REMOVAL OF TOXIC METALLIC IONS CR (VI), Cu (II), Ni (II), Co (II) AND Cd (II) FROM WASTE WATER EFFLUENTS OF TANNERIES BY USING *ORYZA SATIVA (RICE) HUSKS*.

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ABSTRACT: *The adsorption of toxic metallic ions from tannery waste water effluents has been determined with the help of biosorbent prepared by chemical treatment of Oryza sativa (Rice) husks. The results show that the H_2SO_4 treated Oryza sativa (Rice) husks absorb higher concentration of metallic ions from tannery waste water. The contact time of waste water effluent with O. sativa husks has also been studied. The adsorption of metallic ions are observed to be more effective by increasing contact time of chemically modified adsorbent i.e. conc. H_2SO_4 treated Oryza sativa (Rice) husks. A comparison of alkali treated O. sativa husks (NaOH) and acid treated O. sativa husks (with conc. H_2SO_4 and conc. HNO_3) are presented. The maximum adsorption has been observed by conc. H_2SO_4 treated O. sativa husks while least adsorption has been shown by conc. HNO_3 treated O. sativa husks. It has been observed that H_2SO_4 treated O. sativa husks at 301K provide best adsorption of toxic metallic ions from tannery waste water.* *Keywords: Adsorption, Oryza sativa (Rice) husks adsorbent, Renewable sources, Conc.H_2SO_4, NaOH, and Conc.HNO3*

1. INTRODUCTION

Wastes are most often considered as a substitute source of energy, when it cannot be recycled. So, there is a great scrutiny in the proper management of wastes aa a s resource of beneficial materials [1,2]. Many toxic and potentially carcinogenic metals, like Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) are present in leather industries. These heavy metals may be different in concentration from one another. The other metals can also be present in tanneries and leather industrial effluent; like Ca, K, Mg, Fe, Mn, Pb and Zn [3]. The existence of heavy metallic ions like Cr [4], Cd Cu, Co, Ni, [5] can have an adverse effect on the human health [6]. These heavy metallic pollutants can enter in to seed coat then reach to fruits easily if heavy metals contaminated soils are used for the production of crops. Through food chains these toxic metallic ions are become the part of our body as well. Furthermore the heavy metals are said to be biodegradable and start accumulating in living organisms [7].

Pakistan is considered as the major supplier of leather finished products to the Europe and rest of the world market. Pakistan has a world's largest leather shoe manufacturing base (the eighth largest) [8]

Although many common methods are used for the removal of theses toxic metallic ions, but biosorption method has proved to be most effective, attractive and innovative method for removal of toxic metallic ions from tannery effluent. Recently, research has been focused on the evolution of low-cost adsorbents for the treatment of wastewater effluent. [9 , 10]. For this purpose a search for a cheaper and easily available adsorbent has led to the investigation of materials of industrial byproducts as well as agricultural products which are considered as potential metal biosorbent. The application of these low cost adsorbent for the treatment of wastewater prove it more valuable [11]. A variety of materials are being tested which includes *Arthrobacter* sp. and a *Bacillus* sp. Coal [12] , maize (*Zea mays*) leaf [13], palm kernel shell crushed shell [14], *streptomyces sp.* [15], Water hyacinth (*Eichhornia crassipes*) [16], chitosan [17 , 18], palm kernel shell crushed shell [19], Rice husk [20,21], saw dust [22, 23] different fruit's peels like a banana peel [24] pomegranate peel [25] etc. Some adsorbents were passed through different physical and chemical treatment to enhance their efficiency. Phosphoric acid modified rice husk was increased the adsorbing efficiency of rice husk for the removal Chromium [26]. The adsorption of hexavalent chromium from aqueous solution onto formaldehyde treated sawdust and charcoal of sugar cane begasses was also determined at different pH values [27]. Chemically modified pomegranate peels are effectively used for removal of lead (II) and copper (II) from aqueous solutions [28] The objective of the present study is to investigate the biosorption of toxic metallic ions from tannery waste water by using chemically modified *Oryza sativa* husks. The adsorption capacity of these adsorbents was carried out by using batch experiments. The influence of contact time was also studies and the experimental data obtained were evaluated.

