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Optimization of Chromium(VI) and Copper(II) Adsorption on Chemically Treated Sawdust Using Response Surface Methodology

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Chromium(VI) and copper(II) are the most significant industrial effluent whose direct discharge into nearby waterways creates water pollution. Wastewater containing Cr(VI) is released from several industrial activities like electroplating, tanning, plastic surfaces coating and it causes cancer in digestive tract and lungs. Copper(II) is found in industrial effluents including acid mine drainage and galvanizing plants and higher doses leads to anemia, kidney and liver damage. Sawdust is a waste by-product of the timber industry that can be utilized as bio adsorbent for the removal of heavy metals. In the present study, the potential of sawdust for the removal of Cr(VI) and Cu(II) from an aqueous solution through column based adsorption process has been investigated. Response surface methodology is applied for optimization of variables *e.g.* metal concentration, pH and column bed height. The optimum conditions for maximum removal of chromium (89.74 %) and copper (93.17 %) from aqueous medium are: column bed height (20 cm, 20 cm), initial concentration (30 mg/L, 10 mg/L) and pH (2, 4), respectively. The results indicated that sawdust is a promising, effective and an inexpensive material for the removal of Cr(VI) and Cu(II) from industrial wastewater.

Keywords: Sawdust, Bio adsorbent, Wastewater, Response surface methodology.

INTRODUCTION

With the beginning of industrialization till today, the pollution of air, water and soil has been increasing regularly and significantly [1]. The discharge of toxic metals directly into nearby waterways affects its quality and creates a serious water pollution problem. Metal-laden waste effluents generally discharged from mining, electroplating, battery manufacturing and metal finishing industries, without proper treatment, poses severe impact on environment [2]. Day by day industrial activities utilizing heavy metals rises and their inappropriate discharge amplifies the presence of these metals in water bodies. Due to non-biodegradable and toxic in nature, several metals such as Cr(III) and Cr(VI), copper, lead, manganese, mercury, cadmium, *etc*. are hazardous for human beings and have severed health implications *e.g.* skin cancer, blindness, still birth, allergic dermatitis, increase in blood pressure, kidney damage, gastrointestinal stress, liver damage and delay in physical and mental development [3]. Copper is extensively found in wastewater discharges from industries including acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants and its entry into the food chain *via* bioaccumulation leads to severe impacts on human beings such as mucosal irritation, central nervous system irritation, possible necrotic changes in the liver and kidney, *etc*. [2,4]. Chromium mainly in Cr(VI) state is generally used in making pesticides by commercial formulations containing chromium, copper and arsenic such as "chromated copper arsenate (CCA)" for preserving wood [5] and large intake of Cr(VI) compounds causes cancer in humans [6]. Different types of industrial activities such as electroplating, tanning, plastic surfaces coating for water and oil resistance released chromium into environment [7,8]. Chromium compounds may deposition soil and water from airborne particles and can be easily changed from one oxidation form to another [7]. Industrial effluents having high concentration of pollutants need a specialized treatment method [9] and there are several treatment methodologies are available to remove them from industrial wastewater such as ion exchange, membrane filtration, reverse osmosis, electrochemical, evaporation, solvent extraction, emulsion per traction technology and chemical coagulation [8,10-12]. But, all these process have some kind of disadvantages such as

inefficient removal of metal, very costly or not very effective if concentration of metal is in the range of 1-100 mg/L and secondary sludge production [13-15].

Among several treatment methodologies, adsorption is one of the effective and efficient methods for Cr(VI) and Cu(II) removal from industrial effluents as it is a very simple process, no problem of sludge in operation, easy to handle, availability of different types of adsorbents and can remove heavy metals even at lower concentration levels [16]. In the process of adsorption, there is a solid substance known as 'adsorbent' that efficiently binds molecules through physical attractive forces, ion exchange or chemical binding [17-19]. Bio-sorption is a feasible, eco-friendly and promising technology for heavy metal removal as it uses low-cost and non-pollutant material [20].

