



Carbonized agrowastes uses for the removal of heavy metals Cr (VI), Ni (II), Cu (II) and Zn (II) from electroplating effluent at Agra, U.P. (India)

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Abstract

The physico-chemical tests were conducted using an electroplating industry effluent that contained 18.0, 18.9, 8.6 and 15.6 ppm of Cr (VI), Ni(II), Cu(II) and Zn(II) respectively. The work aimed to evaluate the feasibility of using powdered pseudo activated carbon prepared from agro wastes for the removal of heavy metals from electroplating effluents. The ability of coconut coir carbon (CCC), sagaun sawdust carbon (SSC), wheat stem carbon (WSC) and rice husk carbon (RHC) to remove heavy metals from the effluent was studied. The sorption was in the order of Ni > Zn > Cu > Cr over a wide range of initial concentrations: 1-20 mg/l at sorbent dose 1 g/l. The sorption increased with increasing contact time but the equilibrium was attained in two hours for Cr, 3.0 h for Cu, 3.5 h for Zn and 4 h for Ni. The order of metal removal capacities for these chemical sorbents was: RHC > CCC > WSC > SSC. Electroplating effluent showed 4-10% lower removal as compared to synthetic standard solution under similar conditions.

Keywords: carbonized agrowaste, heavy metals, electroplating effluents, Agra

Introduction

There are over 50,000 large, medium and small electroplating effluent units mostly scattered in rural and urban areas in India. The variety of processes and methods of operation in the metal finishing industry gives rise to a wide range of effluent compositions. The processing baths contain a high concentration of potentially polluting materials. The wastewater can be expected to contain cyanides of potassium or sodium, complex cyanides, copper, nickel and zinc in acid solution, hexavalent chromium, oil wastes and solvents. Due to the proprietary nature of many products used in the metal finishing, the precise composition is quite often not known. Dissolved chemicals and metals, which are not toxic to aquatic life at very low concentration levels, are, however, the major concern. A typical wastewater sample from an electroplating industry is likely contain 100-500 mg/l suspended solids, 20-100 ppm for Cr(VI), 30-150 ppm for total Cr, 15-90 ppm for CN⁻, 5-25 ppm for Cu, 15-70 ppm for Ni and 10-200 for ppm Zn, whereas the permitted levels of these contaminants in the electroplating wastewater to be discharged are 100 mg/l, 0.1, 2.0, 0.2, 2.0, 2.0 and 5.0 ppm respectively. The pH is in the range of 4-10, that must be changed to between 6.5 - 8.0 before water is released into the environment. Though the activated carbon is an ideal adsorbent for organic matter due to its organophilic character, It is not economical for wastewater and soil treatment owing to its high production and regeneration costs, and about 10-15% loss during regeneration by chemical or thermal treatment. High cost of activated carbon and synthetic resins has prompted the search for substitutes that are abundant, cheap, Renewable and ecofriendly. So the use of agricultural residues such as sawdust or industrial by-products like bagasse have received considerable attention [1, 2, 3, 4, 5, 6, 7]. Most of these materials contain functional groups associated with proteins and polysaccharides like lignin, cellulose and hemi

cellulose. The pollutant uptake is believed to occur through coulombic attraction and ion exchange processes involving these groups. Though these materials generally do not have high sorption capacity as compared to activated carbon, they are plentiful, inexpensive and renewable. This offers an attractive approach to the removal of metal cations in solution. The sorption capacity of these materials could be enhanced by various physico-chemical modifications to improve their physical and structural properties, making them more suitable for full-scale filter applications. The goal of this research is to evaluate the ability of coconut coir carbon (CCC), sagaun sawdust carbon (SSC), wheat stem carbon (WHC) to remove heavy metals from the electroplating effluent as effective, low cost and biomass sorption.

