Removal of Heavy Metals from Laboratory Wastewater Using Waste Precursors: A Sustainable Approach

Priti Malhotra, Arti Jain

***Abstract*—** Heavy metals remediation of laboratory waste aqueous stream is of special concern due to recalcitrant and persistency of impurities in environment. Conventional treatment technologies for the removal of these toxic heavy metals are not economical and further generate huge quantity of toxic chemical sludge. Use of waste precursors is emerging as a potential alternative to the existing conventional technologies for the removal of metal ions from aqueous solutions. The major advantages of using waste precursors over conventional treatment methods include: Waste management, low cost, high efficiency, minimization of chemical or biological sludge and regeneration of biosorbents. Cellulosic agricultural waste materials, silica containing waste and electronic waste are abundant sources for significant impurities adsorption. The mechanism of sorption process includes chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange etc. Further these sorbents can be modified for better efficiency and multiple reuses to enhance their applicability at industrial scale.

***Keywords*—** Water Purification, Waste Precursors, Agricultural Waste, Electronic Waste, Adsorption

I. INTRODUCTION

DEVELOPING such templates which have been designed from waste material and can be further used effectively to adsorb contaminants are the novel trends of todays research. Their double fold cleaning impact: one using precursors derived from waste material and second trapping their adsorption potential to adsorb impurities like heavy metals present in waste water; makes them highly indispensable. In view of environmental conservation and economical efficiency, it is quite worthwhile to employ waste material obtained from cellulosic agricultural waste materials, silica containing waste and electronic waste and develop active surface by chemical activation and produce a versatile adsorption surface. Removal of toxic materials like heavy metals from waste water which are either laboratory or industrial effluents by employing surfactant-templating assemblies have received extensive attention in the chemistry of materials.

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In this research we attempt to develop ordered mesoporous carbonaceous material from bio waste and electronic waste as well as nano silica from silica containing waste like rice husk, which after surface modification are expected to possess high adsorptive capacity, physiochemical stability, high mechanical strength, and high degree of reactivity. The low cost biomass figure as sustainable resource, encompasses both environmental and economic considerations and in one shot disposes or recycles the waste along with cleaning another aqueous waste. Its collective appeal lies in the ubiquitous potential of finding its applications in diverse fields.

One of the major task faced by many countries around the world is the deteriorating delivery of safe and clean drinking water.[1]

The rise in industrial activities releases effluents containing contaminants such as heavy metal ions into the marine environment, which possess momentous health hazards to living beings and overall deterioration of the environment.[2−8] Because most of the organic molecular pollutants are stable, small in size and not biodegradable, it is difficult to eliminate them from wastewater.[9] Many water purification methods such as chemical coagulation, photo degradation, precipitation, flocculation, activated sludge, membrane separation and ion exchange processes have been tested for removing the pollutants.[2,4,10,11] Yet, it is difficult to find a single effective method that can remove all harmful pollutants from water. Compared to conventional water purification methods, use of bioadsorbents could be advantageous owing to the low cost, easy availability, environmental friendliness and high efficacy.[5] different bioadsorbents such as banana peels,[12] orange peels,[2,12,13] rice husk,[10] tea waste,[14,15] sugarcane bagasse,[16] pine bark[17] and other peels[18−25] were tested for the extraction of heavy metal ions and dyes from water. A notable disadvantage of such bioadsorbents is the release of soluble organic compounds into water, which limits their use in large scale applications. Efficient and universal low cost adsorbents that will not produce a secondary water contamination during the purification process are to be developed. Herein we are showing the formation of adsorbents from agricultural and other wastes (like E-waste and kitchen waste) to adsorb these contaminants in efficient manner without forming any secondary pollutants

II. MATERIAL

The raw material was obtained from an agricultural field of Uttar Pradesh (India). All reagents used were of analytical grade, and their solutions were made up in twice distilled, deionized water. HCl, NaOH, were of laboratory grade from Merck. Boiled rice water extract was taken from different kitchens and dried for 3-4 days to evaporate their water. Then, dried rice water extract (RWE) was powdered and stored in glass bottles. $ZnCl_2$ and HCl were obtained from Merck. Sodium hydroxide, sodium carbonate, and sodium bicarbonate were obtained from Sigma–Aldrich. Non working LCD's are procured from the college.

