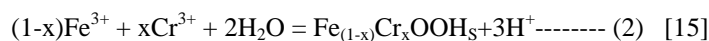
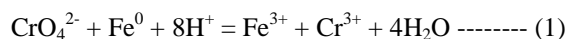
The Lucinda valley in Jaipur District, Orissa, is known for its deposit of chromite ore, producing nearly 98% of the chromite ore in India and one of the prime open cast chromite ore mines in the world (CES, Orissa Newsletter). Due to the seepage of water from the dumped wastes, the nearby water stream gets contaminated with Cr(VI) at a concentration much above the permissible limits. Such incidents happen all over the world. The main diseases include gastrointestinal bleeding, tuberculosis, asthma, infertility, birth defects, and stillbirths. Sources of Cr(VI)

include: industrial operations, including mining, chrome plating, pigments, petroleum refining, leather tanning, wood preserving, textile manufacturing, pulp processing, and electroplating industries [7,8].

Chromium contamination of soil and groundwater is a significant problem worldwide. Cr(VI) tends to be oxidizing in nature, having a tendency to head to the trivalent state., the effluents are treated with ferrous sulfate, chemical reduction, followed by alkaline precipitation or removal by ion exchange; however, the adsorption that suffers from precipitation and additional treatment methods to remove those is to be sorted. There are several methods for the degradation of chromium including biodegradation [9-14]. The one which we chose is iron nanoparticles. Fe<sup>0</sup> is one of the most important reducing agents of Cr(VI). The efficiency of Cr(VI) reduction with GT(Green tea) – Fe Nanoparticles was studied, along with the influence of the starting concentration on the removal efficiency. As time passes the concentration of Cr(VI) in the given sample decreases on addition of iron nanoparticles.

### PRINCIPLE

Iron nanoparticles were biosynthesized and were used for the degradation of chromium present in standards of various concentrations. Chemical reduction is known to remove Cr(VI) rapidly and effectively. Many reactants were employed such as H<sub>2</sub>S, Fe<sup>2+</sup>, and Fe<sup>0</sup>. In this report, we used iron nanoparticles (Fe<sup>0</sup>) to reduce Cr(VI) to Cr(III), iron nanoparticles (Fe<sup>0</sup>) were synthesized from green tea. The reactions of Cr(VI) reduction and co-precipitation of Cr(III) and Fe(III) are:



The main objective of this work is to prepare Fe<sup>0</sup> nanoparticles for the removal of Cr(VI) from any standard solution of chromium. Fe<sup>0</sup> nanoparticles are proved to be best for the degradation as compared to other oxidation states of iron nanoparticles such as Fe<sup>3+</sup>, Fe<sup>4+</sup> or iron fillings. We took K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as a standard reference solution. Iron nanoparticles acts as an adsorbent to which chromium particles adsorb. After the addition of iron nanoparticles in standard solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, we observed that as the time passed the concentration of chromium decreased gradually. The concentration was observed at different time intervals with the help of spectrophotometer.

## EXPERIMENTAL SECTION

### Preparation of Iron Nanoparticles

The preparation of iron nanoparticles can be established by various methods. It can be synthesized chemically by the reduction of ferrous sulphate in aqueous medium or by addition of hydroxides [16], chemical reduction using palladium ion seeds [20]. It is also synthesized by micro emulsion method where the reduction of ferric chloride is done using ammonium borohydride[17]. It can also be prepared from extracts of certain plants and spices [18] or using microbial means for the synthesis of these particles [19]

In this experiment the preparation of iron nanoparticles was done using green tea leaf extracts [21].

Green tea extract was prepared by heating 60.0 g/l green tea until boiling (figure 1). After settling for 1 hour, the extract was filtered using filter paper of pore size 1 to 2 microns. Then, separately, a solution of 0.1 M FeCl<sub>2</sub>·4H<sub>2</sub>O was prepared by adding 19.9g of solid FeCl<sub>2</sub>·4H<sub>2</sub>O in 1 liter of deionized water. Subsequently, 0.1 M FeCl<sub>2</sub>·4H<sub>2</sub>O solution was added to 60.0g/l green tea in 2:3 volume ratio. Following this, 1M NaOH solution was added until the pH was 6.0 and the formation of Green Tea Iron nanoparticles (GT-Fe NPs) was marked by the appearance of intense black precipitate (figure 2). The iron particles were then separated (figure 3) by evaporating water from the iron solution by heating, and then drying it overnight in a fume hood. They appear black and powdery (figure 4) in nature and are stored in 10<sup>-4</sup> M HCl for further usage.

