

The Effectiveness of Different Inexpensive Sorbents on the Toxic Metal Removal in Wastewater

Stephen M. Anderson¹, Khajanchi Lal², Rabin Bhattarai³, Prasanta K. Kalita^{*4}

¹U.S. Department of Agriculture, Natural Resources Conservation Service (USDA-NRCS), Morris, IL 60450, USA

²Division of Microbiology, Indian Agricultural Research Institute, New Delhi, India

³Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

⁴Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

*⁴pkalita@illinois.edu

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Abstract

Expanding agricultural water demand has led to the reuse of wastewaters for irrigation purposes. Left untreated, these reused wastewaters may contaminate agricultural land, plants, and thereby food products. Common contaminants include toxic metals, which are conservative within the soil-plant-water system. The objectives of this study were to assess the effectiveness of widely available inexpensive sorbents in removing toxic metals from native wastewater through sorption capacity and provide a recommendation of best practices for low-cost low-tech treatment. Sugarcane bagasse, ground rice husk, and sawdust, were compared against the conventional metal removal techniques of activated carbon sorption and gypsum pH modification for chemical precipitation. Overall, bagasse, rice husk, and sawdust performed similarly but well below the performance of the activated carbon standard. The results indicate that locally available low-cost materials show promise to be used as metal removal media where activated carbon is unavailable.

Keywords

Contamination; Pollution; Health; Water Quality

Introduction

Significant metal contamination has been detected in Northern Indian waters due to rapid industrialization (Krishna and Govil, 2004). Metal-rich industrial wastewaters get mixed with domestic wastewaters and often receive inadequate secondary treatment,

leaving high levels of metals in wastewater canals. These waters are often used by farmers, for both nutrient-providing capability and also in lieu of declining alternative irrigation sources due to the falling water table, increasing consumptive use of canal waters and growing urban centers (Ahmad et al., 2005). The elevated concentrations of Cadmium, Chromium, and Nickel in agricultural fields after applications of metal-rich waters have been reported by earlier studies (Yadav et al., 2002; Sharma et al., 2007; Bahmanyar, 2008).

A variety of methods have been utilized to remove toxic metals from industrial wastewaters. Included among them are chemical precipitation, ion exchange, and electrochemical methods. These methods tend to be either costly, ineffective at low environmental metal concentrations, or both, are particularly stymied by the presence of organics when domestic wastewaters are mixed with industrial wastewaters (Bailey et al., 1998; Babel and Kurniawan, 2003). Fu and Yang (2011) have reported a thorough review of different methods that have been used to treat heavy metal wastewater. The common solution adopted by the wastewater treatment industry involves primary and secondary settling followed by, when necessary, tertiary treatment via activated carbon filtration. This process handles organics well. Activated carbon is a desirable filtration medium due to its homogeneity, the high

removal density (mg metal/kg carbon), and ability to scavenge metals at low concentrations (Terdkiatburana et al., 2008; Bernard et al., 2013). While effective, such treatment is expensive, requires a substantial up-front investment, and perhaps more significantly requires a network of piping to deliver wastewater to the treatment facility – untenable factors in developing and resource-poor areas (Ahmad et al., 2005). Thus, metal-rich wastewaters are frequently introduced into the riparian environment.

Dilution of metal-rich waste streams by the large amounts of irrigation waters flowing through these contaminated canals does nothing to reduce the metal load, but does complicate removal attempts via sorption methods. Nevertheless, extensive work characterizing metal removal ability has been performed on a wide variety of inexpensive and readily available 'biosorbents' suitable for deployment of metal removal from waters. Bailey et al. (1998) reviewed the spectrum of 'potentially low-cost sorbents for heavy metals' including a variety of biomass- and some mineral-based sorbents, finding chitosan, zeolites, lignin and lignin-based sorbents, and seaweed to have high observed metal absorbency. Bailey et al. particularly noted the variety of methods used to measure the various sorbents precluded comprehensive comparisons and definitive conclusions. Babel and Kurniawan (2003) confirmed in their review that chitosan, zeolites, and lignin were particularly effective in removing metals from wastewaters, additionally noting some substances (ie lignacious biosorbents) often required some chemical modification to improve performance. The lignacious substances reviewed included sawdust, ground rice husk, and sugarcane bagasse.

