

Spectrophotometric Determination of the Efficiency of Lignocellulosic Sludge-Based Adsorbents in the Removal of Cr(VI) and Ni(II) Ions from Aqueous Solution

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Abstract: Advantages such as environmental friendly material, low cost and high regeneration percentage of Lignocellulosic sludge-based adsorbents like activated sawdust powder (ASDP), Paper Mill Sludge carbon (PMSC) and Activated Paper Mill Sludge Carbon (APMSC) make them as suitable adsorbents for the removal of toxic metals such as Cr(VI) and Ni(II) ions from water and wastewater. The mesoporous carbons namely PMSC and APMSC were most effective in adsorption of cationic pollutants than anionic pollutants. Isotherms data indicated that these activated carbons have high adsorption capacity. The dimensionless factor, R_L of the adsorption isotherms revealed that the adsorption process for both ions on both adsorbents was very favorable. The results suggest the feasibility of a good substitute than other commercially available activated carbons produced from natural resources. So, the reuse of organic wastes from any industrial process is a high priority today. Adsorption of Cr(VI) ions and Ni(II) ions using these low-cost sorbents were more effective at pH 2 and pH 5 respectively. Various isotherm, kinetic models and Activation parameters were fitted with experimental data to describe the behavior of diffusion mechanism, solute interaction and nature of adsorption with the adsorbents through batch studies. The best isotherm in these studies was selected by error analysis and the stability of adsorbents was also confirmed through desorption studies.

Keywords: Sawdust, Paper mill sludge, Heavy metals, adsorption, Activation parameters, Isotherms and kinetics modelling, Chi-square (χ^2) test analysis

Introduction

Water contamination by industrial wastes is a major concern because of its toxicity, bio-accumulating tendency and non biodegradable nature. Contaminated water leads to severe health defects to living organisms. Use of chromium and nickel ions in electroplating industry, steel industry, mining *etc.*, is quite extensive. Due to their severe toxicity, Environmental Protection Agency and WHO set the permissible limit for the discharge of Cr(VI) and Ni(II) ions into surface water as 0.1 mg/L and 2 mg/L, respectively and in potable water as 0.05 mg/L and 0.01 mg/L, respectively¹. Thus the removal of Cr(VI) and Ni(II) ions from water and effluents becomes mandatory. Recently, attention has been

diverted towards the biomaterials which are by products or the wastes from large scale agricultural waste and industrial operations materials. So, the reuse of organic wastes originating either naturally or from any industrial process is also a priority today aiming to eliminate/reduce environmental pollution.

Sawdust is one of the cheapest biomass^{2,3} in which the constituents are cellulose (55-60%), hemicellulose (20-25%), lignin (20-25%) used for the preparation of carbon. The functional groups present in the agricultural biomass molecules are like acetamido, amido, amino, carbonyl, carboxyl, sulphydryl groups, phenolic, structural polysaccharides, alcohols and esters. These polar poly functional groups have the high affinity towards metal complexation. Some biosorbents are non-selective and bind to a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals depending upon their chemical composition. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation. Rapidly increasing environmental contamination by solid wastes arising from progressive industrialization is an another important environmental problem⁴. The paper industry is of great environmental importance due to the quantity of paper sludge generated and its disposal. Paper sludge generated by the paper industry is generally composed⁵ of organic fibers (cellulose, hemicelluloses and /or lignin), inorganic fillers and coating materials such as kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), limestone (CaCO_3) and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$).

The possible effective use for paper sludge ash is in the preparation of low cost sorbents for water purification and toxic metal ions removal from water using steam and/or calcination treatments. Preparing the natural lignocellulosic materials (rice husk^{6,7}, sawdust⁸⁻¹⁴, nut shell¹⁵⁻¹⁷, agricultural wastes biopolymers¹⁸, chitosan^{7,19} and sludge-based materials²⁰⁻²²) into activated carbons with specific modification in order to use them for ion-exchange in water- and effluent treatments is a subject of interest nowadays. Adsorption process is one of the efficient methods for Cr(VI) removal due to its simplicity, sludge-free operation, easiness in handling, availability of various adsorbents and more efficient in removal of heavy metals at lower concentration levels^{23,24}. Generally, the adsorption capacity increases with specific surface area due to the availability of adsorption sites. Pore size and pore size distribution are closely related to the composition of the activated carbon, the degree of activation and the frequency of regeneration²⁰. Chemical activation and physical activation are two processes for preparation of activated carbon. Acid treatment leads to enhance the surface chemical properties, adsorptive and textural characteristics²⁵. Acid treatment has been used for cleaning the cell wall and replacing the natural mix of ionic species bound on the cell wall with protons, nitrates and sulphates.

Hence, the present study intends to investigate the preparation of activated sawdust powder (ASDP) produced by the simultaneous treatment of sawdust by the wet oxidizing agents such as H_2SO_4 , HNO_3 and H_2O_2 . Then the mesoporous sludge-based carbons (PMSC and APMSC) also prepared for the adsorption of heavy metal ions such as Cr(VI) and Ni(II) spectrophotometrically and also compare the potentiality of their surface modifications. Surface morphology of ASDP, PMSC and APMSC were characterized by BET, SEM and FTIR. Isotherm and kinetics studies were conducted to evaluate the solute-solid interactions. Thermodynamic parameters were determined to study the spontaneity and feasibility of the adsorption processes. The best isotherm in this study was selected by error analysis (Chi-square (χ^2) test) and the reusability of the activated low-cost lingo-cellulosic adsorbents namely ASDP, PMSC and APMSC were also confirmed through desorption studies.

Experimental

Saw dust was collected from the local saw mill. Paper mill sludge (filter cake) was obtained from Tamil Nadu Newsprint and papers limited (TNPL). Potassium dichromate was used for the preparation of Cr(VI) stock solution purchased from Merck India. Nickel sulphate was used for the preparation of Ni(II) stock solution purchased from Merck, India. The pH of the solutions were maintained by hydrochloric acid - potassium chloride for the range of pH 1-3, acetic acid - sodium acetate for the range of pH 4-6 and boric acid - sodium hydroxide for the range of pH 8-10 purchased from Merck India. Analytical grade reagents of 1,5-biphenyl carbazide and acetone were used for analyzing the chromium ions. Double distilled water was used for preparing all the solutions.