Agricultural by-products are an important source of materials that can be exploited to use as heavy metal adsorbents and also, they are selective in retaining certain metallic ions. Application of agricultural waste products for the treatment of polluted water is an economically attractive and promising option. It provides two benefits on one hand, it unravels the residues disposal problem, which is a major issue, other hand; it transforms these wastes into valuable and economical sorbents for water treatment. Several kinds of adsorbents are studied previously such as water hyacinth [21], bagasse [22,23], carbon cloth [24], fly ash [25,26], rice husk [27], neem sawdust [28] and sunflower [29]. Several research studies have confirmed that among different variety of agricultural by-products sawdust is one of the promising materials which can be utilized for adsorption of heavy metals [30-34], dye [35-39] and some other organic contaminants [40,41] from water. Sawdust is a waste by-product of the timber industry, which is used for cooking fuel purposes or as a packing material [42]. It consists of majorly three important components: cellulose, lignin and hemi-cellulose.

In the present study, optimization of different process variables such as metal concentration, pH of the solution and column bed height for Cr(VI) and Cu(II) removal from aqueous medium using chemically treated sawdust is investigated by employing Box-Behnken model experimental design in response surface methodology, Design Expert software Version 7.0. The effects of the initial metal concentration, column bed height and pH were assessed at constant flow rate of 1 mL/min.

EXPERIMENTAL

Preparation of sawdust by using different chemicals: Raw sawdust (SD) was collected from local sawmill and dried in the sunlight to evaporate all the moisture and then it was ground to a fine powder. The grounded sawdust was treated with the tap water and 1 % of sodium hydroxide, sulphuric acid, hydrogen peroxide and formaldehyde in the ratio of 1:5 (SD chemical, w/v) at 50 °C for 4 h. The sawdust was then filtered through muslin cloth and washed with the distilled water so as to remove free chemicals. Half of the part was kept as water washed sawdust (W) and the remaining portion was activated at 110 °C in an air oven for 24 h and termed as thermally active sawdust (TA) [43].

Preparation of charcoal: Raw sawdust was treated with sulphuric acid until it burnt in acid and converted into black colour and then, it was kept at 100 °C for 2 h. Further, it was washed with distilled water and soaked overnight in 1 % sodium bicarbonate solution for neutralization. The material was dried at 105 °C for in an air oven for 24 h.

Characterization of sawdust: Different physico-chemical characters (ash content, pH and electrical conductivity) of raw sawdust and treated sawdust were determined using standard procedures.

Column experiments: Column experiments were performed using glass columns of 60 cm in height and internal diameter of 4 cm prepared by a series of geotextile cloth, pebbles, sand, sawdust, sand and pebbles, respectively (Fig. 1). Sand was thoroughly washed with distilled water and dried at 105 ± 2 °C for 24 h prior its use.