Based on availability and cost, sawdust, ground rice husk (GRH), and sugarcane bagasse seem likely candidates for further suitability analysis. Activated carbon and gypsum seem to be useful standards against which to test these other materials, based on the homogeneity of the medium. Gypsum has the additional advantage of being inexpensive to procure, particularly in India, where it is widely used to lower high pH soils. The objective of this study is to assess the effectiveness of gypsum, sugarcane bagasse, generic sawdust, and rice husk in removing toxic metals from native wastewater through sorption capacity. We have also used simple models to quantify the effects of treatment practices on toxic metal concentrations under the experimental conditions.

Materials and Methods

Research activities were conducted in Karnal, Haryana, India during 2008-2009. Karnal and the surrounding areas might be considered as a peri-urban environment wherein industrial and sewage waste streams are commonly used as irrigation sources. Likewise, the materials tested for use in remediation, such as rice husk and bagasse, are readily available in India. Experiments were conducted at the main research station of the Central Soil Salinity Research Institute (CSSRI) of Indian Council of Agricultural Research (ICAR).

Amendments were chosen based on low cost and ready availability in India. The amendments chosen to be tested include three biomass-based amendments, a mineral-based amendment, and activated carbon as a standard for water purification. The biomass amendments included sugarcane bagasse (SB), ground rice husk (GRH), and generic sawdust (SD) from a nearby sawmill. The mineral-based amendment was gypsum (G). Powdered activated carbon (PAC) was used as a standard for comparison. Amendments were characterized by sorption kinetics and isotherms. A constant-head column plug flow reactor (PFR) arrangement was used to test sorption capacity and toxic metals breakthrough.

Native wastewater was used to determine the efficacy of amendments. Canal irrigation wastewater was collected from a site near Paniput, Haryana, India (29.39° N, 76.97° E). Paniput is a center for textile and dye industries in northern India. Metals are commonly used in dyes, such as cadmium orange and cadmium yellow. When untreated, the resultant wastewater streams have high toxic metal concentrations and mix into the larger environmental water streams. The wastewater was collected in a 5000L steel tank, and stored at CSSRI for the duration of these experiments, about 6 weeks.

Wastewater for the experiments was siphoned through a cheesecloth into a 200L plastic barrel. The cheesecloth removed some solids from the wastewater, to give consistency and avoid plugging the packed columns. The wastewater in the barrel was spiked with additional Cd, Ni, and Cr to bring effluent concentration up to more easily detectable levels. A concentrated Cd, Ni, and Cr solution was prepared and mixed into the 200L barrel to achieve a 20 ppm metal solution. The addition of Pb was attempted but proved inadvisable due to incompatible salts settling metals out of solution.

Sorption Kinetics

The low but pervasive background toxic metal levels challenge removal according to sorption theory - the low concentration limits the rate of adsorption, while also slowing any absorption occurring. The higher initial concentrations were chosen to allow some resolution in the ending concentrations. Sorption studies were performed with native wastewater spiked to 20ppm of Cd, Ni, and Cr.

Amendments were tested on an equivalent-volume basis. Equal volumes of each amendment were utilized in each column to remove as much variability from the flow regimes as possible. To give meaningful results based on the columns, kinetic tests were performed on an equal volume basis to provide relevant supporting data.

The unpacked density of each amendment was determined. The values were normalized to give the equivalent volume occupied by 5g gypsum. Twenty mL spiked wastewater was combined with the volume-equivalent amounts of amendment in a 50-mL flask. Flasks were shaken for 5 minutes to achieve thorough mixing then allowed to sit for the duration of the experiment. Amendments were tested for 1, 6, 12, 24, and 48-hr durations. At the end of those times, the flasks were again shaken for five minutes and then filtered through Whatman No. 1 filter paper. The filtrate was stored in 100-mL nalgene bottles for later metal analysis. The storage temperature was room temperature for summer (approximately 35°C) in northern India. The first kinetics experiment had three replicates, and the second experiment had two.

Adsorption Isotherms

Adsorption isotherms are a standard method to determine and compare the affinity of sorbents (amendments) and sorbates (toxic metals). Amendments were again tested using equivalent-volume amounts of amendment. The 20ppm spiked wastewater was used as a base stock to prepare 2, 5, 10, 15, and 20-ppm spiked wastewater solutions. Twenty mL of each solution was combined with the volume-equivalent amounts of amendment in a flask. The flasks were shaken for 5 minutes, allowed to sit for 24 hours, again shaken for 5 minutes, and then filtered through Whatman No.1 filter paper. The filtrate was stored in 100-mL nalgene bottles at 35°C for later metal analysis. The degradation of inorganic metals used in this study was not initiated at this temperature. The 24-hr isotherm experiment had three replicates.