Preparation of ASDP

A procedure similar to that followed for the preparation of acid treated sawdust -chitosan composite beads was followed¹⁴. Sawdust was sieved by sieve plate to obtain uniform particles of size 0.5 mm and was treated with concentrated sulphuric acid (50 mL per 10 g) for 2 h. And then treated with sodium carbonate (0.1 N) for neutralization till effervescence stops and again dried in hot air oven 100 °C. The dried sample was then treated with H₂O₂ (10 mL) in a water bath at 50 °C for 30 min, followed by 10% conc. HNO₃ with constant stirring at 70 °C for about 40 min. The sample was then washed, dried and crushed into fine powder form.

Preparation of PMSC and APMSC

The preparative methodology shown below as flow chart is similar as the literature procedure²⁶ Figure 1(a-b).

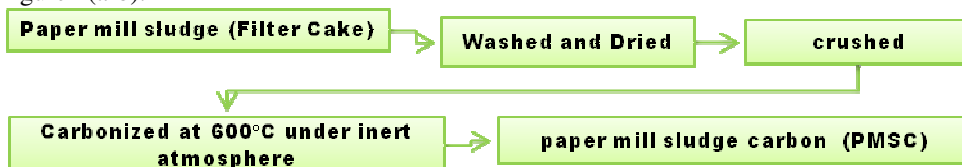


Figure 1(a). Flow chart for getting PMSC

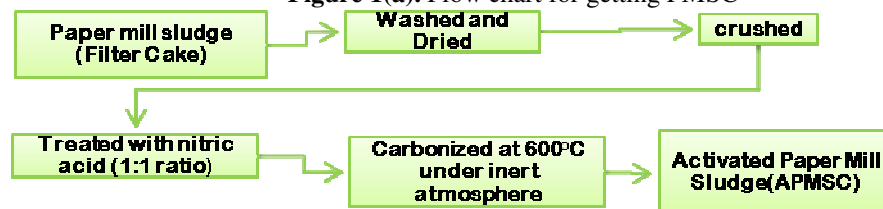


Figure 1(b). Flow chart for getting APMSC

Acid treatment gave best affinity towards the removal of heavy metals because of the introduction of more extractive sites such as -O, -N, -S and -P containing groups which are responsible for adsorption^{11,20}. Significant changes of the functional groups are visible after acid treatment in APMSC.

Analytical method

The lignocellulosic adsorbents namely ASDP, PMSC and APMSC were characterized by using BET analyzer (GeminiV2.00 Micromeritics), SEM and EDAX (Quanta 200 FEG Scanning Electron Microscope Ametek, India.) and FTIR spectra (Perkin Elmer, spectrum RXI) to identify the functional groups present in the surface of adsorbents.

Spectrophotometric method was used to analyze the quantitative Cr(VI) ions at 540 nm using Jasco UV-Visible spectrophotometer and Perkin Elmer Atomic absorption spectrophotometer for Ni(II) ions to calculate the adsorption capacity (q_e) and percentage removal efficiency (%), by using the equations (1) & (2).

$$q_e = (C_o - C_e) V / m \quad (1)$$

$$\text{Percentage removal} = [(C_o - C) / C_o] \times 100 \quad (2)$$

Where C_o and C_e are the initial and equilibrium concentrations (mg/L), V is the volume of solution (l), q_e is the adsorbed quantity (mg/g), m is the weight of adsorbent (g) and C is the solution concentration at the end of the adsorption process (mg/L).

Batch kinetic studies²⁷ were conducted by shaking 25 mL of desired quantity of adsorbate solution with 0.1 g adsorbent at 200 rpm speed with optimum pH and temperature. To explore the stability and reusability of adsorbents regeneration studies were conducted for six cycles. 0.5 g of spent adsorbent was agitated with 25 mL of NaOH solutions for 3 h for both Cr(VI) ions and Ni(II) ions. After desorption the sample was washed and neutralized with distilled water.

Results and Discussion

Characterization of adsorbents

The prepared lignocellulosic adsorbents namely ASDP, PMSC and APMSC were characterized by BET, SEM and FTIR analyses.

BET analysis

Adsorption usually depends on the specific surface area available on it. By BET analysis, specific surface area of ASDP, PMSC and APMSC were found to be 321 m²/g, 73m²/g and 284m²/g respectively. The pore size of PMSC was found as 11.821 nm and hence it was designated as mesoporous carbon^{19,26}. The significant increase in specific surface area of ASDP and APMSC is due to activation. So ASDP and APMSC were considered to possess greater efficiency for the removal of Cr(VI) and Ni(II) ions than PMSC since adsorption depends upon the specific surface area on adsorbent.