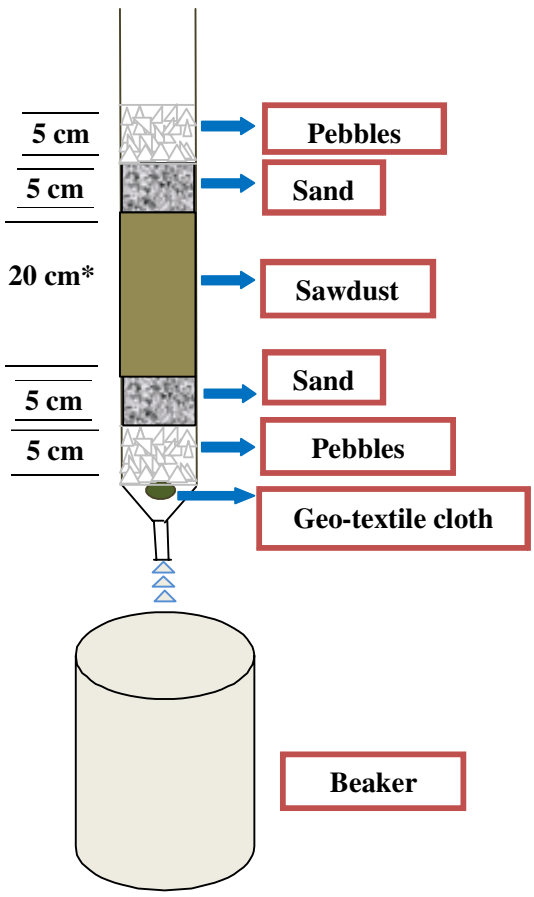

Fig. 1. Column experiment study for adsorption of chromium and copper using sawdust

A glass wool was placed at the bottom of the column to prevent clogging. Initially, a fixed concentration of Cr(VI) and Cu(II) solutions *i.e.* 50 mg/L were passed through the column at a constant flow rate of 1 mL/min so as to find out the best one among the various types of treated sawdust and then, the selected sawdust material was further used in the response surface methodology based experimental study. The methodology of whole experiment is shown in Fig. 2. Chromium(VI) and copper(II) solutions having different concentrations and pH conditions were passed through the column having variable column bed height as suggested by the response surface methodology model at a fixed flow rate of 1 mL/min. 100 mL of eluted fractions were collected time after time and analyzed for Cr(VI)