There are other methods for the green synthesis of iron nanoparticles as well [22]. They include synthesis from plant sources such as coffee, banana and common sources such a table salt. Zero-valent nanoparticles can also be done using chelating agents [23].

Figure: 1 Green tea extract



Figure: 2 Iron nanoparticles in precipitate form



Figure: 3 Separation of iron nanoparticles



Figure: 4 Dried nanoparticles



#### Determination of Standard graph for concentration and optical density

Standard solutions were prepared using varying concentrations of the  $K_2Cr_2O_7$ . A stock solution of .05g/100ml of the potassium dichromate solution is prepared in double distilled water. To determine the standard OD vs. Concentration Graph of  $K_2Cr_2O_7$ , the optical density of the standard solutions was measured at 440 nm (the wavelength of 440nm was determined by trial and error method using a stock of .25g/ml, the table for which is given below in table 1).

Table: 1 Trial and error method for determining the wavelength for measuring absorbance of  $K_2Cr_2O_7$  solution

| Wavelength (in nm) | O.D   |
|--------------------|-------|
| 440                | 3     |
| 475                | 2.99  |
| 510                | 0.14  |
| 540                | 0.041 |
| 560                | 0.037 |
| 590                | 0.022 |
| 650                | 0.033 |
| 700                | 0.032 |
| 720                | 0.036 |

Thus the readings are taken at 440nm as it shows maximum absorbance at this wavelength. Following standard procedure an optical density vs. concentration graph is obtained for the concentration range of 0-500  $\mu\text{g/ml}$  of the  $K_2Cr_2O_7$  solution.

#### Experimental Setup

The aim of the experiment is to determine that the concentration of chromium decreases with time when the solution is treated with iron nanoparticles. For this purpose, a stock solution containing 450 $\mu\text{g/ml}$  of potassium Dichromate is made and 1 ml of it is transferred to each of the 7 test tubes. To each of them .001g of the nanoparticles are added. This way we obtain 7 reactions systems that do not interfere with each other but proceed in a similar manner.

Now at different time intervals (0, 10, 20, 30, 35, 40, 45 minutes) one test tube is taken, its contents are filtered to remove nanoparticles and the optical density of the filtrate is measured at 440 nm. The experiment is repeated with different initial concentration of  $K_2Cr_2O_7$ . In this experiment we take 400 $\mu\text{g/ml}$ , 350 $\mu\text{g/ml}$  and 300 $\mu\text{g/ml}$  initial concentrations to test the GT-Fe NPs. The pH of the system is held constant at 6.

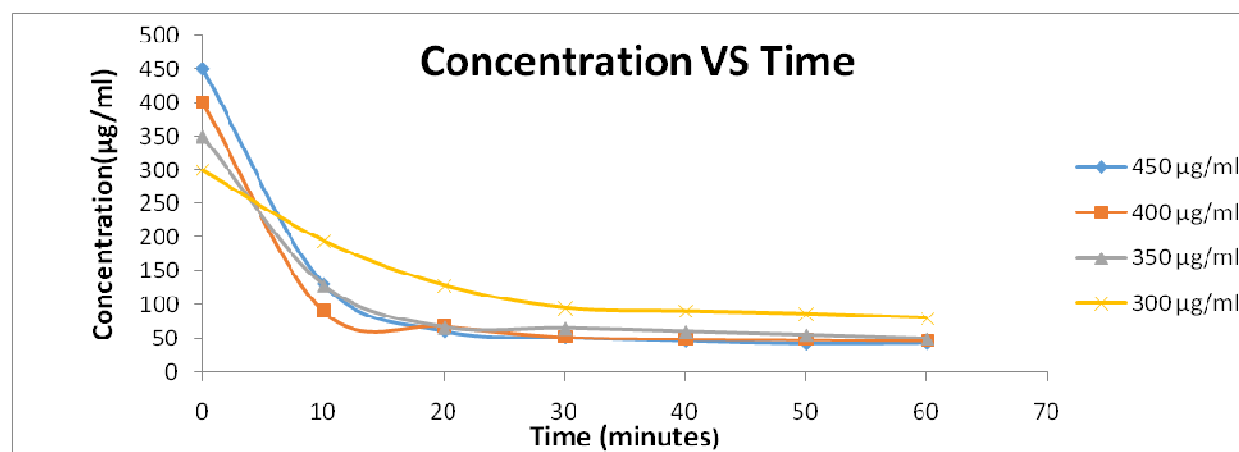
## RESULTS AND DISCUSSION

**Effect of GT-Fe<sup>0</sup> iron nanoparticles on the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>**

The concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is measured at various intervals of 10, 20, 30, 40, 50 and 60 minutes after addition of the GT-Fe<sup>0</sup> iron nanoparticles. It is seen that the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in the solution decreases with time on the addition of the iron nanoparticles. The results are shown in table 2.