2. EXPERIMENTAL WORK

2.1. Materials

Potassium dichromate, copper sulphate, nickel carbonate, cobalt chloride and cadmium chloride has been used for the preparation of stock solutions of 60 ppm for Cr (VI) and 50 ppm for other metals i.e. Cu (II), Ni(II), Co(II) and Cd(II) in distilled water separately. 0.1 N solution of sodium hydroxide, 0.1 M sulphuric acid and 0.1 M nitric acid were also used for the chemical treatments of *Oryza sativa* husk. All experiments were conducted to find out the parameters for the extraction of toxic metallic ion from the sample solution by using Analytical Balance ER-120A, Air Drying Oven 108 L., Orbital Shaker OS-1/02, Muffle Furnace-1473K HTMF-1/07, U.V. Spectrophotometer Beckman Model DB-GT and Atomic Absorption Spectrometer (Aanalyst 100)

2.2. Preparation of Biosorbents

The *O. sativa husks* were crushed washed with distilled water and dried in open air. The final drying was carried out in air dryer at 338 K. Adsorption of metal ion by *O. sativa* husks increases with increase in temperature because as temperature increases, the attractive forces between biosorbent surface and metal ions are weakened and sorption decrease [29]. When

the whole material was cooled down, then divided into four portions. One portion was kept untreated and labeled as "Raw". The second portion was soaked in the solution of 0.1 N sodium hydroxide (CP-1), third portion was dipped in 0.1 M solution of sulphuric acid and marked as CP2. While the fourth portion was soaked in 0.1 M nitric acid (CP-3). All the apparatus was kept for 24 hours. The given materials were then dried before further use.

2.3. Experiments of Biosorbents

Untreated and treated adsorbent (*O. sativa* husks) were used for the removal of toxic metallic ions *i.e.*, Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) commonly found in tannery effluents by making their standard solutions *i.e.* 60 ppm $K_2Cr_2O_7$, 50 ppm $CuSO_4$, 50 ppm $NiCO_3$, 50 ppm $CoCl_2$ and 50 ppm $CdCl_2$ respectively. 50 ml of Standard solution of $K_2Cr_2O_7/CuSO_4/NiCO_3/CoCl_2/CdCl_2$ + sample of biosorbent were taken in six different 100ml of conical flasks and agitated them on orbital shaker for homogenization at 150 rpm for one hour. The samples then filtered and kept safe for further use. The particle size and weight of the sample/biosorbent were calculated and reported in table 1. The best selected adsorbent i.e. CP2, was then mixed with the tannery effluents. The percentage removal of toxic metallic ions was calculated with the help of following formula

$$\%\,Removal = \frac{C_o - C_i}{C_i} \times 100$$

Where C_0 is initial concentration of toxic metallic ions and C_i is the final concentration of toxic metallic ions.

2.4. Preparation of working standards

The working standards were prepared by taking 5ml of $K_2Cr_2O_7$ filtrate in 50 ml of measuring flasks. 1ml of DPC solution and 1ml of O-phosphoric acid were mixed with them. Pink color was developed in case of $K_2Cr_2O_7$. The solutions were level by adding distilled water mixed the solutions gently, all flasks were shaken carefully for a max period of 5 minutes. Pink color that formed as a result of the reaction between Chromium (VI) and 1, 5-diphenyl carbazide in acidic medium, was measured by using UV- Spectrophotometer at fix wavelength i.e. 549nm. The same procedure was used for tannery effluents at the same wavelength i.e. 549nm and their absorbance were calculated with the help of U.V. Spectrophotometer (Beckman Model) which was then converted into concentration by following Beer Lambert Law which resulted in the formation of different color complexes. 10ml volume of each filtrate of other metallic ions [Cu (II), Ni (II), Co (II) and Cd (II)] was placed in 50 ml of different measuring flasks. All flasks were shaken gently and were subjected to atomic absorption spectrometer (Aanalyst 100) to measure the absorbance of Cu (II), Ni (II), Co (II) and Cd (II) at wavelengths of 324nm, 487nm, 416nm, 375nm respectively. Although it can provide reading in concentration directly but we can also calculate it by applying Beer Lambert Law for the conversion of absorbance into concentration and percentage adsorption were calculated by the same method as discussed above.