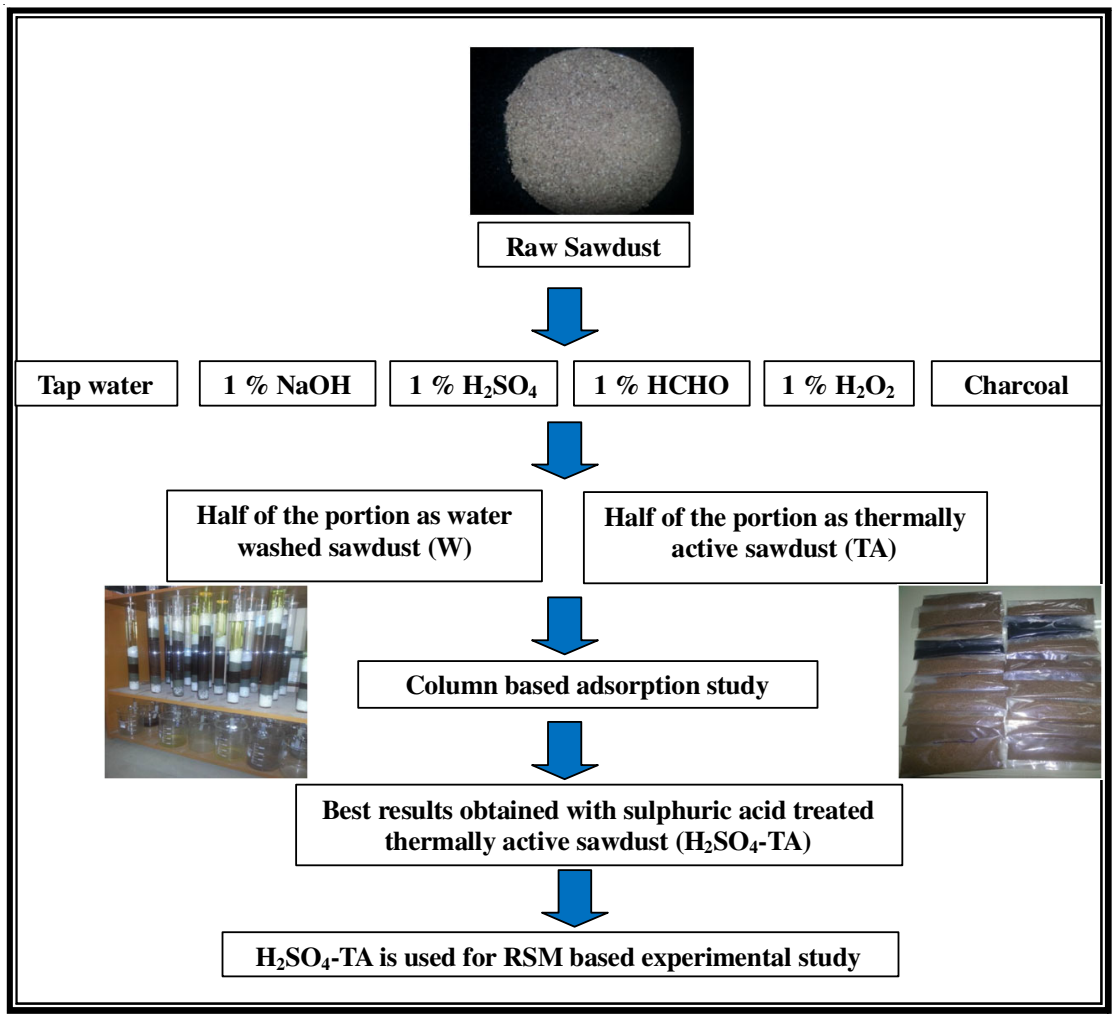

Fig. 2. Methodology of the experimental study

and Cu(II) concentration using atomic absorption spectrophotometer (AAS). All experiments were conducted in triplicate for statistical analysis.

Adsorption studies: Column adsorption studies were conducted to determine the percentage removal of Cr(VI) and Cu(II) ions using sawdust. The percentage removal (%) was calculated as follows:

$$\text{Removal (\%)} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (1)$$

where, C_o = Initial concentration (mg/L); C_t = Solution concentration at the end of the adsorption process (mg/L).

Response surface methodology experimental designs and data analysis: Response surface methodology (RSM) is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable), which is influenced by several independent variables (input variables). For optimization, the user required to supply minimum and maximum values for each factor [44,45]. The conventional method of optimizing the process variables are expensive, difficult and time-consuming as it needs a large number of experimental runs therefore, response surface methodology technique is better, which reduces the number of experiments and provides appropriate model for process optimization. Response surface methodologies are helpful and beneficial technique in order to optimize the responses shaped under the influence of process variables [46-49].

Design Expert software Ver. 7 naming Box-Behnken factorial design (BBD) is used with three factors and three levels, including three replicated at centre point to evaluate the effect of column bed height (cm), initial metal concentration (mg/L) and pH on the removal of Cr(VI) and Cu(II) from aqueous medium using treated sawdust (Table-1). Box-Behnken factorial design (BBD) was used to determine the optimum conditions for adsorption of chromium and copper. The optimization process includes execution of statistically designed experiments, determining the coefficients in the mathematical model, predicting impact on response and verifying the accuracy of the model [50,51]. A polynomial quadratic equation was fitted to evaluate the effect of each independent variable to the response:

$$Y = \beta_o + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (2)$$

where, Y is the predicted response; β_o is a constant; β_1, β_2, β_3 are the linear coefficients; β_{12}, β_{23}, β_{13} are the cross-coefficients; β_{11}, β_{22}, β_{33} are the quadratic coefficients. The response surfaces of the variables inside the experimental domain were analyzed using Design Expert. Subsequently, five additional confir-

TABLE-1
VARIABLES AND LEVELS CONSIDERED FOR THE ADSORPTION OF Cr(VI) AND Cu(II) USING TREATED SAWDUST BY BOX-BEHNKEN FACTORIAL DESIGN

Factors		Range and levels (Coded)		
		-1	0	+1
Column bed height (cm)	A	5	12.50	20
Initial concentration (mg/L)	B	10	30	50
pH	C	2	4	6

mation experiments were conducted to verify the validity of the statistical experimental strategies.

RESULTS AND DISCUSSION

Characterization and comparison of percentage removal efficiency of different types of treated sawdust: Various physico-chemical parameters of raw as well as treated sawdust were shown in Table-2. The results on percentage removal efficiency of chromium as well as copper utilizing different types of treated sawdust (Fig. 3) were indicated that charcoal and sulphuric acid treated thermally active sawdust had the maximum removal efficiency for both Cr and Cu but, because charcoal is highly acidic in nature, it leads to the harmful impact on environment and hence, it is not a good option. Therefore, sulphuric acid treated thermally active sawdust (H_2SO_4-TA) was selected for further response surface methodology based experimental study.

