

PREPARATION OF ION EXCHANGE ACTIVATED CARBON FROM PADDY HUSK AND PRELIMINARY STUDIES ON THE REMOVAL OF MERCURY (II) & CHROMIUM (VI) FROM WATER AND WASTE WATER

K.PAVITHRA
ASSISTANT PROFESSOR
ENVIRONMENTAL ENGINEERING
Sengunthar Engineering College, Tiruchengode, Nammakal, Tamilnadu, India

ABSTRACT

Large quantities of water are used by many industries. The water quantities used by industries are difficult in nature. Water pollution is a situation in which a contaminant is introduced into aqueous system more than the permissible level. Many methods are available for the removal of heavy metals from water and wastewater. Among various physico

chemical processes available adsorption seems to be a promising one because it is capable of removing both organic and inorganic materials whenever activated carbon is employed since a commercial activated carbon are costly from waste organic agricultural materials such as bagasse, paddy husk etc. In recent years, the natural river systems are polluted by heavy metals such as Hg, Ni, Co, Cu, Zn

and Pb etc. for example mercury (Hg) is utilized in many measuring instruments and also used as a cathode in chlor alkali plant producing sodium hydroxide Here am going to prepare activated carbon

from paddy husk and remove heavy metals as mercury from both water and waste water. In the phase – I of the project an ion exchange of carbon with paddy husk will be prepared as tested for the removal of Hg(II) ions from water and wastewater. Therefore in the phase-II of the project studies on Cr(VI) removal by rice husk carbon.

AIM AND SCOPE OF THE PRESENT WORK

- The aim of the present project work is to prepare an activated carbon from a paddy husk an agriculture waste material by suitable methods.
- It is proposed to make use of acid process for the preparation of acid carbon from paddy husk.
- The material thus prepared from paddy husk will be powdered well and sieved to 250- 300 (ASTM) as applied for the removal of Hg(II) from water as wastewater.
- The carbon thus prepared will be subjected to carbon testing process to understand the characteristics of carbon.

- During the adsorption process, Hg(II) removal by paddy husk carbon will be investigated of H, carbon dose and isotherm.
- The material will be checked for wastewater treatment of Hg(II) generated from industries.

Therefore in the phase – I of the project an ion exchange of carbon with paddy husk will be prepared as tested for the removal of Hg(II) ions from water and wastewater.

During the phase-I of the project, paddy husk carbonized under 800°C was utilized for the removal of Hg(II). In the phase-II of the project work it is proposed to make use of the same carbon for the removal of Cr(VI).

1. The paddy husk powdered from the market was washed well with water to remove any extraneous material and charcoal was prepared at 400°C after treatment with H₂SO₄. The charcoal was subjected to activated carbon treatment at 800°C. This carbon was utilized for the removal of Cr(VI) from water.

2. It is proposed to find at the optimum time for removal of Cr(VI) by batch experiments.

3. It is proposed to find at the optimum Ph, optimum carbon dosage and isotherm studies.

4. It is proposed to make use of powdered activated carbon (PHC) for the removal of Cr(VI).

5. The carbon characteristics already have been determined and reported in the phase-I of the project.

6. Finally a synthetic wastewater will be tested for the removal of Cr(VI) using paddy husk carbon (PHC).

REVIEW OF LITERATURE

Mercury is one of the most toxic substances known to humans. It has been introduced into the human environment and has also been widely used in medicine. Since circumstantial evidence exists that the pathology of Alzheimer's disease (AD) might be in part caused or exacerbated by inorganic mercury, we conducted a systematic review using a comprehensive search strategy. Studies were screened according to a pre-defined protocol. Measurements of mercury levels in blood, urine, hair, nails, and cerebrospinal fluid were inconsistent. In vitro models showed that inorganic mercury reproduces all pathological changes seen in AD, and in animal models inorganic mercury produced changes that are similar to those seen in AD. Our mechanistic model describes potential causal pathways. As the single most effective public health primary preventive measure, industrial, and medical usage of mercury should be eliminated as soon as possible. (J. Mutter, A. Curth, J. Neumann, and H. Walach, 2010)