III. RESULTS AND DISCUSSION

Rice husk known to be an agricultural waste material has proved to possess efficient adsorption capacity on its porous surface. Pretreatment of rice husks using various protocols can fabricate a large number of applications in various areas. The pretreated rice husk has proved to remove lignin, hemicellulose, reduce the crystalline nature of cellulose and increase its porosity by enhancing its surface area. Such characteristics of chemically modified rice husk are expected to exhibit higher adsorption capacities towards heavy metal ions and other organic and inorganic compounds. Furthermore, the high mechanical strength, chemical stability and granular structure of pretreated rice husk make them efficient adsorption material for treating various impurities from waste water. By using the rice husk, remediation of waste water can be done by removing toxic heavy metals such as Cd, Cu, Hg, Cr, Pb, Zn and Ni from it. The application of rice husk for waste treatment can evolve as economically sustainable and environmentally friendly approach to remove toxic metals from water and soil. One waste becoming scavenger for another waste material can be well emphasized by this proposal.

Mesoporous carbon has recently generated a great deal of interest due to their multifarious and vital applications in diverse areas of modern science. Owing to their high surface area and physiochemical properties, mesoporous carbon has been extensively used as absorbing materials for separation processes and gas storage. It has been proposed that among various porous materials synthesized so far the mesoporous carbon materials, possessing extremely high surface areas and ordered mesostructures have greater potential as catalysts, separation media and advanced electronic material. Their wide availability adds to their superior physical and chemical properties such as electrical conductivity, chemical stability and low density.

The success of LCDs during the last decade has led to a noticeable amount of LCDs entering in the waste electrical and electronic equipment (WEEE) waste stream. Thus, its recycling is a global concern. Currently, the LCD panel comprising glass, liquid crystal and PVA (polyvinyl-alcohol)-impregnated polarising films is sent for incineration or land-fill, which are potentially hazardous to the environment. Developing a holistic and environmentally acceptable strategy for the recovery and reuse of different materials from LCD panels is of both environmental and commercial interest. We have modified the low value PVA contained in this waste to produce a structured and expanded material. The expansion of PVA mimics the interactions between amylose and amylopectin in starch expansion in which the polymer chains re-organise into a mesoporous structure. The use of recycled material from LCD screens requires no additional iodine and produces the mesoporous material with high surface areas. The expanded PVA obtained from LCD screens has been modified with chitosan to act as precursor which is expected to possess a wide range of applications in environmental sustainability. The PVA/CS blend in the form of a hydrogel is a composite of polyvinyl alcohol and chitosan which forms homogeneous blend with high tensile strength and increased chemical stability due to crosslinking. Chitosan provides an efficient adsorbing surface to the expanded PVA owing to its high proportion of active nitrogen sites. The biocompatible and biodegradable characteristics of PVA/CS blend reinforces its significance along with the fact that PVA is obtained from LCD screens to emphasize on recycling of e-waste.

In course of our search for exploration of adsorption power of rice husk; we tried to extract silica from it. For extraction of silica we tried various methodologies given by various chemists. But by changing some of the steps we got maximum yield of nanosilica from rice husk.

IV. METHODOLOGY FOR THE SYNTHESIS OF NANOSILICA

A.Washing and acid treatment

RH was washed thoroughly with water to remove the soluble particles, dust, and other contaminants present, whereby the other impurities such as grinding particles are also removed. Consequently It was dried in an oven at about 100°C for one day. The dried RH was ultrasonicated with an acidic solution of HCl for nearly 30 minutes by stirring. It was cooled and kept intact for about 20 h. It was then decanted and thoroughly washed with warm distilled water until the rinse became acid free and this was designated as RH'. The wet RH' was subsequently dried in an oven at 110°C for 24 h.