TABLE-2
CHARACTERISTICS OF DIFFERENT TYPES OF TREATED SAWDUST

		pH	EC (dS/m)	Ash (%)
Tap water	W	6.50	0.74	4.08
	TA	6.60	0.75	3.08
Sulphuric acid	W	3.61	0.75	2.99
	TA	3.22	0.75	2.29
Sodium hydroxide	W	8.11	0.74	3.58
	TA	8.20	0.74	3.48
Hydrogen peroxide	W	7.41	0.75	3.39
	TA	6.86	0.75	2.09
Formaldehyde	W	6.70	0.74	3.59
	TA	6.50	0.74	2.89
Raw sawdust		5.86	0.74	2.58
Charcoal		1.56	0.75	3.87

W = Water washed sawdust; TA = Thermally active sawdust

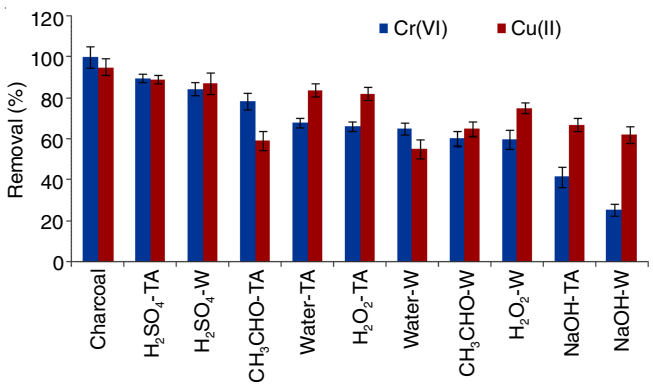

Fig. 3. Percentage removal efficiency of Cr(VI) and Cu(II) from aqueous medium using different water washed (W) and thermally active (TA) treated sawdust

Response surface methodology based experimental design and results: In the present experiment, Box-Behnken factorial design model was employed for optimization of percentage removal of chromium and copper. Design expert software is used for data analysis, analysis of variance (ANOVA), regression coefficients and regression equations. The experimental design matrix comprising independent variables and response for chromium and copper removal is presented in Table-3. ANOVA model represents that the model is significant for chromium and copper at F value 48.02 and 22.14, respectively. If p-value is lower than 0.05, it indicates that the model parameter is significant and thus, data obtained from ANOVA analysis (Table-4) proved that the selected model is satisfactorily represents the data for chromium and copper removal. The coefficient of variation (R^2) for chromium and copper has been found 0.98 and 0.96, respectively and proved that for both Cr and Cu experiments, there is a high correlation between the experimental values and the predicted values. The model appears statistically sound as the lack of fit test used for testing of model shows p value of 0.3917 for Cr and 0.4619 for Cu, which is not significant and non-significant lack of fit test proved that the quadratic model was suitable for the present study [52]. Analysis of residuals showed no abnormality. To depict the interactive effect of independent variables on responses, one variable has been kept constant while the other two variables were varied at different ranges. The interaction between different factors has been shown through the shape of response surfaces. The 3-D responses for chromium and copper are depicted in Figs. 4-6.

Effect of pH and initial metal ion concentration: The combined effect of pH and initial metal ion concentration on percent removal of chromium and copper depicted in Figs. 4(a) and 4(b), respectively. It has been found that as the metal ion concentration increases, the percentage removal of Cr(VI) and Cu(II) decreases because at higher concentrations, the ratio of available surface to initial metal ion concentration is low [49].