**Table: 2 Concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at different time intervals**

| Time (minutes) | OD <sub>450</sub> | Conc. (µg/ml) | OD <sub>400</sub> | Conc. (µg/ml) | OD <sub>350</sub> | Conc. (µg/ml) | OD <sub>300</sub> | Conc. (µg/ml) |
|----------------|-------------------|---------------|-------------------|---------------|-------------------|---------------|-------------------|---------------|
| 0              | 0.623             | 450           | 0.525             | 400           | 0.483             | 350           | 0.418             | 300           |
| 10             | 0.185             | 130           | 0.135             | 90            | 0.182             | 129           | 0.281             | 195           |
| 20             | 0.09              | 60            | 0.112             | 68            | 0.105             | 66.5          | 0.183             | 128.5         |
| 30             | 0.08              | 50            | 0.087             | 52            | 0.097             | 65            | 0.143             | 95            |
| 40             | 0.068             | 45            | 0.077             | 49            | 0.089             | 60            | 0.135             | 90            |
| 50             | 0.057             | 41            | 0.075             | 48            | 0.085             | 55            | 0.13              | 86            |
| 60             | 0.058             | 42            | 0.072             | 46.5          | 0.081             | 49.7          | 0.124             | 80            |

**Figure: 5 Decrease in the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with time on addition of iron nanoparticles**

The figure 5 shows the decrease of the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> due to the degradation of the Cr (VI) ions to Cr (III) by the GT Fe<sup>0</sup>- NP.

**Overall rate of reaction for the process**

If C<sub>i</sub> be the initial concentration, C<sub>f</sub> be the final concentration of the solution and T be the time taken to reach the final concentration then the rate of the reaction can be calculated by the following formulae:

$$R_A = (C_i - C_f) / T$$

**Table: 3 Rate of reaction for all concentrations considered at various intervals**

| Initial concentration (µg/ml) | 450                        | 400                        | 350                        | 300                        |
|-------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Time (minutes)                | R <sub>A</sub> (µg/ml min) | R <sub>A</sub> (µg/ml min) | R <sub>A</sub> (µg/ml min) | R <sub>A</sub> (µg/ml min) |
| 0-10                          | 32                         | 31                         | 22.1                       | 10.5                       |
| 10-20                         | 7                          | 2.2                        | 6.25                       | 6.65                       |
| 20-30                         | 1                          | 1.6                        | 0.15                       | 3.35                       |
| 30-40                         | 0.5                        | 0.3                        | 0.5                        | 0.5                        |
| 40-50                         | 0.4                        | 0.1                        | 0.5                        | 0.4                        |
| 50-60                         | -0.1                       | 0.15                       | 0.53                       | 0.6                        |
| Overall                       | 6.8                        | 5.89                       | 5.005                      | 3.66                       |

Thus we can see from table 3, that the maximum overall rate of reaction, 6.8 µg/ml min is achieved with the highest initial concentration of 450 µg/ml. The rate of reaction achieved in different time intervals decreases with time lapse. Thus the highest rate of reaction is achieved in the first 10 minutes of reaction in all cases considered.

**Efficiency of the process**

The overall efficiency of the reaction can be calculated as below:

$$\text{Efficiency (e)} = [(C_i - C_f) / C_i] * 100$$

Where  $C_i$  is final concentration and  $C_e$  is initial concentration

**Table: 4 The efficiency for all concentrations considered at various intervals**

| Initial Concentration( $\mu\text{g/ml}$ ) | 450            | 400            | 350            | 300            |
|---|----------------|----------------|----------------|----------------|
| Time (minutes)                            | Efficiency (%) | Efficiency (%) | Efficiency (%) | Efficiency (%) |
| 0-10                                      | 71.11          | 77.5           | 63.14          | 35             |
| 10-20                                     | 53.84          | 24.45          | 48.44          | 34.1           |
| 20-30                                     | 16.67          | 23.53          | 2.25           | 26.07          |
| 30-40                                     | 10             | 5.76           | 7.69           | 5.236          |
| 40-50                                     | 8.89           | 2.04           | 8.33           | 4.44           |
| 50-60                                     | -2.4           | 3.125          | 9.63           | 6.97           |
| Overall                                   | 90.66          | 88.375         | 85.8           | 73.33          |