SEM analysis

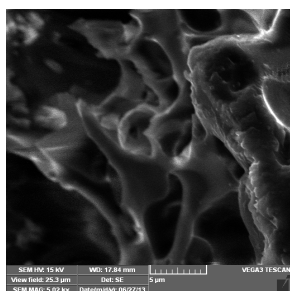
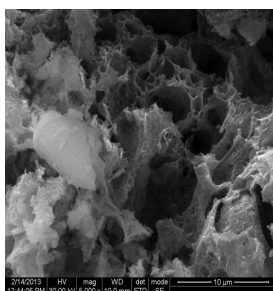
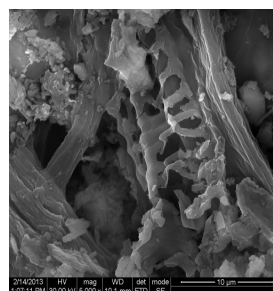
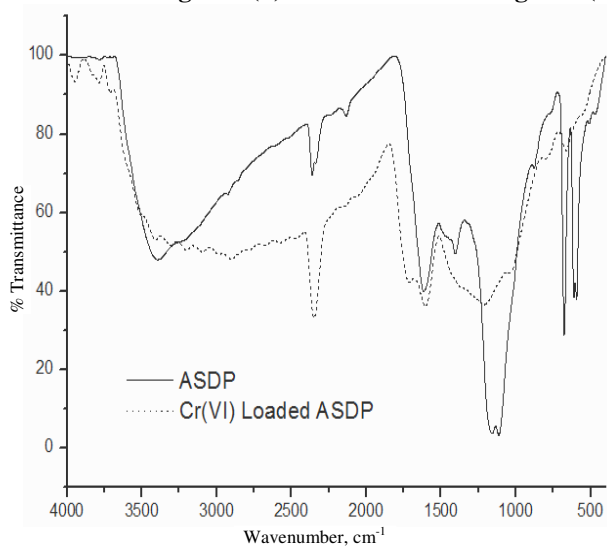
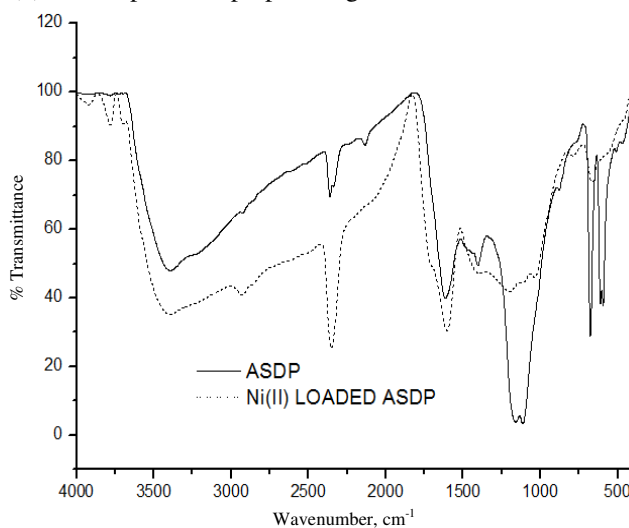
The cross sectional view morphology of ASDP, PMSC and APMSC were investigated using SEM and the images are shown in Figure 2a-c which gives the surface texture and porosity of the ASDP, PMSC and APMSC particle. The SEM image of ASDP (Figure 2a) indicates that it is composed of irregular cracks leads to many pores and the presence of short cellulosic fibers in the mixture agglomerates and aggregates the mineral particles. The SEM images of PMSC and APMSC shown in Figure 2b and 2c indicate the existence of roughness, protrusions and surface coverage in the form of flakes. Roughness is an indicative of maximum surface area.

Based on the particle morphology, these materials are considered suitably as an adsorbents. The image of ASDP and APMSC exhibits abundance of roughness and more crispy nature which may be propitious to its adsorption ability and many pores are clearly found on the surface. Well-developed pores lead to the large surface area and porous structure appeared as elongated fibrous particle in both low-cost adsorbents such as ASDP and APMSC.

FTIR spectra of prepared lignocellulosic adsorbents, Cr(VI) adsorbed and Ni(II) adsorbed sorbents of the corresponding functional groups are shown in Figures 3a-d and reported in Table 1.

Table 1. Functional groups representing in ASDP, PMSC, APMSC, Cr(VI) adsorbed ASDP, PMSC & APMSC and Ni(II) adsorbed ASDP, PMSC & APMSC

Functional Group	ASDP cm ⁻¹	PMSC cm ⁻¹	APMSC cm ⁻¹	Cr(VI) Loaded, cm ⁻¹			Ni(II) Loaded, cm ⁻¹		
				ASDP	PMSC	APMSC	ASDP	PMSC	APMSC
O-H (Hbonded) N-H stretching	3410.7	3420	3404	3306.0 3201.48	3447	3397	3391.5	3421 cm ⁻¹	3384.36
Aliphatic C-H stretching	2926.13	-	-	2901.43	-		2928.31	-	-
Free Amine	2360.83	-	-	2349.53	-		2352.35	-	-
C=C stretch, or (-N ⁺ H ₃)ion	161 7.79	-	1621.9	1603.82	-	1617.40	1604.84	-	1615
N ⁺ H ₄ ,(quaternary amine group) or (C-N),(N-H) stretching	--	1421	1404.39	-	1429.36	1402.89	--	1423 cm ⁻¹	1401
Asymmetric (SO ₃) Stretching	1211.49	-	-	1211.84			1201.65	-	-
(O-H) bending		-	1153.39		-	1158.54		-	1160.74
(C-O) symmetric stretch	1033.79	-	1112	-	-	1114.69		-	1115.89
(C-H) bending	776.48	871 711	872 712		873.35 712.54	874.41 712.61	791.36	873.40 712.54	874.84 712.67
Wagging frequency of metal oxide	614.74 534.74	-	676.98 611.74	665.71	-	673.30		-	676.76 613
-NH wagging		-	595		-	594		-	594

**Figure 2(a).** SEM of ASDP**Figure 2(b).** SEM of PMSC**Figure 2(c).** SEM of APMSC**Figure 3(a).** FTIR spectra of prepared lignocellulosic adsorbent ASDP-Cr(VI)**Figure 3(b).** FTIR spectra of prepared lignocellulosic adsorbent ASDP-Ni(II)

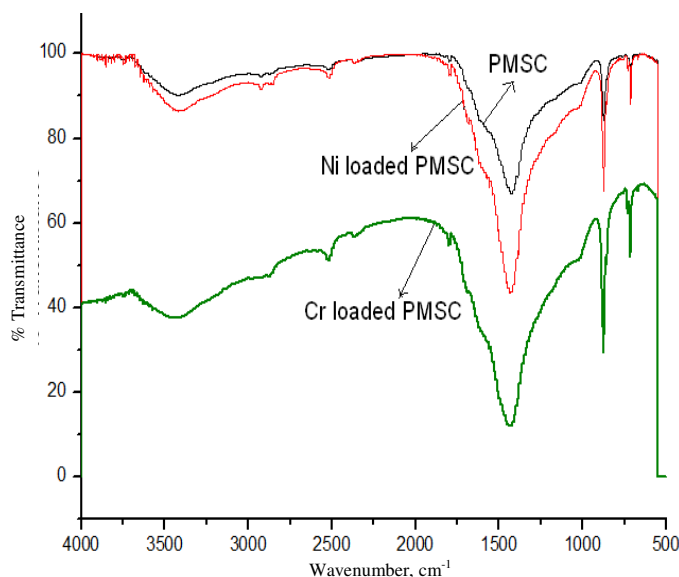


Figure 3(c). FTIR spectra of prepared lignocellulosic adsorbents PMSC-Cr(VI)-Ni(II)