Mercury is a toxic, bioaccumulating trace metal whose emissions to the environment have increased significantly as a result of anthropogenic activities such as mining and fossil fuel combustion^{1, 2}. Several recent models have estimated that these emissions have increased the oceanic mercury inventory by 36–1,313 million moles since the 1500s^{2, 3, 4, 5, 6, 7, 8, 9}. Such predictions have remained largely untested owing to a lack of appropriate historical data and natural archives. Here we report oceanographic measurements of total dissolved mercury and related parameters from several recent expeditions to the Atlantic, Pacific, Southern and Arctic oceans. We find that deep North Atlantic waters and most intermediate waters are anomalously enriched in mercury relative to the deep waters of the South Atlantic, Southern and Pacific oceans, probably as a result of the incorporation of anthropogenic mercury. We estimate the total amount of anthropogenic mercury present in the global ocean to be 290 ± 80 million moles, with almost two-thirds residing in water shallower than a thousand metres. Our findings suggest that anthropogenic perturbations to the global mercury cycle have led to an approximately 150 per cent increase in the amount of mercury in thermocline waters and have tripled the mercury content of surface waters

compared to pre-anthropogenic conditions. This information may aid our understanding of the processes and the depths at which inorganic mercury species are converted into toxic methyl mercury and subsequently bioaccumulated in marine food webs.(

Carl H Lamborg, Chad R. Hammerschmidt,2014)

This study investigates Hg(II) removal onto binary mixed mineral sorbents from simulated mercury contaminated water, in zinc sulfide related sulfidic-anoxic condition. The sorbents used were zinc sulfide, kaolinite, montmorillonite, goethite, and their mixtures. Batch mode studies at room temperature demonstrate a linear increase in mercury sorption with increase in pH up to pH 4, gradually flattening for the rest of pH investigated. Increase in Co-particle concentration does not reveal a corresponding increase in sorption of mercury. Except for zinc sulfide, kaolinite and montmorillonite, increase in residence time could not lead to a corresponding increase in mercury removal. The complex behavior of mineral-mercury interaction under sulfidic-anoxic condition may be attributed to increased hydroxylation of the mineral surface and the presence of thiol (=S-H) and hydroxyl (=Me-OH) functional groups and reactive sites on

surface of metal sulfides.(Ageing D.E. Egirani, 2014)

MATERIALS AND METHODS

Materials For Hg(II) & Cr (VI)

Removal:

1. APPARATUS:

1. Systronics spectrophotometer with 1.0 cm quartz cells for colour measurement.
2. pH meter (Systronics) with combined glass electrodes for the Ph measurement.
3. Horizontal mechanical shaker for equilibrium studies.
4. Systronics digital spectrophotometer with quartz cells for colour measurement.
5. Elico digital pH meter with combined glass electrodes for pH measurement.
6. Rotary mechanical shaker for equilibration studies.

METHODS:

BATCH EXPERIMENTS:

Batch experiments were conducted in polythene bottles of 300 ml capacity proved with screw caps. The polythene were washed well with chromic acid before and after use. 100 ml of the solution containing 10 mg/l of ions under investigation were taken in the bottle. After the addition of carbon, the bottles were equilibrated for specific periods of time in a rotary mechanical shaker. At the end of the equilibration period, the solutions were filtered, using G- 3 crucibles if necessary and the

concentration of Hg (II) & Cr (VI) ions were established by spectrophotometry.

ANALYTICAL PROCEDURE:

DETERMINATION OF MERCURY

A suitable aliquot containing not more than 25 µg of mercury was transferred into a 25 ml volumetric flask. 5ml each, of 0.05M EDTA, buffered potassium iodide, and rhodamine 6G solutions were added with mixing followed by 1ml gelatin. The solution was diluted to mark with water and the absorbance in 1cm cells was measured at 575nm with reference to a reagent blank. A calibration graph in the range of 5- 25 µg of mercury was prepared by following the above procedure and the concentration in the sample aliquot was established

DETERMINATION OF

HEXAVALENT Cr (VI) (59)

A suitable aliquot of the sample solutions containing not more than 50 mg of Cr (VI) in a final volume of 40mL was transferred with a 50mL standard flask. 2.5 mL of diphenyl carbazide reagent was added and mixed well. The solution was diluted upto the mark with distilled water. The absorbance was measured against a reagent blank at 540 nm using 1.0 cells. Measurements were completed within 15 minutes after mixing of the reagents and after allowing a

standing time of 5 minutes. A calibration graph in the range of 10-50 mg of Cr (VI) was prepared by following the above procedure and the concentration of Cr(VI) in the sample aliquot was established.