3. RESULTS AND DISCUSSION:

The study showed that *O. sativa* (Rice) husks was good biosorbents for adsorbing large quantity of Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) ions. The result shows that *O. sativa* (Rice) husks have an influence on the absorbance of relative metals. The chemically activated *O. sativa* (Rice) husks were used for absorption purposes. Then it was passed through different level of treatments to check changes in efficiency. It was observed that *O. sativa* (Rice) husks showed maximum absorption *i.e*. 94.89% - 95.30% for selected metals *i.e*. Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II). There was an appreciable increase in absorption capacity when given at different treatments *i.e.* NaOH, H_2SO_4 whereas the same absorption capacity was decreased when it was treated with HNO_3 treated *O. sativa* husks. For Cr (VI), the absorption capacity was increased from 95.3 % to 99.27 % with conc. H_2SO_4 and 98.85% with NaOH while with HNO_3, it decreased from 95.3 % to 73.97 % (figure 2). The H_2SO_4 treated *O. sativa husks* > NaOH treated *O. sativa* husks >untreated *O. sativa* husks > HNO_3 treated *O. sativa* husks.

The second metal *i.e*. Cu (II) was passed through untreated *O. sativa* husks. The percentage absorption was then 94.93%. This percentage was decreased when the same concentration of standard solution of Cu (II) was treated with HNO_3 treated *O. sativa* husks *i.e.* 72.14 while 97.73% and 99.18% absorption was observed when the same concentration of standard solution of Cu (II) was treated with NaOH treated *O. sativa* husks and H_2SO_4 treated *O. sativa* husks respectively. When 50 ppm standard solution of Ni (II) was treated with untreated *O. sativa* husks 95.02% absorption was observed. This percentage absorption increased to 96.91% by using NaOH treated *O. sativa* husks and to 99.30% by using H_2SO_4 treated *O. sativa* husks. Same pattern was observed for Co (II) and Cd (II).

3.1. Effect of Biosorption on Tannery Effluent

There are about 200 tanneries in Kasur and most of them are located in Niaz Nagar which is becoming the target area of creating pollution and causing different diseases in a particular area [30]. As far as tanneries are concerned, they are generating thousands of metallic ions per day and these substances are becoming the part of our environment as well. There is a great need to adopt such methods that can create less toxicity over there and people will remain safe from different diseases. Use of hazardous chemicals is the main source of pollution especially in drinking water. The water is basically used for the purpose many purposes in tanneries i.e. Cleaning the hides or skin etc. Tannery waste water is extremely polluted in terms of heavy metals like Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) [3, 4.5.6]. The selected samples were then treated with 10 samples of waste water which were gathered from 10 different tanneries of Kasur. According to National Environmental Quality Standard (NEQS) the absorbance or concentration of heavy metals should be in the range of 0.008-0.05 or 0.015-0.09 ml/l. Absorbance if exceeds 0.05/0.09mg/l then it results to a great damage in the environment [31]. In this study, best adsorbent was obtained by the treatment of *O. sativa husks* with the H_2SO_4. The absorbance before and after treatment of H_2SO_4 treated *O. sativa* husks that was found in the tanneries of Kasur, is reported in Figure No. 3 and % removal (Figure No. 4) shows the tremendous change before and after treatments with chemically modified *O. sativa* husks.

3.2. Effect of Contact Time

The removal of Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) ions increases with time and attains saturation in about 5 hours. Figure No. 5 (a, b, c, d) represents the percent removal of Cr (VI), Cu (II), Ni (II), Co (II), Cd (II). The five metals showed a fast rate of biosorption during first hour of the sorbate-sorbent contact and rate of the percent removal becomes almost insignificant due to a quick exhaustion of the adsorption site. The rate of percent removal of metal is more in the beginning on account of a greater surface area of the adsorbent being available for the adsorption of the metals. The tremendous change of adsorption for all other unknown metals that were found in tannery effluent with respect to contact time was also measured (Figure No.6).