Column Plug Flow Reactor (PFR)

A small constant-head column was designed to test amendment sorption capacity and the breakthrough curve. A cylindrical column with 10 cm diameter and 40 cm length was made up of PVC pipe and capped on the bottom end. The cap was drilled to accept small hose barb. The column had 10 cm freeboard at the top followed by three layers of materials: (a) top layer: 5 cm of marble (CaCO₃) chips and 5 cm of sand, (b) middle layer: 10 cm of amendment, (c) bottom layer: 5 cm of sand and 5 cm of marble (CaCO₃) chips. This three-layered configuration with middle amendment layer was designed to act as a packed-bed PFR. The top layer of sand and marble chips prevented the amendment from floating up, maintaining the packed bed. The bottom layer of sand and marble chips was included to prevent the amendment from washing out and plugging the hose barb. Layers of heavy felt were used to separate layers of material. The volume-equivalent masses packed into each column are shown in Table 1.

TABLE 1 COLUMN PACKING MASSES OF AMENDMENTS

Amendment	Unpacked Density (g/L)	Volume-equivalent masses (g)
G	1950	5.0
SB	829	2.1
GRH	700	1.8
SD	368	0.9
PAC	448	1.2

A custom frame was designed and built to hold volumetric flasks upside-down above the columns. The airlock formed by setting the lip of the volumetric flask at the surface of the column water allowed for a constant-head on the water passing through the packed bed of amendment. The valve at the bottom of the column was designed to control flow. By restricting flow, the solution would be forced to saturate the column and all sorptive surfaces contained within, limiting preferential flow paths. Due to the packing process, flow limitation via the valves was not required, as the material retarded the flow of water to the point achieving a 1 L/d flow rate became difficult for activated carbon and gypsum.

Six columns were prepared for each amendment: three for spiked wastewater and three for deionized (DI) water control. For each amendment, columns 1-3 were used for DI water control and columns 4-6 indicated wastewater. Four additional columns with no amendment and only sand and marble chips were prepared as a second control. Two columns were used for spiked wastewater and two for DI water.

With the valves closed, the columns were filled until saturated (water remaining in the 1L volumetric flask). The columns were allowed to sit in this state for 48 hours before beginning to pass water through. After 48 hours, the valves were opened to allow water to pass through. A 1000mL graduated cylinder was used to catch column effluent. When full, samples were taken by pouring off approximately one-third of the graduated cylinder, then swirling the remainder and decanting 100mL into the sample bottle. Thus, the samples were not 'after' each 1L of water but an aggregate sample across the 1L passing through the column. Samples were stored in the lab at 35°C. As immediate metals analysis was not available, DI columns were operated for 15L while wastewater columns were operated up to 20L of collected effluent as much as lab time constraints allowed.

The valves were adjusted as well as possible to a flow rate of approximately 1 L/day. The time of each 1L volumetric flask addition to the top of the column was recorded, as was the time of each sample from the 1L graduated cylinder. Adjustment of the valves continued throughout the study in an effort to achieve a 1L/day rate. Attempts were also made to adjust and standardize flow rate based on drops per minute. This effort was stymied by non-uniform glass geometry at the tip of the valve barbette, causing nonstandard droplet size, and the effort was eventually abandoned. Instead, the columns were checked on roughly 6-hr intervals to empty filled effluent graduated cylinders and refill emptied volumetric flasks. Column effluent samples were stored in nalgene bottles at 35°C in the CSSRI lab until testing could be arranged. Effluent samples were analyzed without further filtering or other manipulation.

Metal Determination

Flame Atomic Absorption Spectroscopy (AAS) analysis was performed by the research team for metal determinations. The instrument used was a Hitachi Z-5000 Polarized Zeeman flame AAS which is a double-beam AAS and provided a more accurate relative absorption measurement instead of an absolute one. Stock standards of 0.5, 1, 2, 4, and 10 ppm were prepared for Cd, Ni, and Cr. The standards were prepared with double-distilled water and stored separately from samples to be analyzed.

The absorbance of each standard was measured, and then samples were processed through the AAS, with care to rinse the aspirator tube with DI water between

each sample. Where sample absorbance readings were greater than the 10ppm reading for an element, samples were diluted. Samples were tested in order of Cd, then Ni, then Cr – from expected lowest concentration to expected highest concentration – to prevent dilutions from pushing the observed concentration below the detectable limits. At the end of a run, the standards were tested against their initial readings to ensure validity across the run. A best-fit polynomial curve between the absorbance reading and concentrations was generated for each run. Sample concentrations were calculated from the best-fit curve.