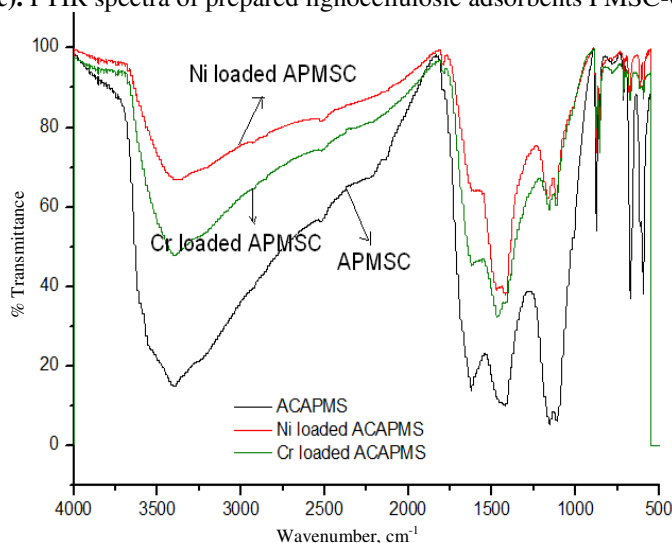


Figure 3(d). FTIR spectra of prepared lignocellulosic adsorbents APMSC-Cr(VI)-Ni(II)

FTIR analysis

Activation of sorbents by acid treatment induces many polar functional groups like O-H, $\text{NH}_2\text{C}=\text{C}$, C-N stretch, C-O symmetric stretch, quaternary ammonium group *etc* and also shifts in transmittance. The Introduction of -N,-O,-S *etc.* are responsible for stretching & bending vibrations²⁰. Deviations in wave numbers of same functional groups are observed after loading of metal ions as indicated in Cr(VI) adsorbed and Ni(II) adsorbed activated low-cost lignocellulosic ASDP, PMSC and APMSC spectra. The shifts in the position of peaks indicate that Ni(II) and Cr(VI) ions are well associated with surface functionality²⁸. Stretching and bending frequencies are responsible for the incorporation of heteroatom in

activated carbon matrix (ASDP, PMSC & APMSC). The presence of polyhydroxyl, quaternary amine is responsible for acidic surface and then positively charged pollutants may be more easily removed by sludge-based activated carbons.

Influence of variables

The adsorption isotherm, kinetics and thermodynamic parameters were determined by examining the variables included (i) effect of pH in the range (2-10) (ii) effect of initial concentration (50 ppm-500 ppm) (iii) effect of contact time (50 ppm- 500 ppm) (iv) effect of agitation speed (100 rpm- 300 rpm) and (v) effect of temperature (30 °C-70 °C). Experiments were repeated in triplicates and the average percentage deviation was found to be 3-5% shown as Tables 2 to 6.

Table 2. Effect of pH on adsorption

pH	[Cr(VI)] ₀ =100 ppm			[Ni(II)] ₀ =100 ppm		
	Adsorption capacity(q _e) mg/g			Adsorption capacity(q _e) mg/g		
	ASDP	PMSC	APMSC	ASDP	PMSC	APMSC
2	12.03	11.6	24.26	21.35	20.74	22.16
3		11.45	20.83	22.86	22.12	23.55
4	10.78	9.68	18.93	24.03	24.03	24.67
5		9.29	16.63	24.37	24.37	24.91
6	9.45	8.67	14.25	22.3	22.3	22.9
7		7.85	12.47			
8	7.83					
10	7.13					

Table 3. Effect of contact time on adsorption

Time	[Cr(VI)] ₀ =100 ppm			[Ni(II)] ₀ =100 ppm		
	qt, mg/g			qt, mg/g		
	ASDP	PMSC	APMSC	ASDP	PMSC	APMSC
10	17.3					
20	18.4			15.19	19.25	19.57
30	19.7					
40		16.93	20.73	18.03	19.84	20.85
60	20.23	17.51	21.71	20.23	20.31	22.52
90	21.28	18.16	22.41	22.3	21.34	23.17
120	22.23	18.78	22.93	23.15	22.31	24.49
150	22.38	19.62	24.14	24.25	23.38	24.91
180		19.68	24.26	24.34	23.68	24.98

Table 4. Effect of agitation speed on adsorption

System	Agitation speed, rpm		
	100	200	300
	Adsorption capacity (q _e), mg/g		
ASDP-Cr	11.6	12.0	11.78
PMSC-Cr	10.18	11.60	10.64
APMSC-Cr	22.50	24.26	23.20
ASDP-Ni	22.28	24.25	23.17
PMSC-Ni	22.06	23.68	22.94
APMSC-Ni	23.12	24.91	24.25

This batch adsorption studies were investigated the adsorption mechanism of the activated low-cost lingocellulosic adsorbents namely ASDP, PMSC and APMSC for the removal of Cr(VI) and Ni(II) ions from aqueous solution.

(i) Effect of pH studies given in Table 2 and Figures 4(a & b). It reveals that at pH 2, the Cr(VI) ions predominantly exist as negatively charged hydrogen chromate ion¹⁰. The surface positive functional groups of the adsorbents carry this oxyanions (negatively charged) of Cr(VI) by electrostatic force of attraction. Therefore, the adsorption capacity is maximum at pH 2. Then at pH 5, the sorption capacity of Ni(II) ions is more and Ni(II) ions exist¹² as Ni^{2+} , $\text{Ni}(\text{OH})^+$, $\text{Ni}(\text{OH})_2$. At pH = 5, ionic and non-ionic active species of adsorbate may be adsorbed on the activated surface with the formation of surface ion-exchange as well as hydrogen bonding ion pair complex between electron donating sites of low-cost lignocellulosic adsorbents and ionic and non-ionic nickel ions. The adsorbents surface acidity and basicity behavior²⁹ can be represented by the following equations 3 and 4;



(ii) In adsorption process, the initial concentration of adsorbate acts as a driving force to overcome the mass transfer between the adsorbent and adsorbate. In the present study, the adsorption capacity increases and percentage removal decreases as the initial concentration increases with same contact time and adsorption temperature. The increase in adsorption capacity may be due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher concentrations. The decrease in percentage removal may be due to the fact that a limited number of active sites in the adsorbent attain saturation above certain concentrations^{30,31}. The percentage removal of Ni(II) ions is 84.4% in ASDP at optimum concentration, but it is only 77% for Cr(VI) ions. The percentage removal of Ni(II) ions at the optimum Ni(II) concentration of 400 ppm is 75.4% in PMSC and 90% in APMSC, but for Cr(VI) ions, it is 61.8% in PMSC and 82.3% in APMSC at optimum Cr(VI) concentration of 300 ppm. But the adsorption capacity of ASDP, PMSC and APMSC is more effective for adsorption of Ni(II) ions when compared to Cr(VI) ions. Thus the sludge based adsorbents namely PMSC and APMSC are most effective in adsorption of cationic pollutants than anionic pollutants.