B. Thermal treatment

A weighed RH' as well as RH were employed to heat treatment to obtain the ash. Samples were burnt inside a programmable furnace (Metrex programmable furnace), and different methods were applied. Different temperatures (500°C, 700°C, and 1,000°C) and rates (2°C/min, 5°C/min, and 10°C/min) were checked. We designated these as ashes (RHAs).

C. Extraction of silica

A sample of 20.0 g RHA was stirred in a 160-mL, 2.5 M sodium hydroxide solution. The solution was heated in a covered beaker for 3 h by stirring constantly and filtered; the residue was then washed with 40 mL of boiling distilled water. The obtained viscous, transparent solution was cooled down to room temperature, and then 10 M H_2SO_4 was added under constant stirring at controlled conditions until it reached pH 2;

NH_4OH was added up to pH 8.5 and was allowed to stand at room temperature for 3 h.

D. Preparation of nanosilica

Nanosilica was prepared by refluxing technique of the above extracted silica with 6.0 M HCl for 3 h and then washed repeatedly using distilled water to make it acid free. It was then dissolved in 2.5 M sodium hydroxide by stirring. H_2SO_4 was added until it reached pH 8. The precipitated silica was washed repeatedly with warm, distilled water to make it alkali free and then dried at 50°C for 48 h in the oven.

Methododology for the Preparation of mesoporous carbon:

Five grams of dWR were inserted into each of five flasks, and $ZnCl_2$ solutions whose impregnation ratios ($ZnCl_2$/dWR) were 0.5/1, 1/1, 2/1, 3/1, 4/1 (w/w) were added to these flasks in order to activate the carbons. The mixtures in the flasks were refluxed below their boiling points for an hour and then dried in petri dishes in an incubator for 24 h at 105 ^{0}C. After drying, the carbonizations of the mixtures were completed by heating in nitrogen atmosphere in a muffle furnace (metrex) at different temperatures, i.e., 400, 500, 600, 700 and 800 ^{0}C for 30, 60, 90 and 120 min. separately. The obtained rice water extract mesoporous carbon (RWEMC) were treated with 0.1 N HCl solutions, and then washed with double distilled water until neutral pH was attained. After an additional drying step in the incubator at 105 ^{0}C, the RWEMCs were stored for future use.

Synthesis of PVA/ CHITOSAN blend:

(a) **Obtaining starting material from LCD screen.**

- Separated polarising film from waste LCD screen.
- PVA was prepared by soaking the polarising film in warm water at 50-60 °C.
- Outer two layers were separated and inner PVA layer was revealed.
- Resulting film was dried.

(b) **Preparation of expanded PVA from waste PVA.**

- LCD PVA film (200mg) and distilled water (4ml) were added in a round bottom flask sealed and heated to 180°C for 20 minutes using oil bath.
- After 20 minutes immediately the PVA solution was allowed to retrograde at 4°C for 12 hours.
- Ethanol (100ml) was added and stirred for 3 hours.
- The resulting precipitate was dried.

(c) **Preparation of PVA/ Chitosan blend:**

- The PVA/CS hydrogels were prepared by mixing 10%w/v PVA solution with 1% w/v CS solution, dissolved in 2% w/v acetic acid.
- Stirred the mixture constantly until homogeneous solution.
- Crosslinking agent was added to the solution under constant stirring.
- Poured the mixture in petri dish and the mixture started forming hydrogel within 30 minutes at room temperature.
- The obtained PVA/CS hydrogel dried and kept at 40°C in a vacuum oven for 48 hours.

The PVA/chitosan blended hydrogel obtained in various ratios are expected to possess mesoporous surface capable of being used as novel adsorbents for adsorption of heavy metal ions from aqueous solutions [26].

