

Short communication

Recycling of agricultural solid waste, coir pith: Removal of anions, heavy metals, organics and dyes from water by adsorption onto $ZnCl_2$ activated coir pith carbon

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Abstract

The abundant lignocellulosic agricultural waste, coir pith is used to develop $ZnCl_2$ activated carbon and applied to the removal of toxic anions, heavy metals, organic compounds and dyes from water. Sorption of inorganic anions such as nitrate, thiocyanate, selenite, chromium(VI), vanadium(V), sulfate, molybdate, phosphate and heavy metals such as nickel(II) and mercury(II) has been studied. Removal of organics such as resorcinol, 4-nitrophenol, catechol, bisphenol A, 2-aminophenol, quinol, *O*-cresol, phenol and 2-chlorophenol has also been investigated. Uptake of acidic dyes such as acid brilliant blue, acid violet, basic dyes such as methylene blue, rhodamine B, direct dyes such as direct red 12B, congo red and reactive dyes such as procion red, procion orange were also examined to assess the possible use of the adsorbent for the treatment of contaminated ground water. Favorable conditions for maximum removal of all adsorbates at the adsorbate concentration of 20 mg/L were used. Results show that $ZnCl_2$ activated coir pith carbon is effective for the removal of toxic pollutants from water.

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1. Introduction

Drinking water sources in developing and underdeveloped countries are facing serious threat from contamination problems due to both man-made industrial and agricultural activities and natural sources such as minerals. In many developing countries ground water is used for drinking purposes and it is polluted with toxic anions, heavy metals, organic compounds and dyes due to effluents from industries. These unwanted chemicals cause health problems, when they exceed the tolerance limits in water. The guidelines for drinking water prescribed by the WHO for nitrate, sulfate, molybdenum, selenium, nickel, chromium(VI) and mercury are 50, 250, 0.01, 0.01, 0.02, 0.05 and 0.001 $mg\ dm^{-3}$, respectively [1]. Germany's drinking water limit for phosphate is 6.7 $mg\ dm^{-3}$ [2]. The tolerance limit for phenolic compounds in drinking water is 0.001 $mg\ dm^{-3}$ [3] and the discharge limit of vanadium in industrial effluents into

surface water is 0.2 $mg\ dm^{-3}$ [4] according to the Bureau of Indian Standards.

Increased nitrate concentrations in public water supplies presents a potential health hazard due to reduction to nitrite in the gastrointestinal human tract. Nitrite causes methemoglobinemia (cyanosis or 'blue baby syndrome') and both nitrate and nitrite have potential to form carcinogenic *N*-nitroso compounds [1]. Sulfate is one of the least toxic anions; however, catharsis, dehydration, and gastrointestinal irritation have been observed at high concentrations [1]. Phosphates cause toxic cyanobacterial blooms in water [2]. Vanadium compounds have harmful effects on the circulatory system and disturb the metabolism including that of plants, as they cause chlorosis and limit growth [5]. Excessive intake of molybdenum causes physiological copper deficiency. Thiocyanate inhibits the uptake of iodine by the thyroid gland, thereby reducing the formation of thyroxine [6]. Selenite and nickel cause liver damage and chromium (VI) is carcinogenic in nature [7]. Phenols are on the priority pollutant list of US EPA [7]. Phenolic compounds have been found to accelerate tumor formation, cancer and mutation [8]. Dye effluents discharged into receiving water bodies affect the aquatic

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flora and fauna and cause many water borne diseases. Some dyes are carcinogenic and others after transformations or degradation yield compounds such as aromatic amines, which may be carcinogenic or otherwise toxic [9]. So the removal of these pollutants from ground water is important before it is used for drinking purpose.

Various treatment techniques available for anions, heavy metals, organics and dyes are reduction, ion exchange, evaporation, reverse osmosis and chemical precipitation. Most of these methods suffer from drawbacks like high capital and operational cost and there are problems in disposal of the residual metal sludge [10]. The use of activated carbons to remove organic and inorganic pollutants from waters is widely extended, because of their high surface area, microporous character and the chemical nature of their surface [11]. Commercially available activated carbons from coconut shell, lignite, peat etc are effective for the removal of various pollutants. However, they are expensive and their regeneration cost is also high. So there is a need for low-cost and readily available materials for the removal of toxic pollutants from water.