4.4 IMPORTANCE OF CARBON CHARACTERISTICS:

The use of carbon in wastewater treatment applications is primarily due to the enormous capacity for the removal of contaminants by adsorption process. Consequently high surface area is desirable. Hardness (or) abrasion resistance is also importance in the case of regenerable carbon, as it must undergo alternate cycles of exhaustion and reactivation with minimum materials loss.

Moisture content through do not affect adsorptive power, dilutes the carbon and therefore necessitates the use of the additional weight of carbon to provide the required weight.

Ash content generally gives idea about inorganic constituent associated with carbon. In any case, the actual amount of individual inorganic constituent will vary from one grade to another as they are mainly derived from source materials or from activating agents during its preparations.

The apparent density may be regarded as a measure of the activity of the carbon in the case of granular

activated carbon; it also gives an idea about the space that would be occupied by the material in the column. When the carbon is contacted with water (or) wastewater (or) acidic wastewater, leaching impurities from the carbon should not be significant so that the desired quality of the effluent is not altered. Consequently, tests pertaining to matter soluble in water and acid present in carbon assumes important.

The pH of the most commercial carbon is due to inorganic ingredients originating in the sources materials and the actual value of pH will be determined by condition under which the carbon is subjected to use. The capacity of the carbon with respects to removal of colour and organics are generally revealed by methylene blue and phenol number test. The determination of iron is considered important only in those instances where release of iron is objectionable.

PREPARATION OF CARBON:

About 50 g of well washed paddy husk was dried in sunlight. This material was treated under acid process to prepare the ion exchange carbon. 50g of paddy husk was missed with concentrated sulphuric acid under the ratio 1:2. After mixing thoroughly, the material was placed in the air oven for 24 hours under the temperature of 140- 160° C. after this, the material was thoroughly washed with

tap water to remove any excess acid and then dried in the oven for 110° C. the dried material was powdered and the particle size over the range of **250 – 300** was used for determination of carbon characteristics and Hg (11) removal. The yield of the carbon was found to be 51- 52 %

BATCH STUDIES FOR THE REMOVAL OF Hg (11)

Batch experiments were performed to establish various parameters for the removal of Hg (11) & Cr(VI) from aqueous solutions. The experiments were carried out using 100ml of solution containing 10 mg of Hg (11). Adjusted to pH 4.0 & **2.0** contained in 300 ml polythene containers. After adding 0.1g of carbon the solutions were equilibrated in a rotary mechanical shaker. The equilibrated solutions were filtered in using G3 crucible if necessary and the amount of Hg (11) & Cr(VI) present in the solution were determined using rodamine 6G methods and S-Diphenyl carbazide as described in materials and methods.

Batch experimental were performed with sulphuric acid treated paddy husk carbon (PHC) using 250-300 powder. Initial testings were done with distilled water solution as finally a synthetically prepared Hg (11) & Cr(VI) was used to assess the carbon potential.

EFFECT OF EQUILIBRATION TIME:

In order to find out the optimum equilibration time for adsorption process, a series of experiments were conducted with 10 mg /l of Hg (11) & Cr(VI) solution as 0.1g.PHC taken in 300ml bottles. The solutions were withdrawn at periodic intervals of 30 minutes as the Hg (11) & Cr(VI) content were determined, using rodamine 6G method and S-Diphenyl carbazide method. It is that a minimum of four hours of equilibration time is sufficient for the maximum removal of Hg (11) & Cr(VI) for PHC. However, further experiments were done with four hours of equilibration time. The extend of removal was founded to be 90%.& 85-86%.