Materials and Methods

The sagaun sawdust used in this study was collected from the saw machine at Panchkuan, Agra in 2018. Coconut coir, rice husk and wheat stem were obtained from the local market at Agra city. All the four agro wastes were dried in the sun, crushed, washed thrice time with distilled water and rinsed with 1% HCl to remove water soluble impurities, particularly metal ions and surface adhered particles. Then they were kept in 0.1 N, NaOH solution overnight to remove lignin and in 0.1 N, CH₃COOH to remove alkalinity developed due to NaOH. Thereafter, they were again washed well with distilled water till the wash water became colour less, they were dried at 110°C in an oven for 2 hours to get rid of moisture and other volatile impurities. Their carbons were prepared by keeping four parts of the above agro wastes with three parts by weight of concentrated H₂SO₄ in an air oven maintained at 150°C for 24 h. The carbonized agro wastes were washed with distilled water to remove free acid (SO₄²⁻ ions).

Then they were soaked in 1% w/v sodium carbonate solution (1% W/V) overnight to remove any residual acid. They were again washed with distilled water and dried at 110°C for 2 hours. The carbons so obtained were ground in a mortar with a pestle and sieved through a standard sieve to get the particle size less than 300 microns throughout the study. The characteristics of adsorbents are listed in the Table-1. Such carbons are expected to be more than 4 times more effective than raw agro wastes compounds [8, 9].

Table 1: Characteristics of Adsorbents

Parameters	RHC	CCC	WSC	SSC
Composition of heavy metal (%)				
Moisture	3.82	4.96	5.67	4.22
Ash	4.56	7.85	5.68	8.36
Carbon	79.89	80.32	78.9	81.73
Silica	2.76	4.36	3.02	4.64
Sodium	0.13	0.11	0.17	0.09
Potassium	0.29	0.31	0.27	0.23
Calcium	0.35	0.39	0.41	0.32
Magnesium	0.03	0.02	0.07	0.01
Phosphorous	0.05	0.04	0.06	0.03
Iron	0.27	0.19	0.32	0.12
Miscellaneous	7.85	1.45	5.34	0.25
Physico-chemical Properties				
pH	8.32	7.64	7.34	7.83
Conductivity(μ S/m)	0.92	0.80	0.75	0.62
Specific gravity(g/L)	1.20	1.34	1.10	1.12
Porosity (ml/g)	1.01	0.92	0.83	0.72
Surface area(m^2/g)	456	397	328	298
Cation exchange capacity(meq/g)	0.70	0.90	0.53	-

All chemicals used were of analytical (AR) grade unless otherwise specified. Distilled deionized water (DDW) was used throughout the experiment. Five standard solutions of 1, 5, 10, 15 and 20 mg/l concentrations of Cr, Ni, Cu and Zn for instrument calibration and sorption study were prepared by diluting their stock solution of 1 g/l, i.e., 1 ml = 1 mg metal. To prepare the Cr (VI) stock, 2.828 g anhydrous $K_2Cr_2O_7$ was dissolved in about 200 ml DDW, 1.5 ml conc. HNO_3 and diluted to 1 litre with DDW. The stock solution of Ni, Cu and Zn were prepared by dissolving 1.000 g of 99.5 % AR 325 mesh metal powder from CDH, in a minimum volume of 1:1 acid (HNO_3 for Ni and Cu, and HCl for Zn) and diluting to 1 litre with 1 % (v/v) acid.

The capacity studies were carried out by transient batch tests. In 25 numbers (5 concentrations of 4 metals each + 5 controls one for each) of 100-ml capacity PVC bottles with screw caps, 0.05 g of sorbent was added to each bottle of 5 sets, each set having 6 bottles 5 for different concentrations of a metal and 1 for its control. The metal solution (50 ml) or effluent was added to each bottle. The solution was buffered with 0.07M sodium acetate, - 0.03 M acetic acid to pH 4.8. Each bottle was shaken in a reciprocating shaker at 180 rpm for 5 hours at room temperature, and the metal concentration was measured per hour until the solution reached equilibrium. The controls without sorbent were to demonstrate metal uptake due to the sorbent, not from other sources such as the walls of the container and centrifuge tube.