(iii) The results shown in Table 3(a & b) and Figures 5(a & b) explicit the effect of contact time for adsorption helps to know the rate of adsorption using different kinetic models. This is obvious that a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules on the solid and bulk phases³⁰. Then the time required to attain equilibrium in the case of adsorption of Cr(VI) ion is nearly at 120 min. for ASDP, 150 min. for PMSC and APMSC and for Ni(II) ion is nearly at 150 min. for ASDP, PMSC and APMSC.

(iv) Table 4 establishes that the rate of adsorption increases with agitation speed. The maximum sorption is obtained at 200 rpm beyond which the increase is not significant. This may be due to the fact that proper contact between the metal ion and active site is developed when increasing the agitation speed. Thus increase of the agitation speed improves the diffusion of Chromium and Nickel ions towards the surface of the adsorbents. Hence the equilibrium agitation speed was fixed at 200 rpm.

Determination of thermodynamic parameters

The effect of temperature on adsorption of Cr(VI) ions and Ni(II) ions was investigated by varying the temperature from 30 °C to 70 °C and the results are compiled in Table 7. The increase in adsorption capacity may be due to the formation of some new adsorption sites

and enlargement of the pores on the surface of the adsorbents. The increased rate of intraparticle diffusion of Cr(VI) ions and Ni(II) ions into the pores of activated low-cost adsorbents namely ASDP, PMSC and APMSC at these temperatures leads to an endothermic adsorption^{18,19}. The thermodynamic parameters, ΔG^0 , ΔH^0 and ΔS^0 for the adsorption of Cr(VI) ions and Ni(II) ions onto ASDP, PMSC and APMSC were determined from Van't Hoff plot, $\ln K$ versus $1/T$ using Eq. 5 and the results are listed in Table 5.

$$\ln K = -\Delta H^0/RT + \Delta S^0/R \quad (\text{where } K=q_e/C_e) \quad (5)$$

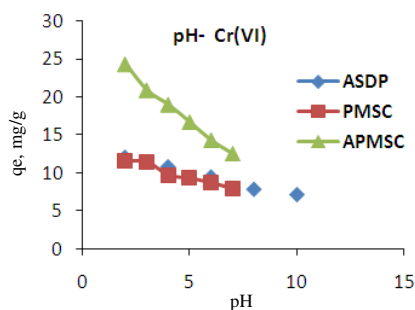


Figure 4(a). Effect of pH on ASDP-PMSC-APMSD-Cr(VI)

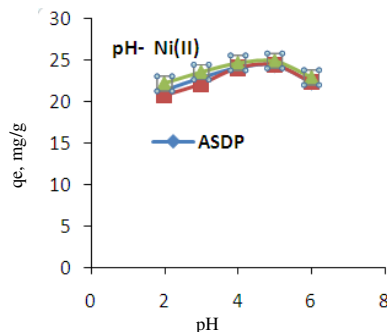


Figure 4(b). Effect of pH on ASDP-PMSC-APMSD-Ni(II)

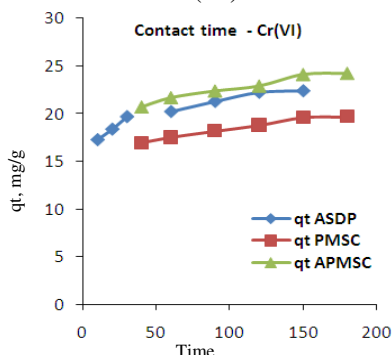


Figure 5(a). Effect of contact time on ASDP-PMSC-APMSD-Cr(VI)

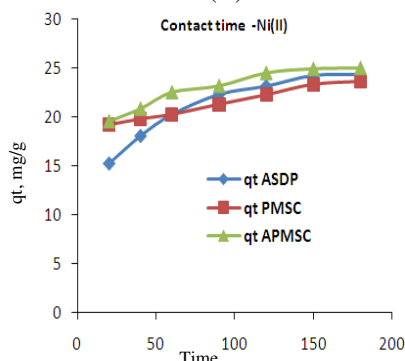


Figure 5(b). Effect of contact time on ASDP-PMSC-APMSD-Ni(II)

Table 5. Thermodynamic parameters for the adsorption of Cr(VI) and Ni(II) ions by ASDP, PMSC & APMSC

S.No	Process	Adsorbent	ΔG^0 kJ/mol @ 303 K	ΔH^0 kJ/mol	ΔS^0 J/K.mol	$T\Delta S^0$ kJ/mol	E_a kJ/mol	R^2
1	Retention of Cr(VI)	ASDP	-1.23	56.81	191.55	58.04	59.33	0.953
		PMSC	-0.04	41.05	135.6	41.09	43.57	0.994
		APMSC	-1.26	55.70	187.6	56.96	58.22	0.966
2	Retention of Ni(II)	ASDP	-0.40	49.67	164.04	50.07	52.19	0.980
		PMSC	-1.74	54.53	184.0	56.27	57.05	0.966
		APMSC	-1.85	63.03	214.1	64.87	65.55	0.998

The energy of activation (E_a) greater than 42 kJ/mol points out that all adsorption process here is a chemically controlled one³². These thermodynamic parameters can be explained the

chemical bonding nature of the absorbent-adsorbate interaction. The negative ΔG° and positive ΔH° and ΔS° indicate that this adsorption is a feasible, spontaneous, endothermic, increased randomness and involve ion-pair chemisorptions. The greater $T\Delta S^\circ$ than ΔH° indicates that the adsorption is dominated by entropy rather than enthalpy. Further, the free energy change becomes more negative with increase in temperature. For Cr(VI)/ASDP, the free energy change ranges from -1.23 to -8.91 kJ/mol, for Cr(VI)/PMSC, ranges from -0.04 to -5.46 kJ/mol, for Cr(VI)/APMSC, from -1.26 to -8.78 kJ/mol, for Ni(II)/ASDP, from -0.40 to -6.91 kJ/mol, for Ni(II)/PMSC, from -1.74 to -9.88 kJ/mol and for Ni(II)/APMSC, from -1.85 to -10.41 kJ/mol with increasing temperature from 30° to 70 °C. Hence, the retention of both ions on these adsorbents are spontaneously feasible.