EFFECT OF pH

In order to determine the effect of pH of Hg(11) & Cr(VI) removal, experiments were conducted with 10 mg / l of Hg (11) & Cr(VI) initially over the pH range 1.0 -10.0 and using 0.1g of carbon. The solutions were equilibrated for four hours and analysed for Hg(11) & Cr(VI) content. From which it is evident that Hg(11) & Cr(VI) removal was maximum over the pH range 3- 5. However for further experiments a pH of 5.0 was maintained.

EFFECT OF CARBON DOSAGE:

In order to find out the maximum carbon dosage required for the maximum removal; of Hg (11) & Cr(VI), experiments were done with 10 mg/l of Hg(11) & Cr(VI) with PHC variation of 5- 250mg/100ml. It can be seen that a maximum removal of 95% be achieved over the carbon dosage of 150-200mg/100ml.

FREUNDLICH ADSORPTION ISOTHERM

Freundlich Adsorption Isotherm is the most widely used mathematical form to explain the adsorption process in aqueous system.

The equation is represented as

$$X/m = K.Ce^{1/x}$$

Where,

X = Amount of solute absorbed.

M = Weight of adsorbent

Ce = equilibrium concentration of the solute

K,1/x = constant characteristics of the system

The above equation is an empirical expression that explains the heterogeneity of the surface and the exponential distribution of sites and energies. The above equation may be returned in the logarithmic form

$$\text{Log } x/m = \text{log } K + 1/x \text{ log } Ce$$

Plotting x/m vs log Ce a straight line is obtained with a slope of

1/x and log k is the intercept of log x/m at log Ce = 0. The value of 1/x obtained for adsorption of most organic compounds and activated carbon is < 1. Steep slopes of 1/x close to 1 indicate adsorption capacity at high equilibrium concentrations that rapidly determinate at lower equilibrium concentration covered by isotherm. Relatively at flat slopes in 1/x < 1 indicate that the adsorption capacity is only slightly reduced at lower equilibrium concentrations.

As the freundlichequations indicate the adsorptive capacity of loading factor on the carbon, x/m is a function of the equilibrium concentrations of the solute. Therefore higher capacities are obtained at high equilibrium concentrations.

The freundlich equation can be used for calculating the amount of activated carbon required to reduce any initial concentration (Co) to a predetermined final concentration (Ce). By substituting Co - Ce for X in equations, where Co is the initial concentration.

Comparison of different activated carbon for the removal of different compounds or removal by the same carbon can be made by using the above equation.

In order to establish the adsorption capacity of carbon using isotherm studies , experiments have been done by taking Hg (11) & Cr(VI)

concentrations over the range 10-60mg/l. the solution were adjusted to pH 4.0 and PHC was added so that 100 mg of carbon for 100 ml was maintained. The solutions were equilibrated for 24 hrs. At the end of equilibrated period Hg (11) & Cr(VI) solution were filtered if necessary & analysed for Hg (11) & Cr(VI) removal. The concentration of Hg (11) & Cr(VI) remaining in solution was subtracted from the respective initial concentrations. The values were divided by carbon dosage to get x/m values. The log values of these data were plotted against the logarithm of concentration of Hg (11) & Cr(VI) remaining in the solutions. A straight line curve can be noticed in the case of Hg (11) & Cr(VI) solutions prepared in distilled water and tap water. These results are shown in FIG 5.

It can be seen from the fig that the overall adsorption capacity was found to be much higher in the case of distilled water than in the case of tap water. It can be seen that the adsorption capacity is more in distilled water than in tap water. The reduction in the adsorption capacity of the tap water might be due to the competition of calcium and magnesium ions for the sites available on the carbon. The corresponding freundlich equations are given below.

For distilled water $x/m = 3.63Ce^{0.77}$

For tap water $x/m = 0.165Ce^{1.24}$

It could be seen that in distilled water Cr(VI) removal was 3.3 times more than in tap water.

