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Research Article

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Batch Studies on Remedy for Cr(VI) and Ni(II) onto Sludge-based Carbons (PMSC & APMSC)

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Abstract

Advantages such as environmental friendly material, low cost and high regeneration percentage of sludge-based adsorbents like 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. These 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, RL 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 Ni (II) ions and Cr (VI) ions using PMSC and APMSC was more effective at pH 5 and pH 2, 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: Paper mill sludge; Heavy metals; Adsorption; Activation Parameters; Isotherms and Kinetics modeling

Introduction

The over exploitation of contamination earth has now brought humankind to a dead end from both an environmental and energy resource standpoint. It is undeniably true that paper sludge reserves are not endless. The main aim of this study was to assess the suitability of the adsorption mechanism to remove both soluble and particulate paper sludge matter from its wastage, the paper industry wastes are main issues. Intensive paper industries paper sludge has led to the excessively increased generation of paper waste, which has resulted in the over-application of manure as a waste of pollution in the environment. Paper sludge generated by the paper industry is generally composed of organic fibers (cellulose, hemicelluloses and/or lignin), inorganic fillers and coating materials such as kaolinite ($Al_2Si_2O_5(OH)_4$), limestone ($CaCO_3$) and talc ($Mg_3Si_4O_{10}(OH)_2$). The development of an innovative process configuration to simultaneously enhance both pollution reduction and the harvesting of paper sludge is required to implement sustainable paper waste treatment systems. Thus, polishing of the high content of paper waste specifically leads to the vertical biomass recycling to rapidly settle the waste based on pollutants removal. It can be used to improve the soil properties and providing beneficial effects on soils that are deficient in organic matter. Paper sludge has been used as fertilizer [1,2].

Nowadays, various kinds of materials are being recycled from paper wastes which based on agricultural residues – to make new applications in various fields is so interesting because it solves two environmental problems: air and environmental pollution. Some of these materials have already been investigated: wood based materials [3], rice straw-wood based materials [4], and hemp wastes based materials [5], tea-leaf fiber wastes [5], Bamboo, and Coconut coir fiber [6-8].

Very most important possible effective use for paper sludge ash is in the preparation of low cost sorbents for water purification and heavy rare earth elements removal. The use of chromium and nickel ions in electroplating industry, steel industry, mining etc., is quite extensive. Cr(III) ions are nontoxic and play an essential role in the metabolism of plant and animals. Cr(VI) ions are highly toxic and lead to carcinogenetic problems. Other health effects include skin allergy, liver problems etc. [9]. Exposure to Ni(II) ions at higher concentrations causes lungs cancer, nose and bone cancer, headache, nausea, rapid respiration etc., [10-12].

This in turn led to find an alternate way for preparing the activated carbon at low cost using waste biomass. Adsorption by inexpensive adsorbents such as neem leaf powder [9], Chitosan [13-15], agricultural wastes [16,17], biomasses like peanut hulls [18,19], Hazelnut shell [20], palm flower [21], apple waste [22], rice husk [23,24], sugarcane bagasse [25,26], activated sawdust [27-33], reuse of solid wastes [34-37] etc., offer a potential alternative for toxic metal ions removal were reported in literature. Hence, the present study intends to investigate the preparation of mesoporous untreated and treated paper mill sludge

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carbon (PMSC and APMSC) for the adsorption of heavy metal ions such as Cr(VI) and Ni(II) spectrophotometrically and also compare the potentiality of surface modifications. Surface morphology of PMSC and APMSC were characterized by BET, SEM, EDAX and FTIR. Isotherms and kinetics studies were conducted to evaluate the solute-solid interactions. Thermodynamic parameters were determined to study the spontaneity of the adsorption processes. Regeneration studies were also done to check the stability of the adsorbents, PMSC and APMSC.

Materials and Methods

Materials

Paper mill sludge (filter cake) was obtained from Tamilnadu 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 [38] 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 PMSC and APMSC: The preparative methodology as shown below in the flow chat is similar as in the literature procedure shown in flowchart (Figures 1a and 1b). 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 [32].

Analytical method: The both Sludge-based Adsorbents 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 (qe) and percentage removal efficiency (%).by using the equations (1) and (2).