Equilibrium isotherms & selection by error analysis

Adsorption isotherm describes the interaction of solute in the liquid phase and the adsorbent in solid phase. Various adsorption isotherm models³¹ are available to fit the experimental data. To quantify the adsorption capacity of adsorbents for the adsorption of Cr(VI) and Ni(II) from aqueous solution Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), adsorption isotherm models were used. Langmuir isotherm indicates surface homogeneity and maximum monolayer adsorption capacity. Freundlich isotherm is an indication of surface heterogeneity and multilayer sorption. Temkin model considers the effects of adsorbent-adsorbate interaction. To determine the adsorption occurred is physical or chemical in nature, the equilibrium data were applied to Dubinin-Radushkevich (D-R) Model. The mean free energy of the adsorption E , which is the free energy for the transfer of one mole of metal ions from the infinity to the surface of the adsorbent, provide information about the nature of adsorption either chemical ion exchange or physical ion exchange adsorption. The values of $E < 8$ kJ/mol, the adsorption process is of a physical ion-exchange via weak electrostatic nature

Ho³³ reported that the non-linear Chi-square test provided a better determination for the experimental data. In this study, both coefficients of correlation (r^2) and Chi-square (x^2) test statistics were used for the determination of best-fitting isotherm with the experimental data. The mathematical equation was given by Equation (6);

$$x^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (6)$$

Where $q_{e,m}$ is the equilibrium capacity obtained by calculation from model (mg/g) and q_e is the equilibrium capacity (mg/g) determined from the experimental data. If data from model are similar to the experimental data then x^2 would be a small number and *vice versa*. The linearized form of these isotherms were applied to the adsorption of Cr(VI) and Ni(II) onto ASDP, PMSC & APMSC and the constants obtained from the slope and intercept of the plots have been compiled in Table 6.

The separation factor, R_L lies between 0 and 1 for all adsorption studies indicates that these are favorable adsorption. For Ni(II) and Cr(VI) ions adsorption, it was observed that the Freundlich isotherms were almost overlapped with the experimental and seemed to be best fitting model for the experimental data. Correspondingly the chi square test analysis showed that the x^2 values for Freundlich are the lowest and Temkin and Dubinin-Radushkevich isotherms are almost lower values when compared to Langmuir isotherms as shown in Table 8. However, Freundlich isotherm displayed the best fitting model than Temkin, Dubinin-Radushkevich and Langmuir isotherm because of the highest correlation coefficient and the lowest Chi-square values thus indicating to the applicability of multilayer coverage of the metal ion by ion-exchange via weak electrostatic nature on the heterogeneity

surface of adsorbents which is evidenced by the constants of all models. So adsorption data fitted well with the Freundlich models for both ions.

Kinetic analysis

In order to investigate the rate of adsorption of Ni(II) ions and Cr(VI) ions onto ASDP, PMSC and APMSC, different kinetic models^{34,35} namely pseudo first order, pseudo second order, simple Elovich and intraparticle diffusion kinetics were tested using the data, the parameters thereby derived from linear plots are collected in Table 7. The R^2 values are close to unity which indicates the appropriateness of the application of these models.

Comparing the correlation coefficients, the best fitting of pseudo second order model indicates that the adsorption of Ni(II) ions and Cr(VI) ions on the activated low-cost lignocellulosic adsorbents were represented by two-phase reactions such as rapid adsorption for shorter duration in initial stage followed by slow adsorption for longer duration later. According to the plot of qt versus $t^{1/2}$ provides a double nature of plots which may be explained the fact that the initial linear portions indicate the boundary layer diffusion effects and the final linear portion is the result of intraparticle diffusion effects. This can be attributed to the instantaneous utilization of the most readily available sites on the ASDP and mesoporous surface of PMSC and APMSC. The multilinearity ($K_{id,1}$, $K_{id,2}$) of Webber and Morris model³⁵ also showed a contribution of film diffusion($K_{id,1}$) on the control of adsorption kinetics and the intraparticle diffusion ($K_{id,2}$) played an important role but was not the rate-determining step because of the positive intercept values.

It was more likely to reflect that the adsorption behavior might involve the weak valence forces of ion exchange and H-bonding through sharing electrons between metal ions and adsorbents. Hence the rate limiting step is finalized as pseudo second order which is an indicative of chemisorptions due to validity of Simple Elovich and intraparticle diffusion models.

Regeneration studies

Desorption studies were also conducted to explore the feasibility of recycling the adsorbents and recovery of the metal resources. NaOH was used for the stripping section for both Ni(II) and Cr(VI) ions⁸. Desorption experiments were conducted by mixing 0.5 g of spent adsorbent with 25 mL of 1 M NaOH. In order to determine the reusability of the adsorbent, the adsorbent was taken out from the solution and washed with double distilled water and protonated with 0.1 M HCl. Consecutive adsorption and desorption studies were repeated six times by using the same adsorbent and is shown in Table 8, which indicates stability of the adsorbent. The recovery experiments show that metal ions are retained by the matrix in non labile forms and that the acid-base reactions are more effective for their displacement than the complexation processes.

Adsorption Mechanism

The adsorption of Cr(VI) and Ni(II) ions onto activated lignocellulosic adsorbents like ASDP, PMSC and APMSC occur as multistep process^{8,11,12} involving (i) Initially ion-exchange rapidly due to weak electrostatic force of attraction between solid-solute interfaces and (ii) diffusion of ions then into the pores slowly by endothermic chemisorptions with active sites of adsorbent. So this is the chemisorptions adsorption mechanism which is evidenced by Elovich kinetics, intraparticle diffusion and activation parameters. Finally the equilibrium is reached due to bonding with binding centers of surface functionality of the low-cost activated carbons. The adsorption mechanisms are shown as the equations 7-10.