The contents were centrifuged at 2000 rpm for 10 min and the supernatant liquid was filtered using a 0.45 μ m membrane filter. The filtrate was analysed for metal ions. The initial and final concentrations of the metal solutions were determined using a Perkin- Elmer AAS Model Analyst 100 AAS by Standard Methods [10]. Experiments were carried out in triplicated and results showed averaged.

The uptake of metal ions at 1, 5, 10, 15 and 20 mg/l concentrations by different sorbents was thus calculated and results are given in Table 2. The data were analysed using the Freundlich and Langmuir equations as follows:

$$\ln a = \ln k + 1/n \ln c \dots \dots \dots \text{Freundlich equation}$$

$$c/a = 1/Qb + c/Q \dots \dots \dots \text{Langmuir equation}$$

Where a (mg/g) is the metal sorbed per unit mass of sorbent ($a = x/m$ where x mg of metal is sorbed on m grams of sorbent), c (mg/l) is equilibrium concentration in aqueous phase, k (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively, Q (mg/g) and b (l/g) are Langmuir constants related to adsorption capacity of sorbent and adsorption maximum (energy of adsorption) respectively.

Table 2: Effect of Cr, Ni, Cu and Zn concentration on their % removal at agitation time 4 h, rpm 240 and sorbent dose 1 g/l, pH 4.8 and temperature 25°C

Metals	Concentration(mg/l)*	RHC	CCC	WSC	SSC
Cr(VI)	1	92.1	90.9	88.3	85.1
	5	89.5	88.2	84.5	80.0
	10	84.2	82.4	76.8	70.9
	15	75.7	71.1	65.9	58.4
	20	68.1	62.3	56.1	48.5
Ni(II)	1	97.6	95.9	94.3	92.8
	5	97.0	94.7	92.7	90.4
	10	95.5	91.9	88.4	84.5
	15	91.3	86.0	79.6	71.2
	20	84.2	76.6	70.9	62.9
Cu(II)	1	94.2	93.6	91.9	88.0
	5	92.7	91.7	89.0	83.6
	10	89.2	86.9	83.9	76.1
	15	81.2	78.9	73.4	62.3
	20	72.5	68.6	63.4	54.1
Zn(II)	1	95.4	94.7	92.3	90.8
	5	94.2	93.2	90.6	87.0
	10	91.5	89.4	84.5	80.2
	15	85.2	80.9	75.2	68.1
	20	78.5	72.1	64.2	56.5
Cr(VI)*	18.0	67.4	61.0	55.7	47.2
Ni(II)*	18.9	83.0	75.2	68.5	60.3
Cu(II)*	8.6	89.0	86.5	83.4	75.5
Zn(II)*	15.6	81.0	75.4	68.3	60.7

*The second set of data is for metal ions present in electroplating effluents.

The Langmuir constants were calculated at five initial concentrations under optimal conditions and results are shown in Table-3.

Table 3: Comparison of Langmuir and Freundlich constants and correlation coefficients (R^2 values) for the sorption of heavy metals by RHC, CCC, WSC and SSC.

System	Langmuir constants and R^2			Freundlich constants and R^2		
	Q,mg/g	b,1/g	R2	k,mg/g	1/n	R2
Cr/RHC	15.5637	0.7730	0.9975	7.422	0.5057	0.9665
Cr/CCC	14.3753	0.7581	0.9986	6.985	0.4686	0.9529
Cr/WSC	13.1134	0.6130	0.9998	6.199	0.4605	0.9759
Cr/SSC	11.4383	0.5978	0.9999	5.102	0.4311	0.9531
Ni/RHC	18.7713	2.3191	0.9993	16.956	0.4823	0.9501
Ni/CCC	17.1763	1.4426	0.9998	11.884	0.4753	0.9484
Ni/WSC	15.8784	1.1181	0.9984	9.430	0.4782	0.9503
Ni/SSC	14.0016	0.9786	0.9965	7.413	0.4551	0.5266
Cu/RHC	17.1083	1.0063	0.9991	9.697	0.4839	0.9512
Cu/CCC	15.6278	0.9955	0.9998	8.936	0.4718	0.9523
Cu/WSC	14.2539	0.8527	0.9995	7.511	0.4501	0.9530
Cu/SSC	12.2523	0.6460	0.9977	5.539	0.4505	0.9534
Zn/RHC	18.3009	1.1852	0.9979	11.151	0.5088	0.9584
Zn/CCC	16.3204	1.1634	0.9987	9.922	0.4744	0.9488
Zn/WSC	14.9322	0.8557	0.9998	8.269	0.8023	0.9445
Zn/SSC	12.5572	0.8492	0.9139	6.878	0.4147	0.9468