Coir pith is one such material, which is generated in the separation process of the fiber from coconut husk. Annual production of coir pith is around 7.5 million tons [12]. Accumulation of coir pith around coir fiber industries is creating a menace. The objective of this work was to evaluate the potential of ZnCl₂ activated coir pith carbon for the removal of inorganic anions, heavy metals, organics and dyes from water.

2. Experimental procedure

2.1. Materials and methods

Coir pith was collected from local coir industries. It was dried in sunlight for 5 h and then zinc chloride activated coir pith carbon was prepared. Coir pith was stirred in a boiling solution containing zinc chloride in the weight ratio of 2:1. The filtered material after drying was carbonized at 700 °C under controlled conditions. After cooling, the excess zinc chloride present in the carbonized material was leached out using dilute HCl. Then the carbon was repeatedly washed to get rid of excess ZnCl₂ and dried. The carbonized material was sieved to 250–500 μm particle size and used for adsorption studies.

The characteristics of ZnCl₂ activated coir pith carbon (ZnCPC) in comparison with coir pith carbon in the absence of ZnCl₂ activation (CPC) are presented in Table 1. Specific surface area and porous properties were determined using Quantachrome surface area analyzer and mercury porosimeter, respectively. The material (ZnCPC) has a high surface area compared to the carbon (CPC) prepared from coir pith in the absence of ZnCl₂ (167 m²/g) [13]. Most of the surface (90%) and pore volume (75%) is made up by pores smaller 2 nm in pore width, the so-called micropores. The SEM photograph of ZnCPC shows that it has honey comb voids (Fig. 1a). On the other hand, CPC shows fractured and fragmented walls of the pores (Fig. 1b). ZnCl₂ makes the interior of the pores expanded uniformly like the flour fermentation. Presence of

Table 1
Characteristics of activated coir pith carbons

Parameter	Presence of ZnCl ₂	Absence of ZnCl ₂
Specific surface area (m ² g ⁻¹)	910	167
Total pore volume (cm ³ g ⁻¹)	0.363	0.1217
Micropore area (m ² g ⁻¹)	284	89.3
Micropore volume (cm ³ g ⁻¹)	0.131	0.0913
Average pore diameter (nm)	1.6	2.75
Average micropore diameter (nm)	0.9	1.2
pH _{ZPC}	3.2	8.0
pH (1% solution)	3.3	10.1
Conductivity (1% solution) (mS/cm)	0.255	2.3
Bulk density (g cm ⁻³)	0.1	0.12
Mechanical moisture content (%)	12.3	6.0
Ash content (%)	3.2	8.0
Specific gravity	1.29	1.74
Porosity (%)	92	93
Volatile matter (%)	19	58
Fixed carbon (%)	81	41
Decolorizing power (mg g ⁻¹)	137	21
Iodine number (mg g ⁻¹)	203	101
Phenol number (mg g ⁻¹)	30	–
Ion exchange capacity (meq g ⁻¹)	0.11	Nil
Zinc (%)	0.0218	–
Zinc leached (%)	0.0095	–
Ash analysis		
Sodium (%)	0.09	0.14
Potassium (%)	0.1	0.18
Calcium (%)	0.78	0.22
Phosphorous (%)	0.009	0.01

ZnCl₂ enhanced the micropore area and hence the surface area. The carbon has a sponge like structure due to the very high value of the fractal dimension with 2.93. The pore size distribution supports the above statements. Surface functional groups [14] and other parameters [15] were determined using standard methods. The acidic surface functional groups present on the ZnCPC are: carboxylic, 0.282 mequiv./g (19.4%); lactones, 0.234 mequiv./g (16.1%); phenolic 0.90 mequiv./g (64.6%) and basic groups, 0.77 mequiv./g.

The reagents used for the analysis are of analytical reagent grade and were obtained from Merck, S.d.fine or Loba Chemicals.