Table 6. Performance evaluation by various isotherm models

Isotherm model			Constants				r^2	x^2
			θ , mg/g	b , Lmg ⁻¹	K_L , Lg ⁻¹	R_L		
Langmuir $C_e/q_e = 1/b\theta + C_e/\theta$	Cr(VI)	ASDP	44.5	0.128	5.69	0.073	0.878	26.6
		PMSC	52.6	0.047	2-49	0.03	0.882	73.9
		APMSC	90.1	0.068	6.13	0.13	0.792	362.8
	Ni(II)	ASDP	112.9	0.064	7.24	0.135	0.881	105.9
		PMSC	90.9	0.05	5.32	0.16	0.866	141.1
		APMSC	128.2	0.11	14.2	0.083	0.786	314.5
Freundlich $\ln q_e = \ln K_F + 1/n \ln C_e$	Cr(VI)	ASDP	$n = 2.72$	$K_F(Lg^{-1}) = 8.81$			0.994	0.34
		PMSC	$n = 2.49$	$K_F(Lg^{-1}) = 7.03$			0.990	0.06
		APMSC	$n = 3.56$	$K_F(Lg^{-1}) = 19.1$			0.990	6.23
	Ni(II)	ASDP	$n = 2.55$	$K_F(Lg^{-1}) = 17.20$			0.994	0.59
		PMSC	$n = 2.86$	$K_F(Lg^{-1}) = 14.9$			0.992	0.55
		APMSC	$n = 3.51$	$K_F(Lg^{-1}) = 32.1$			0.994	0.66
Temkin $q_t = \ln K_T + B \ln C_e$	Cr(VI)	ASDP	$B = 6.92$	$K_T(Lg^{-1}) = 3.69$			0.962	2.97
		PMSC	$B = 9.97$	$K_T(Lg^{-1}) = 0.704$			0.962	3.85
		APMSC	$B = 10.8$	$K_T(Lg^{-1}) = 1.43$			0.962	41.23
	Ni(II)	ASDP	$B = 20.8$	$K_T(Lg^{-1}) = 1.02$			0.968	2.55
		PMSC	$B = 13.1$	$K_T(Lg^{-1}) = 2.56$			0.958	6.76
		APMSC	$B = 17.1$	$K_T(Lg^{-1}) = 6.65$			0.918	4.61
Dubinin-Radushkevich isotherm $\ln q_e = \ln q_m - k\varepsilon^2$ $\varepsilon = RT \ln(1 + 1/C_e)$ $E = (2k) - 0.5$	Cr(VI)	ASDP	q_m mg/g = 32.72	k (mole ² J ²) = 0.897	E (kJ/mol) = 0.75		0.960	6.40
		PMSC	q_m mg/g = 31.85	k (mole ² J ²) = 2.72	E (kJ/mol) = 0.41		0.960	12.69
		APMSC	q_m (mg/g) = 55.20	k (mole ² J ²) = 0.44	E (kJ/mol) = 1.07		0.817	51.77
	Ni(II)	ASDP	q_m (mg/g) = 74.00	k (mole ² J ²) = 1.602	E (kJ/mol) = 0.33		0.770	12.6
		PMSC	q_m mg/g = 75.57	k (mole ² J ²) = 5.77	E (kJ/mol) = 0.29		0.918	8.14
		APMSC	q_m (mg/g) = 101.2	k (mole ² J ²) = 4.53	E (kJ/mol) = 0.56		0.819	9.17

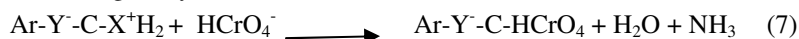
Table 7. Summary of parameters derived for various kinetic models

S.No.	Kinetic model & Equation	Constant	Values for Cr(VI)			Values for Ni(II)		
			ASDP	PMSC	APMSC	ASDP	PMSC	APMSC
1	Pseudo first order $\ln(q_e - q_t) = \ln q_e - k_1 \cdot t$	K_1, min^{-1}	1.96×10^{-2}	1.2×10^{-2}	3.3×10^{-2}	1.65×10^{-2}	1.3×10^{-2}	2.9×10^{-2}
		R^2	0.956	0.934	0.994	0.960	0.728	0.339
2	Pseudo second order $t/q_t = 1/K_2 \cdot q_e^2 + t/q_e$ $h = k_2 q_e^2$	$K_2, \text{g/mg} \cdot \text{min}$	8.21×10^{-3}	4.7×10^{-3}	4.8×10^{-3}	2.11×10^{-3}	3.9×10^{-3}	3.8×10^{-3}
		$q_e, \text{mg/g}$	23.0	21.3	25.6	26.8	25	26.3
		$h, \text{mg/g} \cdot \text{min}$	4.34	2.1	3.1	1.51	2.4	2.6
		R^2	0.998	0.996	0.998	0.998	0.997	0.997
		$\alpha, \text{mg/g} \cdot \text{min}$	6.14	249.5	1380	0.38	153.11	30.41
3	Simple elovich $q_t = \beta \ln t + \beta \ln \alpha \beta$	$\beta, \text{g/mg}$	1.85	1.75	1.84	4.36	2.12	2.63
		R^2	0.978	0.931	0.927	0.994	0.916	0.980
4	Intra Particle Diffusion $qt = K_{id} \cdot t^{0.5} + C$	$K_{id,1}, K_{id,2} \text{mg/g} \cdot \text{min}$	1.02, 0.51	0.39, 0.61	0.53, 0.55	1.31, 0.49	0.40, 0.56	0.75, 0.17
		C_1, C_2	14.0, 16.4	14.7, 12.1	18.5, 17.1	10.0, 18.0	17.3, 16.3	16.3, 22.7
		R^2	0.985, 0.955	0.99, 0.99	0.94, 0.84	0.998, 0.829	0.97, 0.92	0.97, 0.77

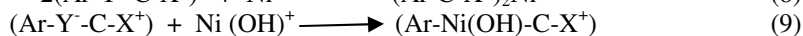
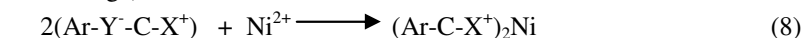
Table 8. Recycling of the adsorbents