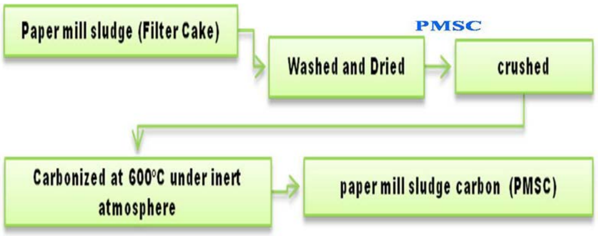

Figure 1a: Flow chat for getting PMSC.

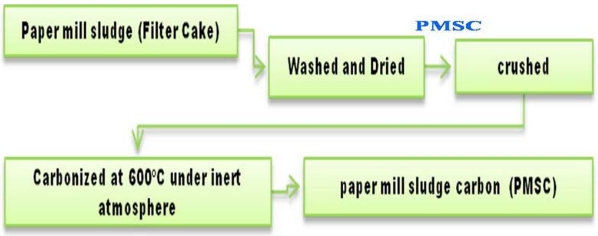

Figure 1b: Flow chat for getting APMSC.

$$qe=\{(C_0-C_t)V\}/M \quad (1)$$

$$\text{Percentage removal}=[(C_0-C_F)/C_0]\ X100 \quad (2)$$

Where C_0 and C_t (both in mg/l) are the initial concentration and the concentration at any instant, C_F is the final concentration, V is the volume of the solution (l), M is the mass of adsorbent (g).

Batch kinetic studies 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 [28]. 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 PMSC and APMSC were characterized by BET, SEM, FTIR and EDAX analyses.

BET analysis: The specific surface area of PMSC and APMSC were found to be 73 m^2/g and 284 m^2/g respectively. The pore size of PMSC was found as 11.821 nm and hence it was designated as mesoporous carbon [8,39]. The significant increase in specific surface area of APMSC is due to activation. So, APMSC is 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 surface morphology images of PMSC and APMSC obtained using scanning electron microscope are shown in Figures 2a and 2b. These images indicate the surface texture and porosity of the PMSC and APMSC. These surfaces seem to be rough and protrusions are seen. Surface coverage in the form of flakes is evident, showing the presence of inorganic elements as confirmed by EDAX analysis shown in Figures 3a and 3b. Roughness is indicative of maximum surface area.

Based on the particle morphology, these materials are suitable to be used as adsorbent. The image of 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 APMSC.

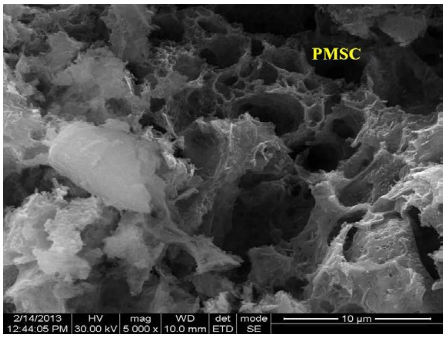

Figure 2a: SEM analysis of PMSC.

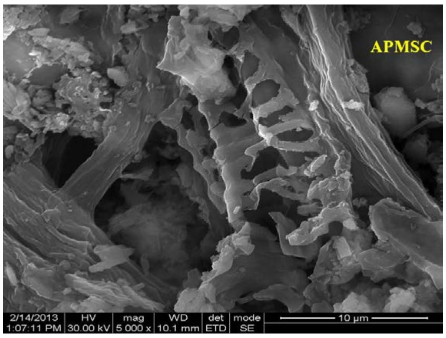

Figure 2b: SEM analysis of APMSC.

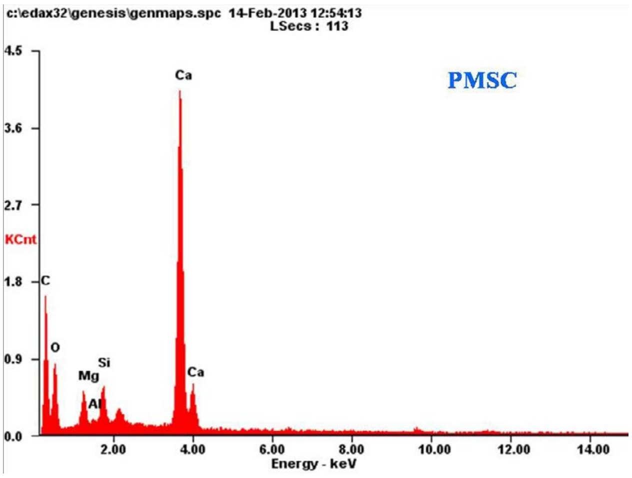

Figure 3a: EDAX analysis of PMSC.