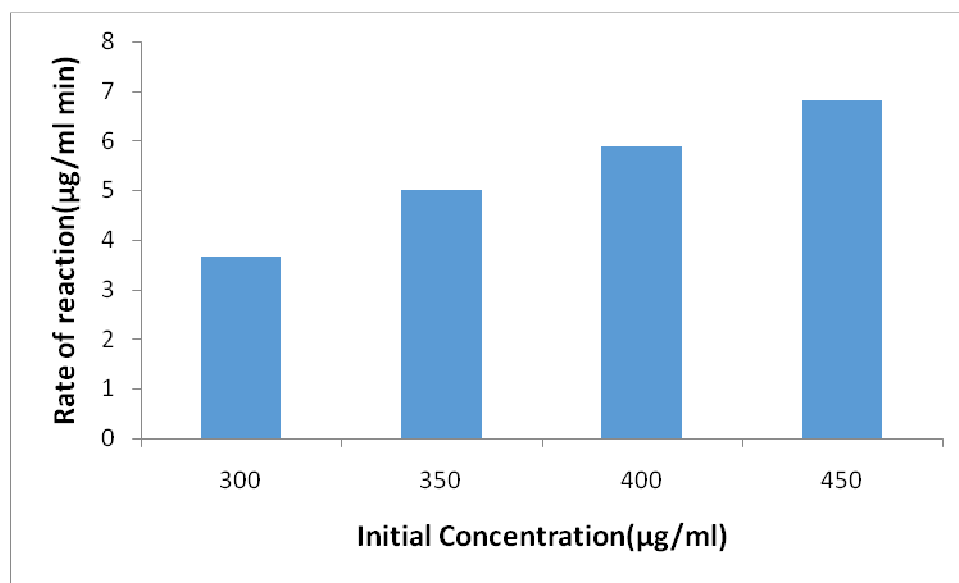
As it is evident from the table 4, the efficiency is maximum in the first 10 minutes of the reaction and then decreases rapidly in the subsequent steps.

**Effect of Initial concentration ( $C_i$ ) on the reaction rate and efficiency**

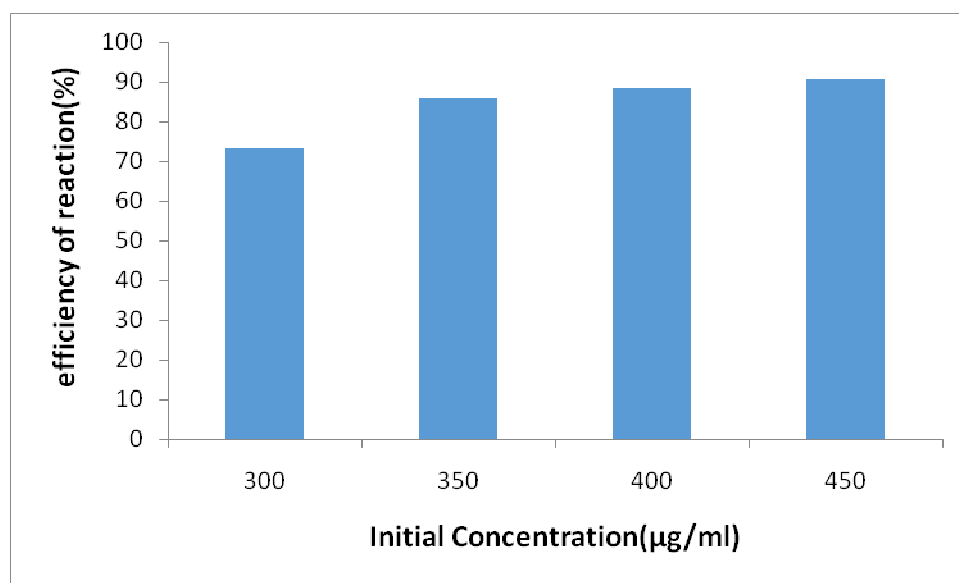
The results obtained show that the reaction is positively related to the initial concentration of Cr(VI) present in the system. With high initial concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$ , the efficiency obtained is much higher than that achieved with the lower concentrations. Even the rate of reaction significantly increases when the initial concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$  is higher. This can be seen in figure 6 and 7.

Higher the initial concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$ , higher is the initial concentration of Cr(VI) ions. Thus lowering of the  $\text{K}_2\text{Cr}_2\text{O}_7$  is indicative of conversion of Cr(VI) ions to Cr(III) ions, thus breaking the compound  $\text{K}_2\text{Cr}_2\text{O}_7$ .