Due to broad scatter in metal results from the initial batch of metal sorption lab experiments, repeat experiments were performed for removal kinetics, isotherms, and column studies. The repeat kinetics and isotherm experiments utilized 10g of amendment in 60 mL of wastewater spiked to 20ppm of each metal (Cr, Cd, and Ni). The columns were operated for further volumes of water passing through. Results from the repeat experiments are presented here. Errors in the analysis of the initial samples were attributed to the combination of the utilization of native wastewater and long storage time, allowing residual organics to form colloids and precipitate metals from solution, preventing them from being detected in the AAS experiments. The storage time was much shorter between PFR flow and analysis the second time and the native wastewater was used again.

Kinetics and Sorption Modeling

Kinetics and sorption models were used to generate standard comparisons between sorbents. Both linear and nonlinear kinetics models were fitted to the data based on concepts from Kumar and Sivanesan (2005). 48-hour concentrations were assumed to be equilibrium values.

1) Pseudo First-Order Model

The model used was a linearized form based on the pseudo first-order Lagergren kinetics (Lagergren, 1898),

$$\ln(q_e - q) = \ln(q_e - K_1 t)$$

where q (mg/g) is the amount of metal ion sorbed to the surface of the sorbent at any time t (hr), q_e (mg/g) is the amount at equilibrium, and K_1 (mg/g-hr) is the sorption rate constant.

2) Pseudo Second-Order Model

The plotted concentrations were fitted to a pseudo

second-order kinetic model from Ho and McKay (1998) as used by Guo et. al. (2008) for rice husk sorption modeling,

$$t/q = 1/(K_2 \times q_e^2) + (1/q_e)t$$

where K_2 (g/mg-s) is the sorption rate constant.

The two common sorption isotherms are described below. Both isotherms assume monolayer adsorption onto active soil surfaces.

3) Freundlich Isotherm

The Freundlich equation is given as

$$q = K_f \times C^n$$

Where q (mg/g) is the mass adsorbed per mass adsorbate, C (mg/L) is the liquid concentration, and K_f (mg/g) and n are constants. The equation can be linearized to

$$\log(q) = \log(K_f) + n \log(C)$$

4) Langmuir Isotherm

The Langmuir equation is given as

$$q = (q_e \times K_a \times C) / (1 + K_a \times C)$$

Where q_e (mg/g) is the equilibrium mass adsorbed per mass adsorbate and K_a (L/mg) is a constant. The equation can be linearized to

$$1/q = 1/q_e + 1/(K_a \times q_e \times C)$$

Model Performance Evaluation

Using simple R^2 values is a weak comparison technique for the determination of goodness-of-fit. Adjusted- R^2 for these models will be identical to R^2 , as both models are linearized for parameter determination. These non-nested models further forestall the use of the t- and F-tests for statistical comparison.

The models may be compared for goodness-of-fit using Akaike's Information Criterion (AIC) and Bayesian Information Criterion (BIC). In spite of low n -values causing possible bias, both models use identical sets of observations to formulate the model. This suggests AIC and BIC may provide a more informed goodness-of-fit than simple R^2 .

AIC may be calculated from the following equation, adjusted for small sample set bias as unadjusted AIC tends to overfit models:

$$AIC = n \times \ln(RSS/n) + 2K + 2K(K+1)/(n-K-1)$$

where RSS is the residual sum of squares, n is the

number of observations, and K is the number of parameters in the model (2 for the linearized forms). A superior model will have a lower AIC than other models.

BIC is calculated very similarly:

$$BIC = n \times \ln(RSS/n) + K \times \ln(n)$$

with a built-in adjustment for sample size. As for AIC, a lower BIC value suggests less error is present in the model.

Results and Discussion

Removals were tested by sorption kinetics, adsorption isotherms, and column modeling. Samples from the initial round of experiments awaited analysis for up to 6 weeks. The wait time is believed to have allowed settling of suspended organics present in the native wastewater, reducing aqueous sorbed metals. The settled organics and metals would not have been aspirated by the AAS feed tube, leading to inaccurate representations of metal contents, and is one possible explanation for the inexplicably low concentration results of the initial experiments.

Sorption Kinetics

The sorption kinetics data and results are presented for Cr and Ni in the following section. Using flame AAS, we were unable to resolve Cd from background levels in samples. It is likely that Cd may have a higher sorption affinity than either Cr or Ni, and is thus scavenged to lower concentrations during preferential sorption.