2.2. Adsorption studies

Adsorption experiments were carried out by agitating 20–400 mg of adsorbent with 50 ml of adsorbate solution of 20 mg/L concentration at pH from 2.0 to 11.0, 200 rpm, 35 °C in a thermostated rotary shaker (ORBITEK, Chennai, India). pH was measured using pH meter (Elico Instruments, model LI-107, Hyderabad, India). The pH of the solutions was adjusted by means of 0.1 M HCl and 0.1 M NaOH solutions. The samples were withdrawn from the shaker at predetermined time intervals and the supernatant was centrifuged at 20,000 rpm for 20 min. Then the centrifugate was analyzed spectrophotometrically for the residual adsorbate by the appropriate method (Specord 200 UV–vis spectrophotometer, Analytic Jena, Germany).

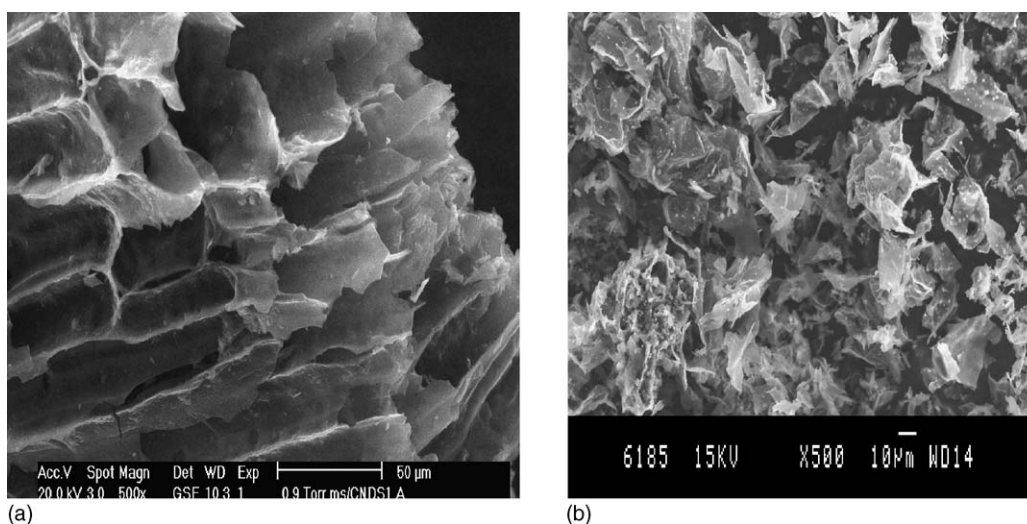


Fig. 1. SEM Photographs of ZnCPC(a) and CPC(b).

2.2.1. Removal of oxyanions and heavy metals

Analysis of inorganics was carried out spectrophotometrically by using the following methods: Direct screening method for nitrate [14], gallic acid and hydroxylamine method for molybdate [16], stannous chloride method for phosphate [14], hydrogen peroxide method for vanadate [17], diphenyl carbazide method for chromium(VI) [14], turbidimetric method for sulfate [14], ferric nitrate method for thiocyanate [14], dimethyl glyoxime method for nickel [18] and rhodamine 6G method for mercury(II) [19].

2.2.2. Removal of organics

Analysis of organics was carried out spectrophotometrically by monitoring them at their respective wavelength of maximum absorption: 276 nm for resorcinol [20], 318 nm for 4-nitrophenol [21], 276 nm for catechol [20], 278 nm for bisphenol A, 272 nm for 2-aminophenol, 291 nm for quinol, 271 nm for *O*-cresol [20], 270 nm for phenol [22] and 273 nm for 2-chlorophenol [13].

2.2.3. Removal of dyes

Analysis of dyes was carried out spectrophotometrically by measuring the absorbance of dye solutions at their respective wavelengths of maximum absorption: 660 nm for methylene blue, 559 nm for rhodamine B, 550 nm for acid brilliant blue, 551.4 nm for acid violet, 539 nm for procion red, 493 nm for procion orange, 525 nm for direct red - 12B and 495.7 nm for Congo red. Experiments were carried out in duplicate and the mean values are presented. Maximum deviation was 3%.