Effect of pH and column bed height: The combined effect of pH and column bed height on percent removal of chromium and copper was shown in Figs. 5(a) and 5(b), respectively. As the pH increases from 2 to 6, the percentage removal of Cr(VI) and Cu(II) decreases. Adsorption is higher in nearly acidic pH range due to the presence of ionizable surface charge of the adsorbent. In case of chromium, at pH 2, main species is $HCrO_4^-$ that creates electrostatic attraction between positively charged adsorbent surface and negatively charged chromium species [49].

Effect of initial metal ion concentration and column bed height: The combined effect of initial metal ion concentration and column bed height on percent removal of chromium and copper analyzed at constant pH is presented in Figs. 6(a) and 6(b), respectively. With the increase in column bed height, the removal efficiency of both the metal ion increases due to presence of more active sites as well as utilization of all active sites in adsorbent by metal ions [53].

Confirmatory experiments: The optimum conditions for percentage removal of chromium and copper obtained from the model is shown in the Table-5. Further, the confirmatory

TABLE-3
EXPERIMENTAL DESIGN MATRIX AND RESPONSES FOR CHROMIUM(VI) AND COPPER(II) REMOVAL USING H_2SO_4-THERMALLY ACTIVE

Runs	Column bed height (cm)	Initial concentration (mg/L)	pH	Removal of Cr(VI) (%)		Removal of Cu(II) (%)	
				Actual	Predicted	Actual	Predicted
1	5.00	10.00	4.00	80.59	81.23	89.15	88.98
2	20.00	10.00	4.00	87.12	85.56	93.17	92.56
3	5.00	50.00	4.00	77.86	76.41	86.95	85.92
4	20.00	50.00	4.00	86.23	79.27	90.35	91.27
5	5.00	30.00	2.00	78.26	82.32	88.55	88.32
6	20.00	30.00	2.00	89.74	86.21	91.63	90.11
7	5.00	30.00	6.00	77.12	78.26	87.55	85.64
8	20.00	30.00	6.00	87.53	82.65	90.86	88.72
9	12.50	10.00	2.00	78.23	80.12	88.56	87.43
10	12.50	50.00	2.00	78.45	81.29	87.25	86.54
11	12.50	10.00	6.00	82.26	81.55	89.21	88.59
12	12.50	50.00	6.00	77.63	76.21	87.11	86.21
13	12.50	30.00	4.00	75.68	76.21	86.93	85.95
14	12.50	30.00	4.00	75.58	74.29	85.78	85.11
15	12.50	30.00	4.00	75.52	74.25	86.92	86.75
16	12.50	30.00	4.00	77.43	75.11	85.85	85.24
17	12.50	30.00	4.00	76.65	75.21	85.91	86.11

TABLE-4
ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE QUADRATIC MODEL OF CHROMIUM(VI) AND COPPER(II) REMOVAL

Source	Sum of squares	Degree of freedom	Mean square	F- value	P-value	
ANOVA for chromium(VI)						
Model	343.90	9	38.21	48.02	0.0001	Significant
A	169.19	1	169.19	212.60	0.0001	
B	14.18	1	14.18	17.82	0.0099	
BC	5.88	1	5.88	7.39	0.0298	
A2	122.73	1	122.73	154.23	0.0001	
B2	17.42	1	17.42	21.89	0.0023	
C2	3.69	1	3.69	4.64	0.0682	
Residual	5.57	7	0.80			
Lack of fit	2.74	3	0.91	1.29	0.3917	Not Significant
ANOVA for copper(II)						
Model	71.46	9	7.94	22.14	0.0002	Significant
A	23.84	1	23.84	66.48	0.0001	
B	8.88	1	8.88	24.77	0.0016	
A2	28.92	1	28.92	80.66	0.0001	
B2	4.26	1	4.26	11.88	0.0107	
C2	2.36	1	2.36			
Residual	2.51	7	0.36			
Lack of fit	1.11	3	0.37	1.05	0.4619	Not Significant