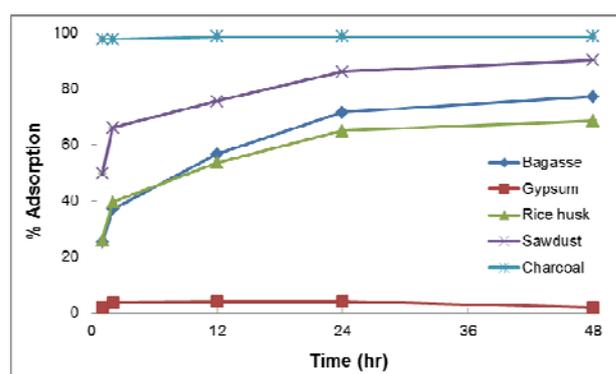


FIG. 1 CHROMIUM ADSORPTION (%) VS. CONTACT TIME

1) Chromium Kinetics

Transforming the concentration data to show the percent of chromium adsorbed, Figure 1 shows the effect of sorbent contact time on chromium. The immediate (1-hr) 100% removal of Cr by carbon suggests the sorption sites were not saturated,

rendering the carbon experiment invalid for complete comparison to the other sorbents. However, the other sorbents did not reach 100% saturation, allowing for comparison between them.

Gypsum was nearly completely ineffective at precipitating Cr. Sawdust led both rice husk and bagasse in performance for Cr removal, eventually removing over 80% of the Cr. Sawdust, bagasse, and rice husk shared similar trends in adsorbance. While the rate of removal slowed with time, removal slowly continued throughout the 48 hours. This suggested that additional sorption sites became available throughout the experiment, possibly through decay and exposure to additional surfaces. It was possible that more finely processing the material would result in improved removal through exposure to more active surfaces.

At the low initial concentration of 20 ppm, chromium achieved a maximum 48-hr loading capacity of 0.90, 0.78, and 0.68 mg Cr/mg of sawdust, bagasse, and rice husk sorbents, respectively. In general, the loading rates achieved were expected to be far below the maximum rates found in the literature. The relatively dilute nature of the solution, combined with the relatively low amount of solution placed into contact with the sorbent, would not suggest otherwise. It's possible that a repeat experiment would place a much smaller amount of sorbent in contact with the solution to achieve higher loading rates. However, such a repeat experiment would not mimic the realistic conditions of low environmental metal concentrations as used in this study.

It was observed that the activated carbon neared 100% Cr removal within the first hour – the sorption was rapid. Without any data points in the first hour, and without saturating the sorption sites, an accurate sorption model for carbon cannot be accurately fit. The opposite was true for gypsum – minimal removal was accomplished throughout the 48-hr test period. However, for bagasse, ground rice husk, and sawdust sufficient resolution appears present to fit sorption models. By assuming the 48-hr concentration to be the equilibrium concentration and linearizing the Lagergren equation, pseudo-first and pseudo-second order models were fitted to the data.

With linear best-fit lines applied to the data, regression coefficients for pseudo-first and pseudo-second order models, AIC and BIC values for the

three sorbents responsive to the metal loading are given in Table 2.

TABLE 2 CHROMIUM KINETIC MODEL CONSTANTS AND CORRELATION VALUES

Sorbent	1st-order				
	q _e	K ₁	R ²	AIC	BIC
Bagasse	-0.093	-2.729	0.99	-23.6	-33.6
Rice husk	-0.101	-2.967	0.98	-52.7	-62.7
Sawdust	-0.091	-3.107	0.96	-25.9	-35.9
	2nd-order				
	q _e	K ₂	R ²	AIC	BIC
Bagasse	0.097	3.26	0.99	5.5	-1.3
Rice husk	0.086	5.04	0.99	7.0	0.2
Sawdust	0.110	6.67	0.99	6.9	0.1

While criticism of linearizing such models exists in the literature (McCuen and Surbeck, 2008; Kumar and Sivanesan, 2006), in particular suggesting linearization overstates the accuracy of said models, the standard method for reporting results has been via linearization of pseudo-first and pseudo-second order models (Ho and McKay, 1998; Kumar and Sivanesan, 2006; Kumar and Bandyopadhyay, 2006; Guo et al., 2008). Lower AIC and BIC values indicate models more closely represent the observed data. For chromium, contrary to R² values, the first-order model appears superior to the linearized second-order model.