For distilled water $x/m = 11.75 Ce^{0.35}$

For tap water $x/m = 3.54 Ce^{0.62}$

Conc In Tap Water	Ce	x/m	log Ce	logx/m
10	5.380	4.630	0.730	0.665
20	9.750	10.25	0.989	1.011
30	15.750	14.25	1.197	1.154
40	19.00	21.00	1.279	1.322
50	21.25	28.75	1.327	1.459
60	27.00	33.00	1.431	1.519

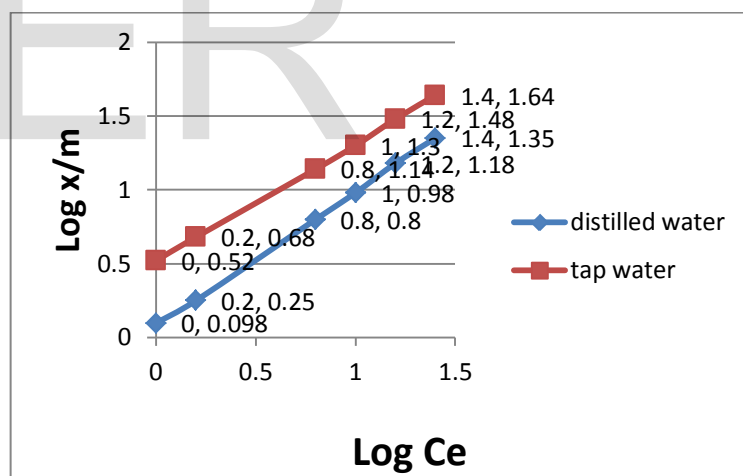
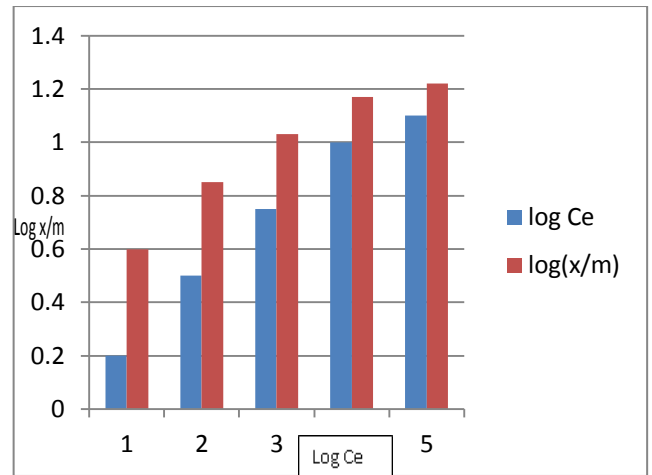
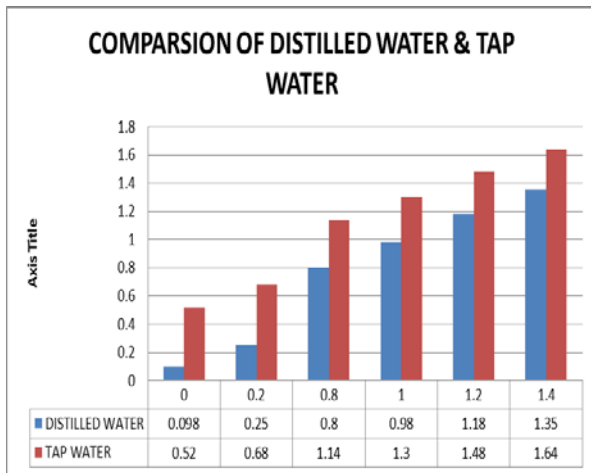


FIG:1.6

**FREUNDLICH ADSORPTION
ISOTHERM**



5. RESULTS AND DISCUSSION

In this connection, chlor alkali plant waste synthetically prepared was used for the experiment. The characteristics of the final effluent can be manufacturing unit is given below.

log Ce	log(x/m)	log Ce	log(x/m)
0.2	0.6	0.2	1.18
0.5	0.85	0.48	1.2
0.75	1.03	0.77	1.3
1	1.17	1	1.38
1.1	1.22	1.1	1.4

1.	pH value	1.4
2.	Total suspended solids mg/l	12
3.	Total dissolved solids mg/l	680
4.	Acidity (as CaCO ₃)	
	Methyl orange acidity mg/l	82500
	total acidity mg/l	82500
5.	Chlorides (as Cl ₂) mg/l	62000
6.	Mercury mg/l	120