4. CONCLUSION:

Chemically treated *O. sativa husks* with NaOH and chemically treated *O. sativa* husks with H_2SO_4 shows an increasing trend in case of Cr (VI) removal whereas the same adsorbent when treated with HNO3, it shows the decreasing trend. The similar increasing as well as decreasing trends were also observed for other metallic ions Cu (II), Ni (II), Co (II) and Cd (II). It is further concluded that biosorption of Cr(VI), Cu (II), Ni(II), Co(II) and Cd(II) with pomegranate membranes/peels follow the following trend in terms of removal efficiency : The H_2SO_4 treated *O. sativa husks* > NaOH treated *O. sativa* husks >untreated *O. sativa* husks > HNO_3 treated *O. sativa* husks. The percentage absorption has been found an increasing function of contact time.

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APPENDICES

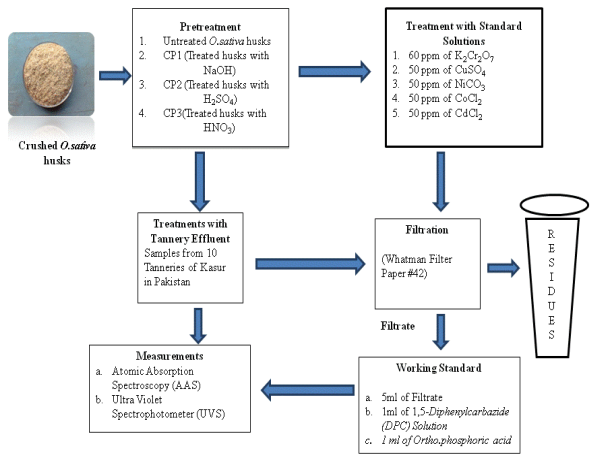

Figure 1. A schematic representation of different steps for the removal of toxic metallic ions Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II) from waste water effluents of tanneries by using *O. sativa* (Rice) husks

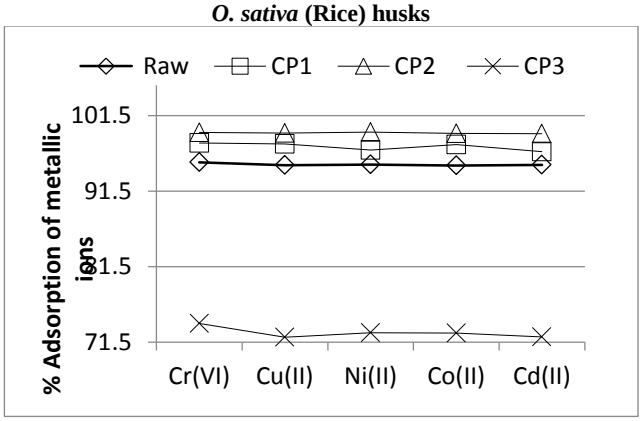

Figure 2. Percentage absorption of metals on chemically treated *O. sativa* husks.

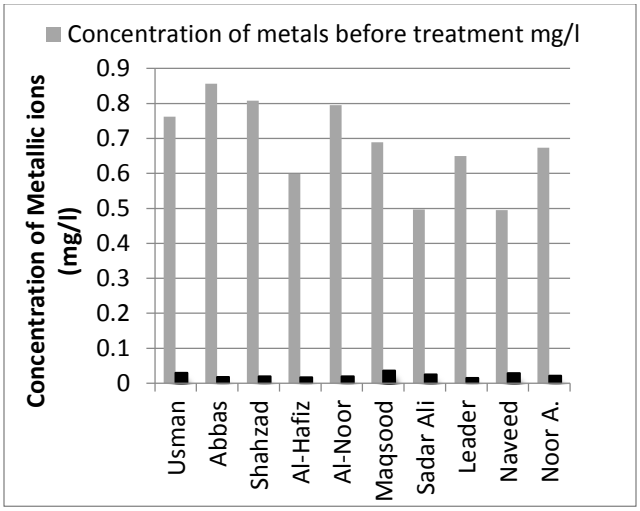

Figure 3. The absorbance of metals in effluent of tanneries of Kasur before and after treatment of biosorbent