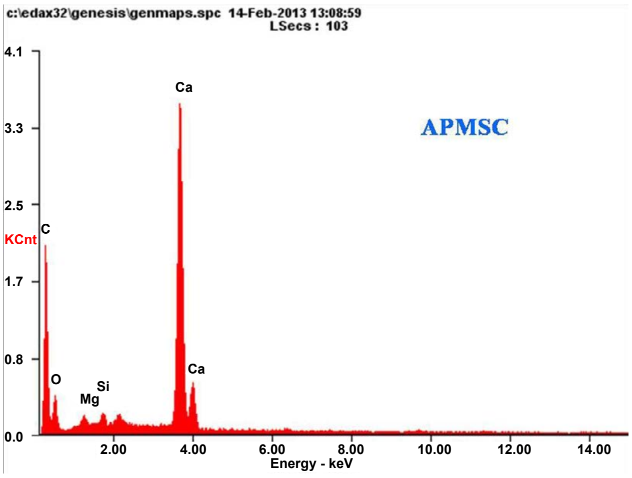

Figure 3b: EDAX analysis of APMSC.

EDAX analysis: The elemental analysis of PMSC and APMSC was done by using EDAX analysis. The spectra are presented in Figures 3a and 3b and the data are listed in Table 1. It can be seen from the table that the major component present in both the samples is carbon. Mg, Al, Si and Ca are also present in PMSC. On acid treatment these elements are washed or diminished in APMSC. The removal of trace amount of Al may be due to the acid treatment.

Element	PMSC		APMSC	
	Wt%	At%	Wt %	At %
C	48.43	61.33	59.52	72.62
O	31.54	29.99	22.29	20.42
Mg	02.68	01.68	00.97	00.59
Si	00.45	00.26	00.49	00.26
Ca	02.09	01.13	16.73	06.12
Al	14.79	05.61	_	_

Table 1: EDAX analysis results of PMSC and APMSC.

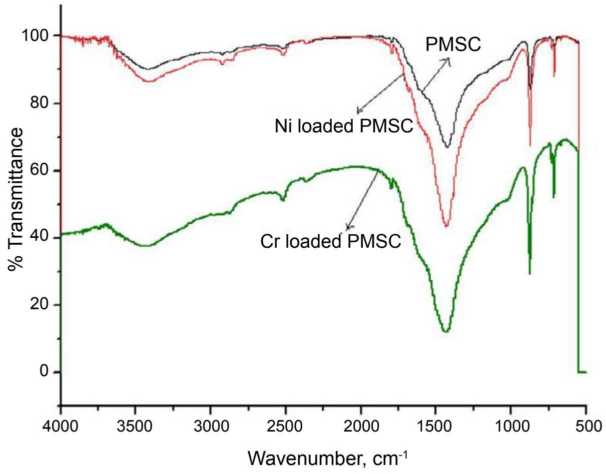

Figure 4a: FTIR analysis of PMSC.

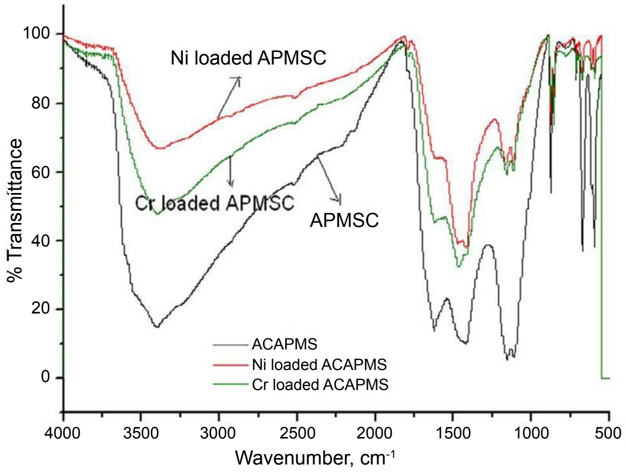

Figure 4b: FTIR analysis of APMSC.