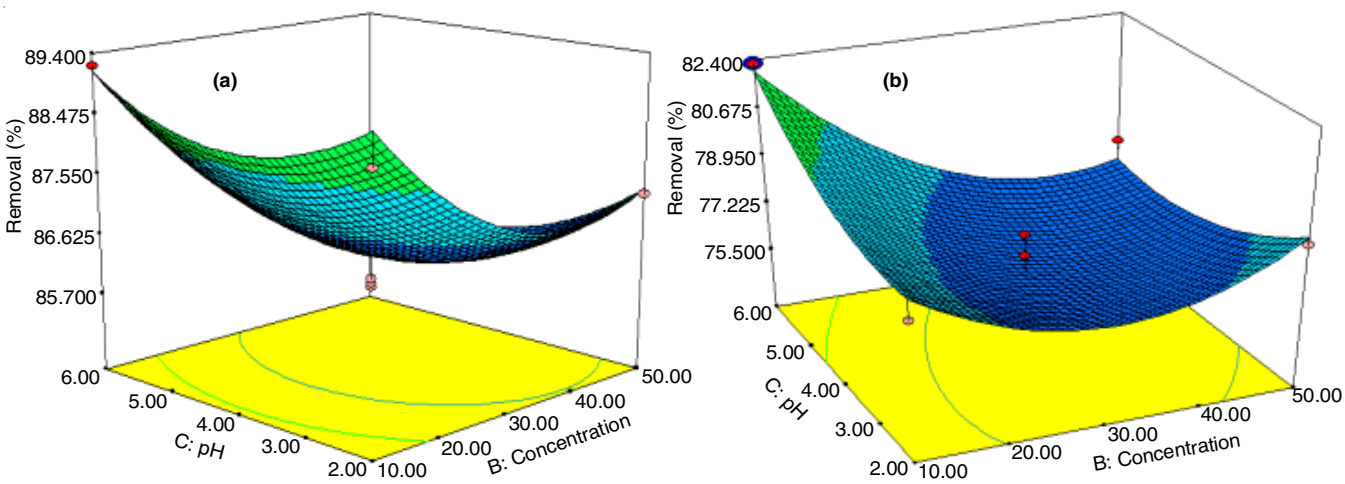

Fig. 4. Effect of pH and initial metal ion concentration on percentage removal of (a) Cr(VI) (b) Cu(II)

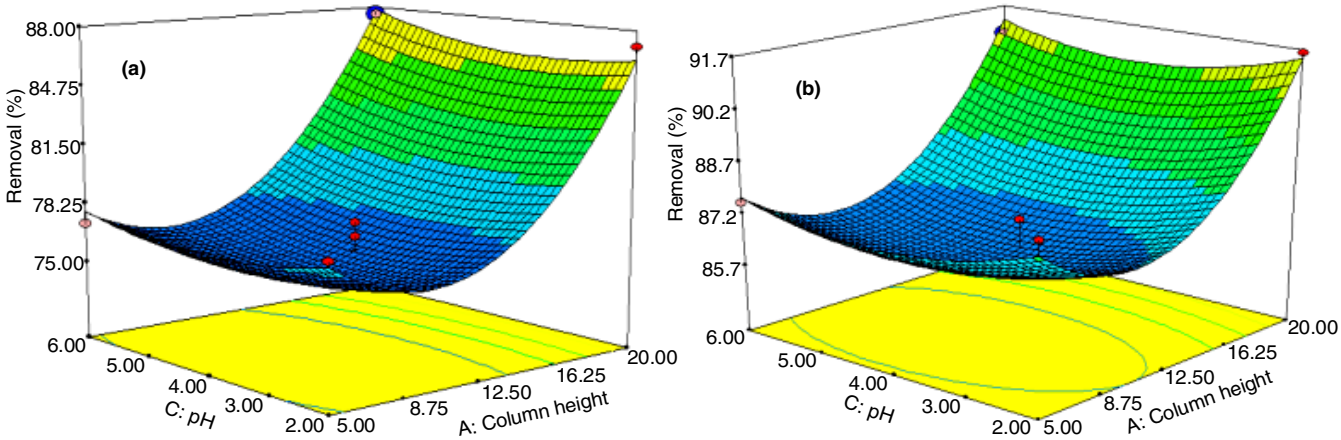

Fig. 5. Effect of pH and column bed height on percentage removal of (a) Cr(VI) (b) Cu(II)