No. of cycle	% Removal					
	$C_o = 25 \text{ mg/L}$	$C_o = 100 \text{ mg/L}$	$C_o = 25 \text{ mg/L}$	$C_o = 100 \text{ mg/L}$	$C_o = 100 \text{ mg/L}$	$C_o = 100 \text{ mg/L}$
	ASDP	ASDP	PMSC	APMSC	PMSC	APMSC
	Cr(VI)	Ni(II)	Cr(VI)	Cr(VI)	Ni(II)	Ni(II)
1	98.2	97.9	97.3	97.04	94.7	99.6
2	97.8	97.8	96.4	96.8	93.5	99.2
3	95.3	96.2	92.8	95.2	91.8	97.4
4	90.6	94.2	82.0	90.2	87.4	94.6
5	84.2	89.7	79.2	88.5	81.2	92.9
6	71.9	75.6	69.8	81.2	72.4	89.7

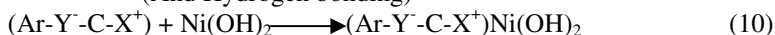
For Cr(VI) ions: (Ion exchange only)



For Ni(II) ions: (Ion exchange)



(And Hydrogen bonding)



Ar is the matrix of the low-cost activated carbons (ASDP, PMSC & APMSC) with X⁺ & Y⁻ binding centres such as -O, -N, -S, (C-H), (-C=C), (C-O), (C-N), etc.

Performance evaluation

The results from this study show that the biosorption is a viable process for the retention of toxic metal ions like Cr(VI) and Ni(II) from aqueous solutions onto lingo-cellulosic biopolymers, namely activated sawdust powder (ASDP) and sludge-based carbons (PMSC and APMSC). The findings of this research correlate well and in some cases even superior to the results reported in the literature. The acid treatment has enhanced the uptake capacity of activated carbons (ASDP, PMSC and APMSC) used in this study. In addition, the chemicals used and methods of modification followed are of economically viable. These low-cost activated carbons possess excellent adsorption capacity towards Cr(VI) and Ni(II) ions, because these charred adsorbents consist of small crystallites, disorganized carbon, extraordinary large specific surface area, cracked and rough tunable surface functionalities. In general, all the adsorbents examined in this study are referred as low-cost lignocellulosic activated carbons.

Usually acid treated adsorbents gave best affinity towards heavy metal remediation than alkaline and any other activation method²⁰. It can be observed that a pH of 2.0 for Cr(VI) and pH of 5.0 for Ni(II) was found to be an optimum in nearly all cases whatever be the method of activation. During the surface activation all of them have H-bonded poly hydroxyl ion, quaternary ammonium ion, free amine group and conjugated olefinic bond as surface tunable adsorption sites as acidity or basicity surface behaviour which causes for better ion-exchange for Cr(VI) and ion-exchange as well as H-bonding mechanism for Ni(II). They have comparable Ea(observed activation energy) and B (Temkin heat of adsorption) values. The maximum adsorption capacity of both Cr (VI) & Ni(II) onto ASDP, PMSC and APMSC as given below:

Cr(VI): θ (mg/g): ASDP(44.5), PMSC(52.6), APMSC(90.1)

Ni(II): θ (mg/g): ASDP(112.9), PMSC(90.9), APMSC(128.2)

On comparing the Langmuir maximum adsorption capacities obtained for the studied systems, the following points may be summarized:

- (i) The adsorption capacity of both Cr(VI) and Ni(II) onto APMSC is comparatively greater than ASDP and PMSC due to basic surface morphology, well-developed pores appeared as elongated fibres on the rough surface in APMSC by acid treatment which was also indicated by its highest θ (mg/g), q_m (mg/g), $K_L(\text{Lg}^{-1})$, $K_F(\text{Lg}^{-1})$, $K_T(\text{Lg}^{-1})$, n and B values of adsorption isotherm models. The experimental data has been suitably fitted with heterogenic multilayer chemisorptions in each studies by the error analysis.
- (ii) The sorptions of Cr(VI) and Ni(II) on sludge-based mesoporous adsorbents, viz., PMSC (θ (mg/g): Cr(VI) = 52.6; Ni(II) = 90.9) and APMSC (θ (mg/g): Cr(VI) = 90.1; Ni(II) = 128.2) are also comparable. The increase in adsorption capacity of both ions onto

APMSC may be due to the formation of some new adsorption sites, increased BET area, enlargement of pores (PMSC = 73 m²/g; APMSC = 284 m²/g) on the surface of APMSC which improves the rate of diffusion of ions into the pores.

- (iii) Finally, the removal of both ionic and non-ionic form of Ni(II) ions onto ASDP is more effective than the removal of ionic form of Cr(VI) ions because of the existence of acidity and basicity surface behaviour of ASDP. This well-behaved ion-pair formation of Ni(II) ions is implied by the appearance of significant shift in peak from 1211.49 cm⁻¹ to 1201.65 cm⁻¹ than Cr(VI) ion loaded peak (*i.e.* 1211.49 cm⁻¹ to 1211.84 cm⁻¹).

Conclusion

In this study, each examined adsorption system exhibits an effective efficiency in batch operations. The probable mechanism of Cr(VI) adsorption may be ion-exchange only and for Ni(II) ion adsorption the ion-pair formation is due to *H*-bonding along with ion-exchange chemisorptions which was confirmed by very less negative value of ΔG° . The thermodynamic study further reveals the endothermic, randomness and feasibly spontaneous nature of the adsorption processes. Desorption studies suggested that metal ions are retained by the matrix in non-labile forms and that acid-base reactions are more effective up to six cycles. Hence, these three low-cost lignocellulosic activated carbons can be considered to be viable adsorbents for the removal of Cr(VI) and Ni(II) ions from dilute solutions (*i.e.* >90%). But APMSC can be considered to be viable adsorbent for Ni(II) ions from dilute aqueous and effluent solutions because positively charged pollutants may be more easily removed by sludge-based activated carbons by both ion-exchange and ion-pair formation due to the presence of surface polar poly functional groups as adsorption sites which were indicated by FTIR results.

Conversion of waste sludge to the cost-effective carbons synthesized from paper mill sludge which can produce comparable results for removal of contaminants from water. It is a novel and environmentally friendly process. So, the organic waste from industrial process is utilized successfully today.

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