FTIR analysis: FTIR spectra of PMSC and APMSC, Ni(II) adsorbed and Cr(VI) adsorbed PMSC and APMSC and the corresponding functional groups are shown in Figures 4a and 4b and reported in Table 2. Activation of PMSC by acid treatment induces many polar functional groups like O-H, C=C, C-N stretch, C-O symmetric stretch, etc. and also shifts in transmittance. The Introduction of –N,-O,-S etc., are responsible for stretching and bending vibrations. Deviations in wave numbers of same functional groups are observed after loading of metal ions as indicated in Ni(II) adsorbed PMSC and APMSC and Cr(VI) adsorbed PMSC and APMSC spectra. The shifts in the position

Functional Group	PMSC	APMSC	Ni(II) Loaded		Cr(VI) Loaded	
			PMSC	APMSC	PMSC	APMSC
O-H (H bonded) and N-H stretching	3420 cm^{-1}	3404 cm^{-1}	3421 cm^{-1}	3384.36 cm^{-1}	3447 cm^{-1}	3397 cm^{-1}
C=C stretch, or (-N^+H_3)ion	-	1621.9 cm^{-1}	-	1615 cm^{-1}	-	1617.40 cm^{-1}
-N^+H_4,(quaternary amine group) or (C-N),(N-H) stretching	1421 cm^{-1}	1404.39 cm^{-1}	1423 cm^{-1}	1401 cm^{-1}	1429.36 cm^{-1}	1402.89 cm^{-1}
(O-H) bending	-	1153.39 cm^{-1}	-	1160.74 cm^{-1}	---	1158.54 cm^{-1}
(C-O) symmetric stretch	-	1112 cm^{-1}	-	1115.89 cm^{-1}	--	1114.69 cm^{-1}
(C-H) bending	871 cm^{-1} 711 cm^{-1}	872 cm^{-1} 712 cm^{-1}	873.40 cm^{-1} 712.54 cm^{-1}	874.84 cm^{-1} 712.67 cm^{-1}	873.35 cm^{-1} 712.54 cm^{-1}	874.41 cm^{-1} 712.61 cm^{-1}
Wagging frequency of metal oxide	-	676.98 cm^{-1} 611.74 cm^{-1}	-	676.76 cm^{-1} 613 cm^{-1}	-	673.30 cm^{-1}
-NH wagging	-	595 cm^{-1}	-	594 cm^{-1}	-	594 cm^{-1}

Table 2: Functional groups representing in PMSC, APMSC, Ni (II) adsorbed PMSC & APMSC and Cr(VI) adsorbed PMSC & APMSC.

of peaks indicate that Ni(II) and Cr(VI) ions are well associated with surface functionality [40].

Stretching and bending frequencies are responsible for the incorporation of heteroatom in activated carbon matrix (PMSC and APMSC). The presence of quaternary amine as acidic surface and then positively charged pollutants may be more easily removed by sludge-based activated carbons.

Influence of Parameters

The adsorption isotherm and kinetics were determined by examining the different parameters included(i) effect of pH in the range(2-7) (ii) effect of contact time(100 ppm-500 ppm) (iii) effect of agitation speed(100 rpm- 300 rpm) (iv) effect of initial concentration (50 ppm–500 ppm) and (v) effect of temperature (30–70°C). Experiments were repeated in triplicates and the average percentage deviation was found to be 3-5%.

Effect of pH

The adsorption of Cr(VI) and Ni(II) ions is highly influenced by pH. Studies were conducted to determine the effect of pH by varying the pH of solution from 2 to 10 at fixed adsorbent dosage and metal ion concentration. The results are shown in Figure 5. It is observed that the adsorption capacity is high at pH 5 for Ni(II) ion and pH 2 for Cr(VI) ions. For Ni(II) ions, at pH 5.0 the active form of Ni(II) ions are Ni^{2+}, $Ni(OH)^+$ and $Ni(OH)_2$ [32]. The maximum adsorption of Ni(II) at pH 5.0 may be due to the hydrogen bonding along with electrostatic attraction between the adsorbent and the Ni(II) ions whereas at lower pH the entire active sites of the PMSC and APMSC are occupied by protons due to the high mobility of H^+ than nickel ions, thereby decreasing the adsorption capacity. At pH 2. The Cr(VI) ions exist as [39] hydrogen chromate ($HCrO_4^-$: 90%), dichromate ($Cr_2O_7^{2-}$: 5%) and chromic acid (H_2CrO_4: 5%) and at higher pH, the predominant species of Cr(VI) ion is CrO_4^{2-}. The surface positive functional groups of the adsorbents carry the oxyanions (negatively charged) of Cr(VI) by electrostatic force of attraction [9,11,17]. Therefore, the adsorption capacity increases at lower pH. At higher pH, the increased negative charges on the adsorbent surface decrease the attraction of oxyanions of Chromium on the adsorbent [26].