3. Results and discussion

3.1. Removal of inorganics, organics and dyes

The per cent removal of inorganic anions and heavy metals by using ZnCPC and CPC are presented in Table 2. It was generally found that the per cent removal increased with increase in contact time and adsorbent dose. More than 90% removal of nitrate, phosphate, vanadium(V), thiocyanate, molybdate, mercury and

chromium(VI) was obtained by using ZnCPC, for an adsorbate concentration of 20 mg/L, temperature 35 °C, 200 rpm and agitation time 3 h. The per cent removal of sulfate, selenite and nickel by ZnCPC was found to be 70, 74 and 41%, respectively under the same adsorption conditions (Table 2).

The per cent removal of the above ions was also tested at the same adsorption conditions by using the adsorbent CPC. Except mercury(II) and chromium(VI), the removal of all the ions by CPC was found to be negligible. Per cent removal of mercury(II) and chromium(VI) by CPC was found to be 80 and 18%, respectively (Table 2).

3.2. Removal of organics

The per cent removal of organic compounds is presented in Table 3. It was generally found that the per cent removal increased with increase in contact time and adsorbent dose. Almost quantitative removal of 2-chlorophenol, bisphenol A, *O*-cresol, quinol and 2-aminophenol, resorcinol, 4-nitrophenol, phenol and catechol was obtained by using ZnCPC, for an adsorbate concentration of 20 mg/L, temperature 35 °C, 200 rpm and agitation time 3 h. The per cent removal of phenols by ZnCPC was greater than that for CPC.

Table 2
Removal of inorganic anions and heavy metals by using ZnCPC and CPC

Adsorbate	Initial pH	Adsorbent dose (mg/50 ml)	Per cent removal	
			ZnCPC	CPC
Nitrate	6.2	400	95	Nil
Phosphate	4.0	450	91	Nil
Vanadium(V)	4.0	250	99	Nil
Thiocyanate	6.2	250	100	Nil
Molybdate	4.0	200	99	Nil
Sulfate	4.0	300	70	Nil
Selenite	6.0	600	74	Nil
Chromium(VI)	2.0	50	99	18
Nickel(II)	5.0	600	41	58
Mercury(II)	5.0	200	100	80

Table 3
Removal of organics by using ZnCPC and CPC

Adsorbate	Initial pH	Adsorbent dose (mg/50 ml)	Per cent removal	
			ZnCPC	CPC
Phenol	2.0	100	98	65
Resorcinol	4.0	100	99	61
4-Nitrophenol	4.0	100	100	50
2-Chlorophenol	4.0	50	99	67
Bisphenol A	2.0	50	97	57
Catechol	2.0	100	98	54
O-Cresol	2.0	50	98	52
Quinol	2.0	50	100	76
2-Aminophenol	2.0	50	100	50

Table 4
Removal of dyes by using ZnCPC and CPC

Adsorbate	Initial pH	Adsorbent dose (mg/50 ml)	Per cent removal	
			ZnCPC	CPC
Acid brilliant blue	4.0	200	99	92
Acid violet	2.0	200	99	92
Methylene blue	9.0	50	100	50
Rhodamine B	9.0	300	98	70
Direct red 12B	2.0	200	99	62
Congo red	2.0	200	93	79
Procion red	2.0	300	95	65
Procion orange	2.0	200	97	42

3.3. Removal of dyes

The per cent removal of dyes is presented in Table 4. It was generally found that the per cent removal increased with increase in contact time and adsorbent dose. Almost quantitative removal of all dyes except for congo red and procion red was obtained by using ZnCPC for an adsorbate concentration of 20 mg/L, temperature 35 °C, 200 rpm and agitation time 3 h. The per cent removal of dyes by ZnCPC was greater than that for CPC at the same adsorption conditions.

Further work is in progress on the kinetics of the adsorption of organics and inorganics, fixed bed studies and applications to real ground water treatment using ZnCl₂ activated coir pith carbon.

4. Conclusions

These studies show that the ZnCl₂ activated coir pith carbon developed from agricultural solid waste, coir pith, is an effective adsorbent for the removal of a number of inorganic anions, heavy metals, organics and dyes from water. The removal efficiency for the inorganic anions, organics and dyes was almost quantitative for an adsorbate concentration of 20 mg/L and is better than the carbon developed from coir pith in the absence of ZnCl₂.

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