Results and Discussion

The carbonized agro wastes used in the study has shown that the sorption capacity is found to decrease with increase in metal concentration. The higher uptake at lower initial concentration can be attributed to the availability of more isolated metal ions. Sorption rate is very rapid during initial the contact period of contact due to the availability of more sites for sorption and more than 60% of sorption is reached within 1 hour. However, equilibrium was attained after 2 hours for Cr, 3 hours for Zn, 3.5 hours for Cu and 4 hours for Ni. RHC could remove a greater amount of these metals than any other carbon studied. It was found to remove 92.1% for Cr (VI), 97.6% for Ni, 94.25% for Cu and 95.4% for Zn at concentration 1 mg/l, sorbent dose 1 g/l, rpm 240, agitation time 4 h, pH 4.8 and temperature 25°C. The order of metal removal capacities for these chemical adsorbents was RHC > CCC > WSC > SSC. The order of removal/sorption of metals was Ni > Zn > Cu > Cr. The effect of various parameters affecting the adsorption such as initial metal concentration, adsorbent dose, contact time and pH was determined. Adsorption decreases with rise in metal concentration but increases with increase in adsorbent dose.

The rate of adsorption is high in the beginning as sites are available and unimolecular layer increases. Adsorption and desorption occur together and rates become equal at a stage called adsorption equilibrium when isotherms are applied. That is why there is little increase in the percentage removal on increasing contact time is increased from 4-5 hours. The subsequent slow rise in the curve may be due to adsorption and intra-particle diffusion taking place that occurs simultaneously with dominance of adsorption. The physico-chemical properties of carbonized agro wastes vary widely from plant to plant and method to method of carbonization. They depend on the variety of a plant and area in which it is cultivated, temperature of carbonization, operational features and efficiency of the heating equipment like oven or furnace, The peaks of their X-ray diffractogram can be used to identify major components, such as crystalline quartz, amorphous silica, calcium orthosilicate, cristobalite, sillimanite, crystalline carbonate etc^[11]. Their scanning electron micrographs can depict their morphology, particularly linear or curved type fibers with holes in the fibers and other places in the skeletal

structure. The number and size of pores of a carbon can also be determined. More numerous and larger-sized pores but smaller particle size make a better sorbent. The bands of their FTIR spectra can indicate the presence of carboxy, hydroxyl and sulphonic groups responsible for cation exchange.

The pseudo activated carbons may consist of oxides of silicon, calcium, magnesium and iron. They may have anion adsorption sites similar to minerals like alumina and clay. Such sites are aquo groups ($-M-OH_2-$) and hydroxo groups ($-M-OH$). The surface chemistry of an oxide in contact with an aqueous solution is determined to a large extent by deprotonation or a hydroxyl ion association reaction. However, some evidence suggests that an anion like Cr_2O_7 can be adsorbed by an ion exchange mechanism even though the surface is neutral. Had Cr (VI) not been in dichromate form, it would have been adsorbed to the maximum extent based on its ionic size and potential.

The optimum pH for metal removal was found in the acidic medium^[12]. This may be attributed to the large number of H^+ ions in the acidic medium that neutralize the negatively charged adsorbent surface, thereby reducing hindrance to diffusion of dichromate ions. At higher pH, the abundance of OH^- ions create increased to diffusion of dichromate ions. The data generated may be used for designing treatment plants for industrial effluents having low levels of heavy metals and hold a promise for the commercial exploitation.

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