Effect of contact time

Initial concentrations for adsorption of both Cr(VI) and Ni(II) ions onto PMSC and APMSC shown in Figure 6, corporate with the results the adsorption capacity increases with increase of contact time for all

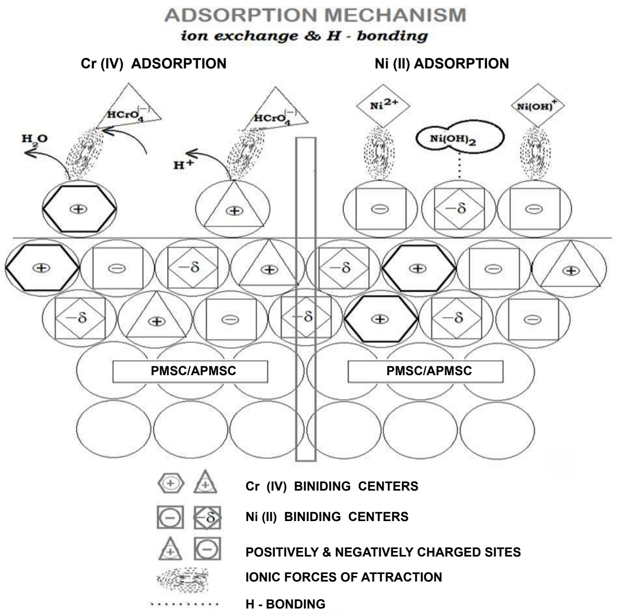

Figure 5: Adsorption mechanism of Cr(IV) and Ni (II) binding centres.

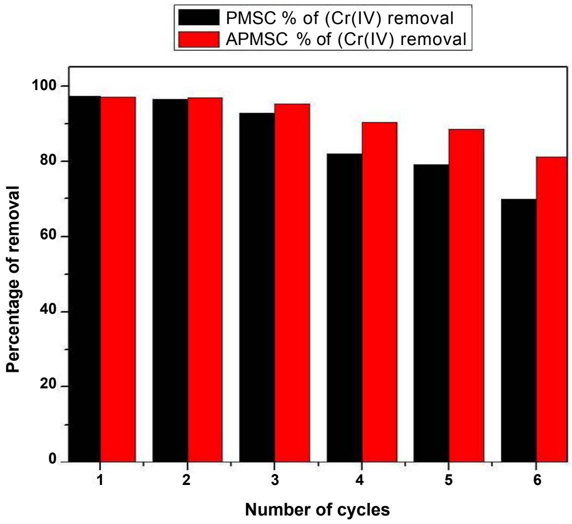

Figure 6a: Removal of Cr(IV) of PMSC and APMSC.

initial metal ion concentrations, also chemical activation increases the initial rate of adsorption due to the availability of a large number of vacant sites. Slow adsorption for longer duration then reaches equilibrium nearly at 150 min. This may be due to the availability of a large number of vacant sites for adsorption. The adsorption capacity is tailed off due to the saturation of vacant sites [39,40].

Effect of agitation speed

The effect of agitation speed (100 rpm to 300 rpm) on adsorption capacity of PMSC and APMSC for the removal of Cr(VI) and Ni(II) ions for initial concentration of 100 ppm at pH 5 for Ni(II) and 100 ppm at pH 2 for Cr(VI) ions with adsorbent dosage of 0.1 g for 25 mL of solution. The maximum adsorption capacity is obtained at 200 rpm beyond which the increase is not significant. The increase in adsorption capacity in all the four systems, viz., PMSC-Cr, PMSC-Ni, APMSC-Cr and APMSC-Ni with increase in agitation speed from 100 rpm to 300 rpm which is due to improve the diffusion of ions towards the surface of the adsorbents. Hence the optimum agitation speed is fixed at 200 rpm for further studies.