**Figure: 6 Rate of reaction and initial concentration**



**Figure: 7 Efficiency of reaction and initial concentration**



### CONCLUSION

The results show that the GT-Fe nanoparticles synthesized by the given method are very efficient in degradation of Cr(VI) to Cr(III). The results obtained are also in consensus with the existing results [7, 12]. Thus Fe<sup>0</sup> nanoparticles are successfully used to reduce the present Cr(VI) ions to Cr(III). Good process efficiency is obtained when the reaction conditions (pH 6, room temperature etc.) are kept constant during the reaction and a high initial concentration of Cr(VI) ions is present.

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### REFERENCES

- [1] Gerd Anger; Jost Halstenberg; Klaus Hochgeschwender; Christopher Scherhag; Ulrich Korallus; Herbert Knopf; Peter Schmidt; Manfred Ohlinger. Ullmann's Encyclopedia of Industrial Chemistry, Wiley online library, **2000**.
- [2] Savita Verna; Rani Devi. National seminar on Environmental Challenges, **2010**.
- [3] MM Altaf; F Masood; A Malik. *Turkish Journal of Biology*, **2008**, 32, 1–8.
- [4] Gerd Anger; Jost Halstenberg; Klaus Hochgeschwender; Christopher Scherhag; Ulrich Korallus; Herbert Knopf; Peter Schmidt; Manfred Ohlinger. Ullmann's Encyclopedia of Industrial Chemistry, Wiley online library, **2005**.
- [5] Zeid Al-Hourani, Mansour Al-Sarhani, *European Scientific Journal*, **2013**, 9(21), 260.
- [6] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Chromium, U.S. Dept. of Health and Human Services, Atlanta, Georgia, **2000**.
- [7] G.Pinder, *Water Resources Research*, **1973**, 9(6), 1657–1669
- [8] Xu, Xiangrong; Reductive detoxification of hexavalent chromium and degradation of methyl tertiary butyl ether and phthalate esters, The University of Hong Kong (Pokfulam, Hong Kong), Hong Kong, **2005**.
- [9] YT Wang; C Xiao. *Water Research Resources*, **1995**, 29, 2467-74.
- [10] A Prasad Dasand; S Mishra. *Journal of Carcinogenesis*, **2010**, 9(6), 1-6.
- [11] EM Nkhalambayausi-Chirwa; YT Wang. *Water Research*. **2001**, 35(8), 1921-32.
- [12] Vandana Swarnkar, Nishi Agrawal and Radha Tomar, *J. Chem. Pharm. Res.*, **2011**, 3(3), 520-529
- [13] Meby Mary Mathew, Thomas Binitha Mancy and Shaleesha A Stanley, *J. Chem. Pharm. Res.*, **2013**, 5(4):301-309
- [14] S. Thillai Natarajan, R. Jayaraj, P. Jeyasingh Thanaraj and P. Martin Deva Prasath, *J. Chem. Pharm. Res.*, **2011**, 3(2):595-604
- [15] Nguyen Thi Nhung; Nguyen Thi Kim Thuon. *VNU Journal of Science, Natural Sciences and Technology*, **2008**, 24, 233-237.

- [16] P Razvan-Ioan; JU Gheorghita; P Eugenia; O Antoaneta Filcenco; R Rozalia. *Scientific Bulletin*, **2010**, 72(4), 208-218.
- [17] Z Guandong; PI Daniel Cullen; B Ian. Center for Nanomaterials Research at Dartmouth Research Experience for Undergraduates Program, **2008**, 1-2
- [18] P Monalisa; PL Nayak. *International journal of plant, animal and environmental sciences*, **2013**, 3(1), 15-21.
- [19] Abhilash ; K Revati; BD Pandey, *National Metallurgical Laboratory*, **2011**, 34(2), 191-198.
- [20] Kuo- Cheng Huang; Sheryl H. Ehrman. Springer, **2007**, 23(3), 1419-1426.
- [21] T Shahwan; S Abu Sirriah; M Nairat; E Boyaci; AE Eroglu; TB Scott; KR Hallam. *Chemical Engineering Journal*, **2011**, 272 (1), 258-266.
- [22] OV Kharissova; HV Rasika Dias; I Boris Kharisov; B Olvera Perez; Victor M. Jimenez Perez, *Cell press journal*, **2013**, 10 (1) , 215-268.
- [23] Murad Basha Allabaksh, Badal Kumar Mandal, Mohan Kumar Kesarla, Koppala Siva Kumar and ,Pamanji Sreedhara Reddy, *J. Chem. Pharm. Res.*, **2010**, 2(5): 67-74