It is also appropriate to recognize that the range over which these kinetics have been fit is on the high end of the literature. These experiments test kinetic results over a 48-hr period, similar to that of Mohan and Singh (2002) and Celik and Demirbas (2005), as opposed to the shorter 1-6 hour periods in the literature (Wong et al., 2003; Kumar and Bandyopadhyay, 2006). It is interesting to note that removals continued up through 24 hours, as opposed to more typical equilibrium times of some 1-2 hours found in the literature.

The relative paucity of equilibrium points also brings into a question whether the 48-hr value does accurately represent the equilibrium (q_e) value for kinetics modeling purposes. The 24-hr data points would suggest the 48-hr points to be approaching equilibrium; it appears however somewhat risky to consider the value at the outside of the data range to be a typical equilibrium value.

2) Nickel Kinetics

Figure 2 shows percent adsorption of Ni in solution onto sorbent materials. While activated carbon scavenged all Cr from the solution within the first

hour, the efficacy for Ni was much less. Conversely, whereas gypsum was ineffective for Cr, it performed nearly as well as rice husk for Ni removal.

Overall, the adsorbents are less responsive to Ni adsorption than Cr adsorption. Activated carbon remains the superior treatment, but sawdust and sugarcane bagasse, responding similarly to Ni adsorption, perform to within 85% of activated carbon's sorption capacity. Nickel is sorbed at a capacity of 0.98, 0.90, 0.86, 0.69, and 0.64 mg/mg of activated carbon, sawdust, bagasse, gypsum, and rice husk sorbents, respectively.

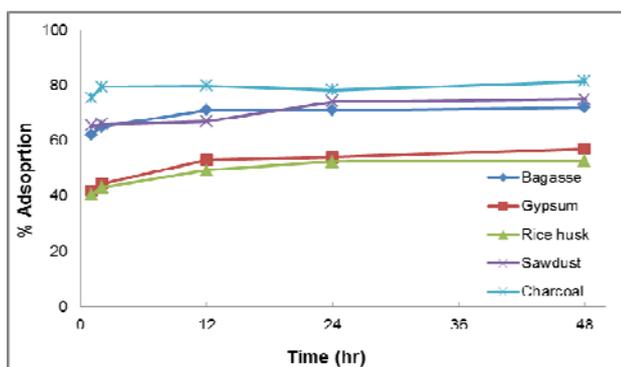


FIG. 2 NICKEL ADSORPTION (%) VS. CONTACT TIME

The Lagergren first order kinetics and a pseudo-second order kinetic model were fitted to the nickel sorption capacity data for all sorbents but activated carbon, which reached saturation levels at one hour.

Table 3 shows the R² and constant values for the two kinetic models, AIC and BIC values. While simple R² would suggest the linearized second-order model to be superior, AIC and BIC indicate the first-order model most closely represents the observed data for all sorbents. The goodness-of-fit value for bagasse pseudo-second order sorption illustrates the concerns of using model linearization techniques.

TABLE 3 NICKEL KINETIC MODEL CONSTANTS AND CORRELATION VALUES

Sorbent	1st order				
	q _e	K ₁	R ²	AIC	BIC
Bagasse	-0.102	-4.67	0.78	-40.7	-47.5
Gypsum	-0.071	-4.10	0.89	-35.6	-42.4
Rice husk	-0.150	-4.03	0.98	-38.1	-44.9
Sawdust	-0.099	-4.17	0.83	-38.4	-45.2
	2nd order				
	q _e	K ₂	R ²	AIC	BIC
Bagasse	0.087	50.00	1.00	8.4	1.7
Gypsum	0.069	19.14	0.99	7.7	0.9
Rice husk	0.064	29.35	0.99	8.1	1.3
Sawdust	0.091	19.19	0.99	7.7	0.9

Equilibrium Isotherms

Results for the 12-hour isotherms are presented in the following section. While twelve hours is a different period of time than the 48-hr equilibrium concentrations used for kinetics modeling, the kinetics show overall the 12- and 48-hr ending concentrations are substantially the same in comparison to the initial concentrations.

1) Chromium

The data were fitted to 12-hr Freundlich and Langmuir isotherm for chromium. The fit constants, K_f and n for Freundlich and K_a for Langmuir isotherms, respectively, are shown in the Table 4, along with the R² value from the linear best fit line from which the constants were derived.