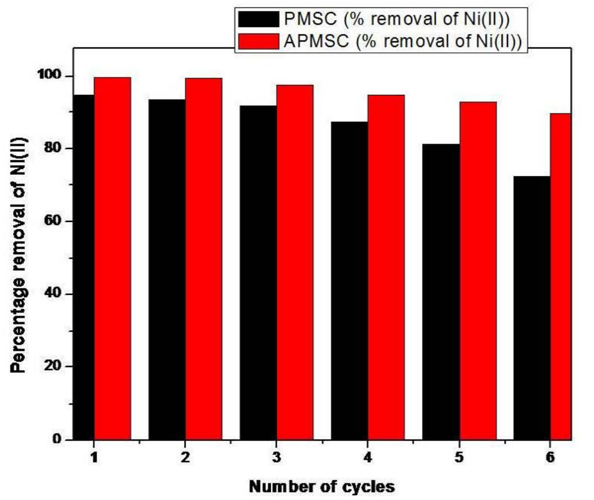

Figure 6b: Removal of Ni(II) of PMSC and APMSC.

Effect of initial metal ion concentration

In adsorption process, the initial concentrations of adsorbate acts as a driving force to overcome the mass transfer between the solid and solute. The effect of initial concentration of Ni(II) and Cr(VI) ions on the adsorption potential of PMSC and APMSC were investigated at pH 5.0 and 2.0, respectively. The results were used to derive parameters for various isotherm models which are shown in Table 3. The adsorption capacity of both the adsorbents for both the ions increases, while the percentage removal decreases with increase in metal ion concentration. 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. But the adsorption capacity of PMSC and APMSC is more effective for adsorption of Ni(II) ions when compared to 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. Thus the sludge based adsorbents namely PMSC and APMSC are most effective in adsorption of cationic pollutants than anionic pollutants.

Adsorption isotherms

Adsorption isotherm describes the interaction of solute in the liquid phase and the adsorbent in solid phase [40-44]. 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 monolayer adsorption. This is also analyzed by separation factor, R_L which is between 0 and 1 for favorable adsorption. 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 adsorption potential (**ε**) is independent of the temperature, but it depends upon the nature of the adsorbent and adsorbate. The mean free energy of the adsorption E, provide information about the nature of adsorption either chemical ion exchange or physical ion exchange adsorption. The values of E lies between 8–16 kJ/mol depicts

Isotherm model			**Constants**				r^2	**x^2**
			θ(mg/g)	**b(Lmg^{-1})**	**K_L(Lg^{-1})**	**R_L**		
Langmuir Ce/qe=1/b.θ+Ce/θ	PMSC	Cr(VI)	52.6	0.047	2.49	0.030	0.882	73.9
		Ni(II)	90.9	0.05	5.32	0.16	0.866	141.1
	APMSC	Cr(VI)	90.1	0.068	6.13	0.130	0.792	362.8
		Ni(II)	128.2	0.111	14.2	0.083	0.786	314.5
Freundlich lnqe=lnK_F+1/n lnCe	PMSC	Cr(VI)	n=2.49		K_F(Lg^{-1})=7.03		0.990	0.06
		Ni(II)	n=2.86		K_F(Lg^{-1})=14.9		0.992	0.55
	APMSC	Cr(VI)	n=3.56		K_F(Lg^{-1})=19.1		0.990	6.23
		Ni(II)	n=3.51		K_F(Lg^{-1})=32.1		0.994	0.66
Temkin qt=ln K_{T+}B ln Ce	PMSC	Cr(VI)	B=9.97		K_T(Lg^{-1})=0.704		0.962	3.85
		Ni(II)	B=13.1		K_T(Lg^{-1})=2.56		0.968	6.76
	APMSC	Cr(VI)	B=10.8		K_T(Lg^{-1})=1.43		0.962	41.23
		Ni(II)	B=17.1		K_T(Lg^{-1})=6.65		0.968	4.61
Dubinin-Radushkevich isotherm ln qe=ln q_m − kε2 ε=RT ln (1+1/Ce) E=(2k)−0.5	PMSC	Cr(VI)	q_m(mg/g)$_=$31.85		K (mole$^{2/}$$J^2$)=2.72	E (kJ/mol)=1.07	0.891	12.7
		Ni(II)	q_m(mg/g)=75.57		K (mole$^{2/}$$J^2$)=5.77	E (kJ/mol)=0.29	0.918	8.14
	APMSC	Cr(VI)	q_m(mg/g)=55.20		K (mole$^{2/}$$J^2$)=0.44	E (kJ/mol)=1.07	0.892	51.77
		Ni(II)	q_m (mg/g)=101.19		K (mole$^{2/}$$J^2$)=4.53	E (kJ/mol)=0.33	0.819	9.17