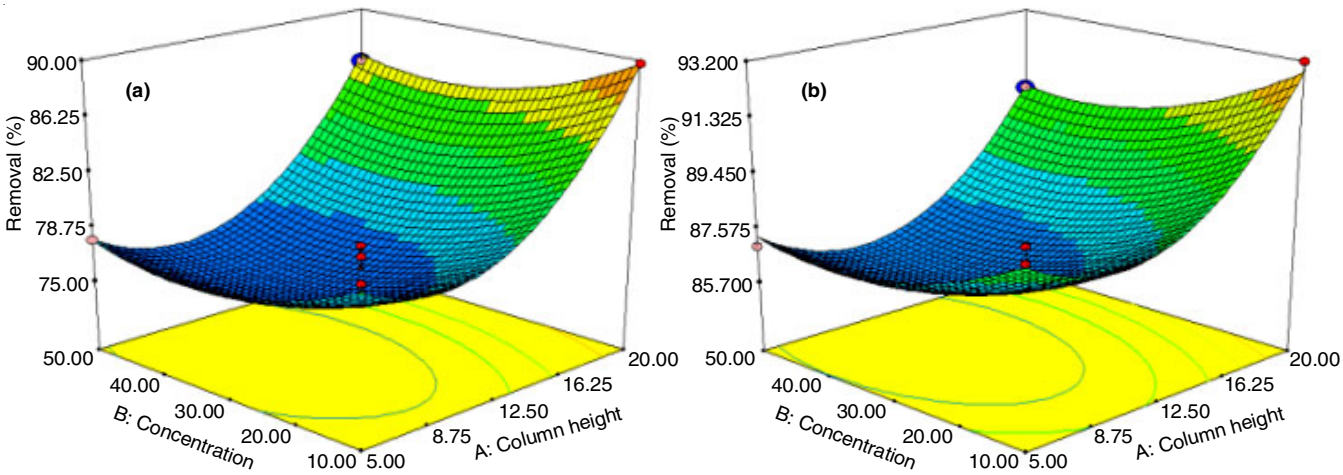

Fig. 6. Effect of initial metal ion concentration and column bed height on percentage removal of (a) Cr(VI) (b) Cu(II)

TABLE-5
OPTIMUM CONDITIONS FOR PERCENT REMOVAL OF CHROMIUM(VI) AND COPPER(II) USING H_2SO_4-THERMALLY ACTIVE

	Column bed height (cm)	Initial concentration (mg/L)	pH	Removal efficiency (%)	
				Actual after confirmatory experiments	Prediction given by model
Chromium(VI)	20	30	2	89.74	86.21
Copper(II)	20	10	4	93.17	92.56

experiments were performed with the variables suggested by the model for supporting the optimized data. The effect of column bed height, metal concentration and pH on the removal efficiency were also analyzed and it was determined that the data are in accordance with the suggested model given by response surface methodology.

Conclusion

In the current study, different types of chemically treated sawdust was employed for removal of chromium and copper from aqueous medium and it was ascertained that among various types of treated sawdust, chromium and copper removal efficiency of H_2SO_4-TA was maximum. A detailed column adsorption study using H_2SO_4-TA determined the optimum conditions for chromium and copper removal using response surface methodology. The optimum conditions for maximum removal of chromium (89.74 %) and copper (93.17 %) from aqueous medium are: column bed height (20 cm, 20 cm), initial concentration (30 mg/L, 10 mg/L) and pH (2, 4), respectively. Availability and cost effectiveness of sawdust makes it very viable adsorbent for the removal of Cr and Cu from the wastewater. It can be concluded that exploitation of sawdust for wastewater treatment is an effective, eco-friendly and economical process.

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