TABLE I
Composition of the PVA/CS hydrogel used in this study

(PVA/CS) Hydrogels	50/50	25/75^a
CS (mL)	5.00	5.00
PVA (mL)	5.00	2.50
Crosslink (mL)	2.86	1.43
1.25% GA (mL)	0.04	0.06

Adsorption of Cr(VI) from $K_2Cr_2O_7$ stock solution and Mn(VII) from $KMnO_4$ stock solution.

The adsorption of Heavy metals (from the solution of $K_2Cr_2O_7$ and $KMnO_4$**)** onto 0.2 g prepared adsorbents i.e on nanosilica and mesoporous carbon and PVA/CS blend was carried out by using standard solutions of $K_2Cr_2O_7$ and $KMnO_4$ (50 mg L^{-1}) and the results are shown in Fig. 1A and 1B. It was found from the absorbance graph taken from UV spectrophotometer (Motras instrumentation) that nanosilica, mesoporous carbon and PVA/CS are showing promising results than activated carbon and ordinary silica. This is due to the more prone active sites presents at treated adsorbents.

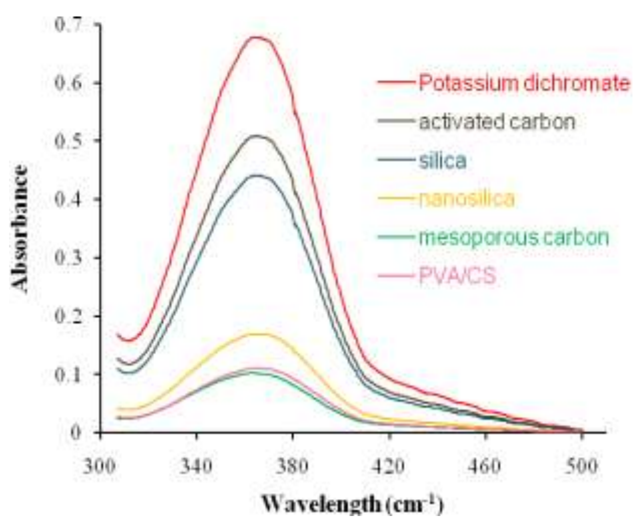

Fig 1A: Absorbance graph of $K_2Cr_2O_7$ showing adsoption of heavy metal (Cr(VI)) on various adsorbent

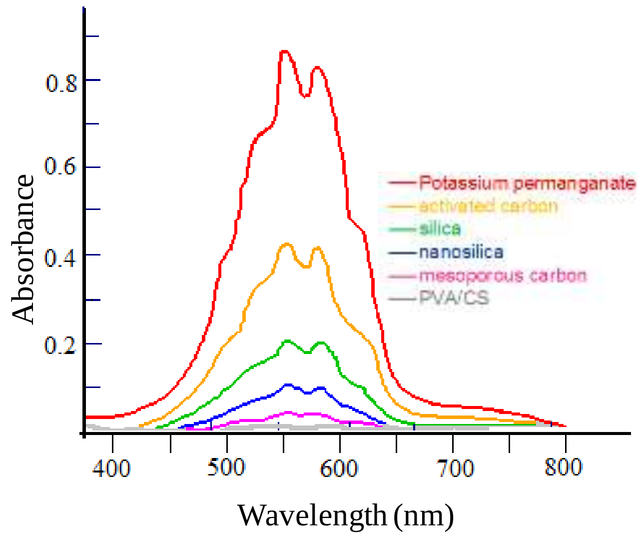

Fig 1A: Absorbance graph of $KMnO_4$ showing adsoption of heavy metal (Mn(VII)) on various adsorbent

V. CONCLUSIONS:

This environmental benign procedure offers several promising features for the treatment of waste water. The application of rice husk, rice water extract and LCD screens for waste treatment can evolve as economically sustainable and environmentally friendly approach to remove toxic metals from water and soil. One waste becoming scavenger for another waste material can be well implemented and evident by this paper.

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