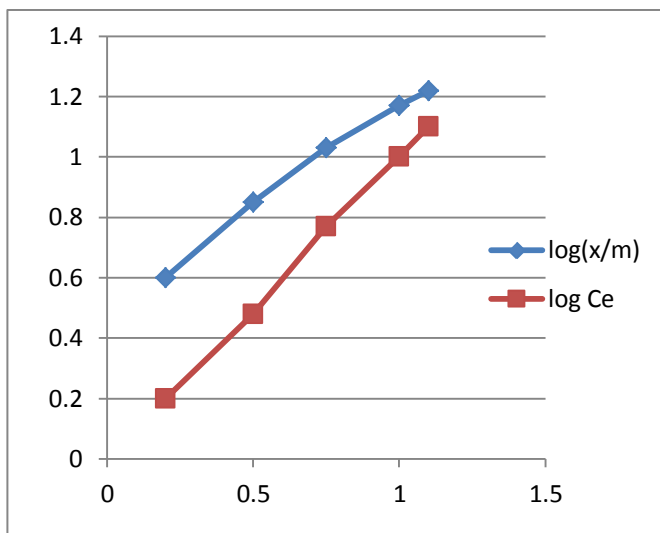


Fig:5 Frenldich isotherm

The above wastewater adjusted to pH condition using sodium hydroxide to a pH level 5.0 – 6.0. about 1litre of the wastewater was taken in a 2 litre beaker and sufficient quantities of paddy husk carbon was added and stirred for sufficient time of 5 hrs using magnetic stirrer. About 12-13 g of carbon was added initially and stirred well at the end

of equilibration time; the effluent was filtered through a sand filter bed created on a funnel under gravity conditions. The filtered effluent was analyzed for Hg(11) content. The percentage removal of Hg (11) was found to be 98 %.

CHARACTERISTICS OF SYNTHETIC WASTEWATER

1.	pH value	3-4.5
2.	Total suspended solids (mg/L)	50
3.	Total dissolved solids	500
4.	Chlorides	100
5.	Sulphates	250
6.	Chromium	75-100
7.	Ion salts	20

The above wastewater adjusted to pH 2.5 conditions having sodium hydroxide. About 1 litre of the wastewater was taken in a 2 litre beaker and sufficient quantities of paddy husk carbon was added and stirred for sufficient time over the range of 5-6hrs. using magnetic stirrer.About 6-7 g of carbon was added initially and stirred well.At the end of the equilibrium period,the effluent was filtered through a sand filter bed treated on a funnel under gravity contions.The filtered effluent was analysed for Cr(VI) content.The removal of Cr(VI) was found to be 98-99%.

CONCLUSION

Mercury is widely used in amalgams, scientific instruments, batteries etc. Its salt is used as fumigants in combating plant diseases and insects pets. It is also used as an antifoulant in ship paints. The most spectacular incident of mercury poisoning in humans resulted from the ingestion of sea food taken from minamata bay, japan.

The yield of the carbon was found to be 52 %. Thus when 100g of paddy husk was used, the resulting weight of the carbon was found to be 52g.

1. The paddy husk carbon showed a good ion exchange capacity and sufficient surface area.
2. Thus the carbon was able to remove Hg (11) ions by adsorption and ion exchange mechanism.
3. Preliminary studies indicated that the paddy husk carbon required about 4 hrs of equilibration time to achieve about 90 % removal of Hg (11).When an initial concentration of 10mg/l of Hg (11) ions were employed.
4. The optimum pH of the Hg (11) was found to be over the range 4.0- 6.0.
5. The optimum carbon dosage was found to be 250 mg / 100 ml for an initial concentration of Hg(11) equal to 10 mg/l under optimum pH conditions.
6. Experiments were conducted to know the potential of this paddy husk carbon using synthetically prepare chlor alkali plant

waste in which concentration of Hg (11) was 50 mg/l. proportionate quantity of carbon powder was added (12.5g/l) to this waste water. After adjusting to a pH of 5-6, the Hg (11) removal was found to be 98%.