TABLE 4 CHROMIUM ISOTHERM MODEL CONSTANTS AND CORRELATION VALUES

Sorbent	Freundlich			Langmuir		
	K _f	n	R ²	q _e	K _a	R ²
Bagasse	0.010	0.776	0.99	0.081	0.167	0.99
Gypsum	0.002	0.301	0.99	0.005	0.556	0.94
Rice husk	0.010	0.753	0.99	0.082	0.148	0.99
Saw dust	0.019	0.812	0.98	-0.121	-0.056	0.99
Charcoal	0.422	1.187	0.98	-0.162	-1.373	0.99

From the table, it appears that, generally, the chromium isotherms fit very well and are very closely grouped in goodness of fit with the exception of the Langmuir isotherm for gypsum. While the goodness-of-fit may seem high, similar R² values (> 0.95) have been achieved by many authors for metal sorption onto these alternative sorbents, including Cd, Zn, Pb, Ni, and Cr (Mohan and Singh, 2002; Kumar and Bandyopadhyay, 2006; Krishnani et al., 2008; Guo et al., 2008).

2) Nickel

The data were also fitted to the 12-hr Freundlich and Langmuir isotherm for nickel. The fit constants, K_f and n for Freundlich and K_a for Langmuir isotherms, respectively, are shown in the Table 5, along with the R² value from the linear best fit line.

TABLE 5 NICKEL ISOTHERM MODEL CONSTANTS AND CORRELATION VALUES

Sorbent	Freundlich			Langmuir		
	K _f	n	R ²	q _e	K _a	R ²
Bagasse	0.012	1.022	0.99	-0.204	0.054	0.99
Gypsum	0.007	0.838	0.94	0.058	0.171	0.91
Rice husk	0.009	0.838	0.99	0.143	0.067	0.99
Saw dust	0.003	1.516	0.98	-0.024	0.124	0.95
Charcoal	0.017	1.243	0.99	-0.081	0.159	0.99

As discussed above, such high R^2 values have been widely achieved throughout the literature. In contrast to chromium above, the Freundlich isotherm appears to describe the behavior of nickel sorption onto these treatments marginally better than the Langmuir isotherm. However, all treatments have R^2 values greater than 0.90, suggesting the trends and assumptions inherent in the Langmuir and Freundlich isotherms are reasonable for these removal approaches.

Column Studies

The column studies were expected to provide the most realistic and applicable results of any of the modeling experiments performed in this work. It was unfortunate that the packing process slowed hydraulic conductivity to the point that it was not possible to collect the desired amount of leachate in the experimental time available. As discussed in the methods section, a top limit of 25L was selected for leachate collection as immediate analysis was not available to detect metal breakthrough. Those samples were later discarded due to sample testing latency, and subsequent quantities of water were passed through the columns.

The repeat column experiment for nickel was operated through 16, 12, 11, 9, and 5 liters of effluent for the sugarcane bagasse and control, gypsum, rice husk, sawdust, and charcoal treatments, respectively. As these figures highlight, the packing process was extremely effective in achieving complete saturation of the treatment media. Equivalent packing efforts resulted in notable differences in flow rate through the columns. Finer-sized media, such as the powdered activated carbon, was packed to very low flow rates, while coarser particles such as gypsum, ground rice husk, and sawdust had higher conductivities. The highest flow rate was observed for the coarsely ground and spongy sugarcane bagasse media.

Although the columns were not subject to any appreciable head pressures (<10cm H₂O), this does suggest standard approaches used to force water through activated carbon PFR's would have to be modified for head pressure, packing density, and/or depth to achieve equivalent contact times, beyond any modifications which may be desirable to achieve longer contact times due to media less activated than PAC.

The volumetric concentration breakthrough curve results are presented in the following sections. As with

the kinetic and isotherm results, cadmium was unable to be resolved from column effluent.

1) Nickel

The nickel breakthrough curves are presented below in Figure 3. The initial wastewater spiked 20ppm Ni concentrations fell below 3ppm for the first liter of effluent, before rising to as high as 6ppm. No columns appeared to have reached total breakthrough – not even the control columns.

The DI water control treatments had an average 0.94ppm concentration, with a 0.33ppm standard deviation. While this might suggest all detections were 1ppm too high, the 5 liters of effluent passed through activated carbon all had lower detections than the control, suggesting either some link in the CaCO₃/sand/felt chain was contaminated with pervasive low Ni concentrations or that the DI control water source was contaminated.