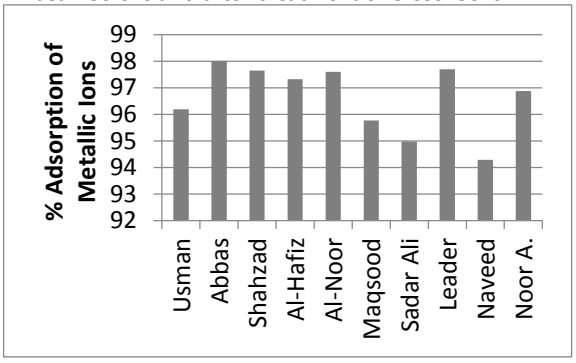

Figure 4. The Percentage Adsorption of metals from the effluent of tanneries of Kasur

a)

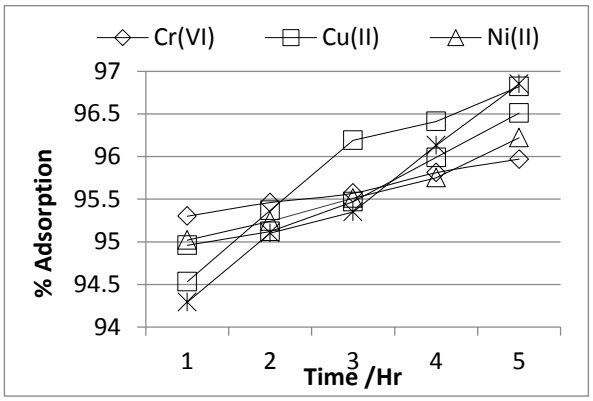

Figure 5(a). The experimental data of % removal efficiency of heavy metals on biosorbent (Raw) surface as a function of time.

b)

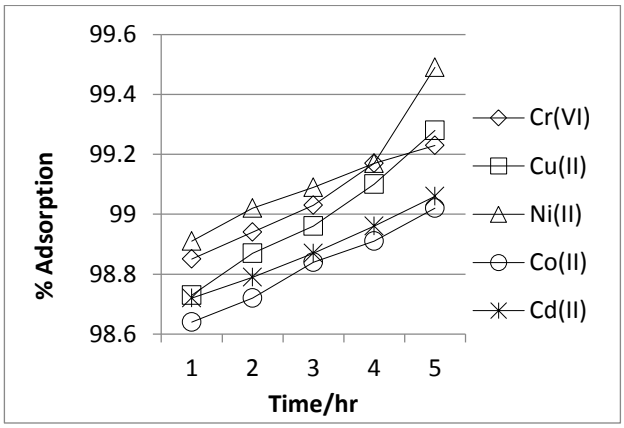

Figure 5(b). The experimental data of % removal efficiency of heavy metals on CP_1 biosorbent surface as a function of time.

(c)

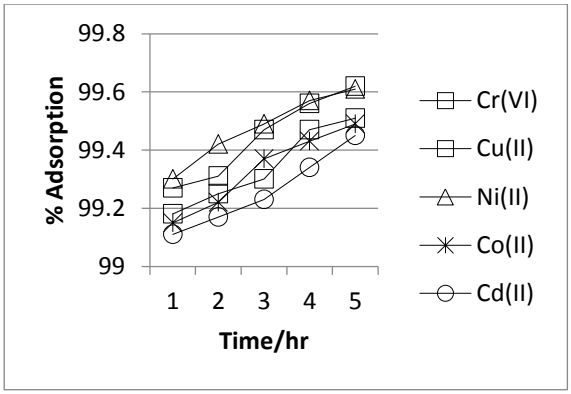

Figure 5 (c). The experimental data of % Adsorption of heavy metals on biosorbent (CP2) surface as a function of time.

(d)

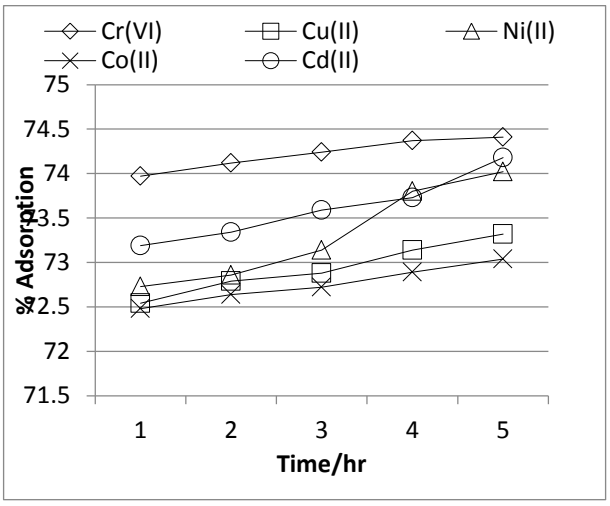

Figure 5(d). The experimental data of % removal efficiency of heavy metals on CP_3 biosorbent surface as a function of time.