7. Isotherm studies showed that this material (PHC) followed freundlich adsorption type. Experiment with distilled water and tap water showed that the removal of Hg (11) was found to be more in distilled water than tap water. This indicates that common cations in tap water are able to interfere with the adsorption of mercury. Thus it can be concluded that paddy husk carbon can be effectively used for the removal of Hg(11) from aqueous system. Chromium and its salts are widely used in plating industries, stainless steel manufacture and in the preparation of chromium pigments used in paints industries. Chromium salts especially, Cr(VI) salts are toxic and tend to give chromium dermatitis, an itching problem. Chromium (VI) salts are 150 times less toxic than Cr(VI) salts.

1. The yield of the carbon was found to be 48%.

3. Preliminary studies indicated that the paddy husk carbon required about 5 hrs of equilibration time to achieve about 85% removal of Cr(VI).

4. The optimum Ph for the removal of Cr(VI) was found to be over the range 2-3.

5. The optimum carbon dosage was found to be 500mg/ml for an initial concentration of 10mg/L for Cr(VI) under optimum conditions.

6. The Cr(VI) followed freundlich adsorption isotherm. The removal of Cr(VI) in distilled water was found to be 3.3 times higher than in tap water. The lower adsorption capacity in tap water may be due to compaction of common cations such as Ca^{+2} and Mg^{+2} for sites on the carbon.

7. Experiments with synthetic wastewater indicated that 6-7 g/L of carbon is capable of removing 98% of Cr(VI) ions over a period of 5hrs, where an initial concentration of Cr(VI) was 50mg/L. Thus it can be concluded that PHC (Paddy Husk Carbon) can effectively be used for the removal of Cr(VI) from aqueous system.

REFERENCES

1. J. Mutter, A. Curth, J. Neumann, R. Deth, and H. Walach, "Does inorganic mercury play a role in Alzheimer's disease? A systematic review and an integrated molecular mechanism," Journal of Alzheimer's Disease, vol. 22, no. 2, pp. 357-374, 2010.

2. MajidSa'idi Experimental studies on effect of Heavy Metals presence in Industrial Wastewater on Biological Treatment international journal of environmental sciences Volume 1, No 4, 2010

3. BiebyVojjant * Anuar, A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation .international journal of 9. Pacheco, S., Medina, M., Valencia, F., and Tapia, J. (2006). "Removal of Inorganic Mercury from Polluted Water Using Structured Nanoparticles." J. Environ. Eng., 132(3), 342–349.

10. AgeingD.E. Egirani1, J.E. Andrews2, A.R. Baker2 Vol.4, Issue 4 (April 2014) Mercury Removal from Aqueous Solution Using Mixed Mineral Systems Injected with Zinc Sulfide in Sulfidic- Anoxic ConditionsII.

11. K. Nakamura, J. Aoki, K.Morishita, M. Yamamoto Mercury volatilization by the most mercury-resistant bacteria from the seawater of Minamata Bay in various physiological conditions November 2000

12.Burger J, Jeitner C, Gochfeld M. Locational differences in mercury and selenium levels in 19 species of saltwater fish from New Jersey. Journal of Toxicology and Environmental Health. chemical engineering 2011

4. S. S. Krishnan,A. Cancilla,R. E. Jarvis Industrial wastewater treatment for toxic heavy metals using natural materials as

adsorbants, Journal of Radioanalytical and Nuclear Chemistry March 1987, Volume 110, Issue 2, pp 373-378

5. T W Clarkson, L Magos, C Cox Tests of efficacy of antidotes for removal of methyl mercury in human poisoning during the Iraq outbreak

6. John Wiley & Sons Ltd Human Health Concerns of Lead, Mercury, Cadmium and Arsenic Monitoring and Assessment Research Centre, U.K.1987

7. Carl H. Lamborg, Chad R. Hammerschmidt A global ocean inventory of anthropogenic mercury based on water column measurements Nature 512, 65–68 (07 August 2014)Published 06 August 2014

8 .Xixin Lu, XiaoliuHuangfu, Xiang Zhang, Removal of trace mercury (II) from aqueous solution by in situ MnOx combined with poly-aluminum chloride in June 2014

2011;74(13):863–874. [PubMed]