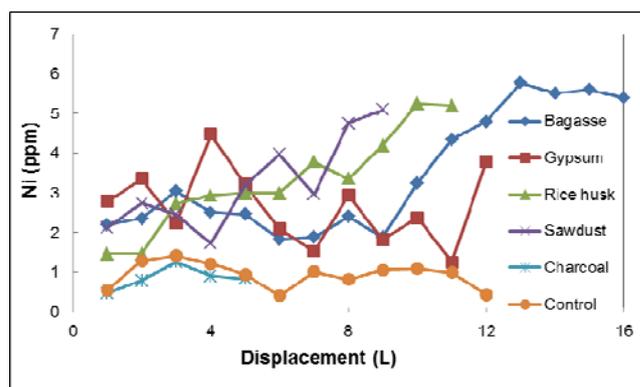


FIG. 3 NICKEL BREAKTHROUGH CURVES FOR DIFFERENT SORBENTS

The bagasse, gypsum, and sawdust treatments exhibited a trend where a local concentration maximum existed between 3-6 liters of effluent. The nonlinear trend appeared to continue for the control sawdust, and bagasse treatments. Rice husk and sawdust treatments were not operated through sufficient effluent volumes to determine if the trend continues.

Bagasse, rice husk, and sawdust treatment exhibited a positive overall trend. Although breakthrough was not a linear process, this suggested the three treatments were headed towards breakthrough. The slightly negative trend for gypsum was consistent with the gypsum metal removal mechanism, which was chemical precipitation via pH modification. This trend might be expected to continue until all gypsum was dissolved into the passing effluent stream.

2) Chromium

Chromium breakthrough curves are presented below in Figure 4. Contrary to the nickel breakthroughs shown above, three distinct breakthrough patterns were apparent for Cr. Gypsum was completely ineffective at Cr removal, closely tracking the DI control effluent concentrations. Bagasse, rice husk, and sawdust performed consistently, leaving 4-7ppm Cr in the effluent. Activated carbon scavenged all Cr present down to trace levels. These findings reinforced the sorbent-Cr sorption trends discussed above.

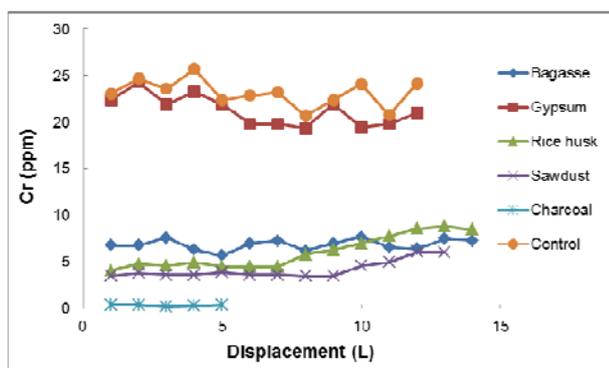


FIG. 4 CHROMIUM BREAKTHROUGH CURVES FOR DIFFERENT SORBENTS

Conclusions

This research utilized novel concepts to characterize cadmium, nickel, and chromium in the water system near Panipat, India and assessed the effectiveness of sugarcane bagasse, sawdust, gypsum, and ground rice husk to remove metals from environmental wastewaters. These inexpensive sorbents were compared to powdered activated carbon for sorption capacity and speed, and metal scavenging ability. Bagasse, ground rice husk, and sawdust all trended similarly for Cr removal, while gypsum was an ineffective treatment. For Ni removal, gypsum and rice husk performed similarly, as did sawdust and bagasse, with the latter scavenging metals to lower concentration than the former. Cadmium concentrations were too low to be identified from background noise. The processes employed competitive sorption, wherein all metals were present in solution simultaneously. Cadmium may have outcompeted Cr and Ni for sorption sites on sorbent materials.

In an effort to standardize comparisons, the sorbents were fit to linearized first- and second-order kinetic models and Langmuir and Freundlich isotherms. High R^2 values were achieved for linearized kinetics fits,

particularly for the second-order equations. Conventional F- and t-tests were not suitable to test these non-nested models for statistical validity. However, the information-theoretic based approaches of AIC and BIC indicated that first-order sorption kinetics were a better fit for all sorbents than the linearized pseudo-second order sorption model.

Both Langmuir and Freundlich isotherms described the observed data. The low number of sample points may have contributed to the high R^2 values (> 0.95), although other authors have achieved similar values. This suggested the assumptions inherent in the Langmuir and Freundlich isotherms, i.e. monolayer absorption, were appropriate for these sorbents.

Sorbents were used to fill constant-head packed-bed column reactors (PFR's) to mimic actual field-use situations. Breakthrough curves were inconclusive, likely due to the relatively dilute and low volumes of wastewater passed through them. Further investigation along this vein appears warranted to generate the realistic data required to successfully engineer and implement alternative sorbent-based PFR's.

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