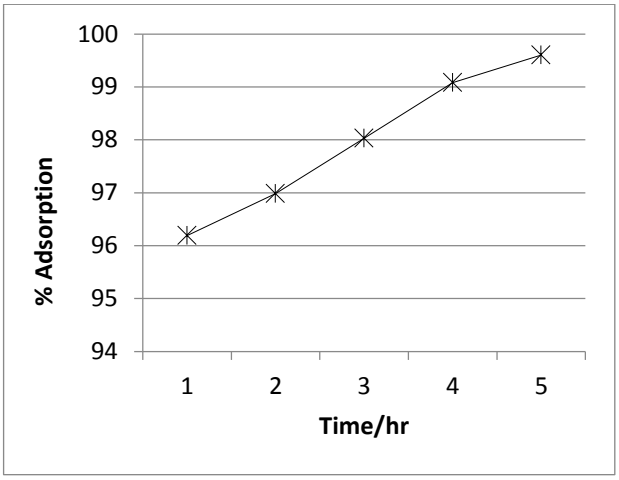

Figure 6. Effect of contact time on the removal of heavy metals of Tanneries.

Table 1: Particle size and weight of biosorbent taken for treatment

		Weight of the samples taken for 50ml of standard solutions in ppm at different wavelength				
Sample No.	**Particle Size in nm**	**60 $K_2Cr_2O_7$ at 549nm**	**50 $CuSO_4$ at 324nm**	**50 $NiCO_3$ at 487nm**	**50 $CoCl_2$ at 416nm**	**50 $CdCl_2$ at 375nm**
1	10-100	5.0234g	5.0596g	5.0425g	5.0372g	5.0821g
2	10-100	5.0476g	5.0651g	5.0329g	5.0482g	5.0986g
3	10-100	5.0391g	5.0467g	5.0521g	5.0630g	5.0576g

Table No: 2: Percentage Absorption of metals [Cr (VI), Cu (II), Ni (II), Co (II) and Cd (II))] by using *Oryza sativa* husks

Serial No.	Treatments	PERCENTAGE ABSORPTION OF DIFFERENT METALS				
		Cr(VI) %	Cu(II) %	Ni(II) %	Co(II) %	Cd(II) %
1	**Un treated** (Raw)	95.30	94.93	95.02	94.89	94.96
2	**CP1** (NaOH)	98.85	97.73	96.91	98.64	98.72
3	**CP2** (conc.HNO_3)	99.27	99.18	99.30	99.15	99.11
4	**CP3** (conc.HNO_3)	73.97	72.14	72.73	72.68	72.19

TABLE No. 3: Percentage Removal of Heavy Metals by using Physico-chemically treated Pomegranate Membranes/Peels

Sample No.	Name of Tannery	Concentration of metals before treatment mg/l	Concentration of metals after treatment/mg/l	% Removal of metals
1	Usman	0.762	0.029	96.19
2	Abbas	0.856	0.017	98.01
3	Shahzad	0.807	0.019	97.64
4	Al-Hafiz	0.598	0.016	97.32
5	Al-Noor	0.794	0.019	97.60
6	Maqsood	0.689	0.036	95.77
7	Sadar Ali	0.471	0.025	94.97
8	Leader	0.649	0.015	97.69
9	Naveed	0.495	0.028	94.28
10	Noor Ahmed	0.673	0.021	96.88

Table No. 4: Change in Concentration/Percentage Absorption of metals in Tannery Effluent with respect to time

S. No.	Time	Concentration in mg/l	% Absorption
1	1.00 hrs	0.029	96.19
2	2.00 hrs	0.023	96.98
3	3.00 hrs	0.015	98.03
4	4.00 hrs	0.007	99.08
5	5.00 hrs	0.003	99.60