Table 3: Summary of parameters for various isotherm models.

the adsorption process follows the chemical ion-exchange and if E<8kJ/mol, the adsorption process is of a physical ion-exchange via weak electrostatic nature [40,42]. The linearized form of these isotherms were applied to the adsorption of Cr(VI) and Ni(II) onto PMSC & APMSC and the constants obtained from the slope and intercept of the plots have been compiled in Table 3. But the maximum adsorption capacity of APMSC for both the ions is due to the larger surface area and presence of more active sites in APMSC than PMSC due to activation. Significant changes of the functional groups are visible after acid treatment. 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 and nitrates. So APMSC was considered as an efficient adsorbent for Ni(II) ions because positively charged pollutants may be more easily removed by sludge based activated carbons.

Selection by error analysis

The linear regression and the non-linear χ^2 analysis gave different models as the best-fitting isotherm for the given data set, thus indicating a significant difference between the analytical methods. Ho [45] reported that the non-linear χ^2 test provided a better determination for the experimental data. In this study, both coefficients of correlation (r^2) and χ^2 test statistics were used for the determination of best-fitting isotherm with the experimental data.

The mathematical equation was given by equation (3)

$$x^2 = \sum \frac{\left(q_e - q_{e,m}\right)^2}{q_{e,m}} \qquad (3)$$

where $q_{e,m}$ is the equilibrium capacity obtained by calculation from model (mg/g) and *qe* is the equilibrium capacity (mg/g) determined from the experimental data. If data from model are similar to the experimental data then χ^2 would be a small number and vice versa [46]. In linear analysis the different forms of equation would affect the regression coefficient (r) and coefficient of determination (r^2) value significantly and it will affect the final determination. This can be avoided by using nonlinear χ^2 test analysis.

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 χ^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 3. However, Freundlich isotherm displayed the best fitting model than Temkin, Dubinin-Radushkevich and Langmuir isotherm because of the highest correlation coefficient and the lowest χ^2 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. So adsorption data fitted well with the Freundlich models for both ions.

Effect of temperature

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 as shown in Table 4. 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 adsorbent. The increased rate of intraparticle diffusion of Cr(VI) ions and Ni(II) ions into the pores of PMSC and APMSC at higher temperatures leads to the endothermic adsorption [28,29]. The thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o for the adsorption of Cr(VI) ions and Ni(II)ions onto PMSC and APMSC were determined from van't Hoff plot, ln K vs. 1/T using eqs. (4)

$$\ln K = -\Delta H^0/RT + \Delta S^0/R \ [(ie) K = q_e/C_e] \qquad (4)$$

and the results are listed in Table 4.

The energy of activation ($Ea = \Delta H^0 + RT$) values greater than+42 kJ/mol points out that all adsorption process here is a chemically controlled one [47]. These thermodynamic parameters can be explained the chemical bonding nature of the absorbent-adsorbate interaction [47,48]. The negative ΔG^o and positive ΔH^o and ΔS^o indicate that this adsorption is a feasible, spontaneous, endothermic, increased randomness and involve ion-pair chemisorptions. The greater $T\Delta S$ 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. Hence, the retention of both ions on both the adsorbents is feasible.

Adsorption kinetics

In order to investigate the rate of adsorption of Ni(II) ions and Cr(VI) ions onto PMSC and APMSC, different kinetic models [41-47] 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 5. The pseudo second order model indicates that the adsorption of Ni(II) ions and Cr(VI) ions on the surface of PMSC and APMSC is represented by two-phase reactions such as rapid adsorption for shorter duration in initial stage followed by slow adsorption for longer duration. 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 mesoporous surface of PMSC and APMSC. The R^2 values are close to unity which indicates the appropriateness of the application of this model. The multilinearity ($K_{id,1,}$ $K_{id,2}$) of Webber and Morris model [49] 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.

Comparing the correlation coefficients, it was more likely to reflect that the adsorption behavior might involve the weak valence forces through sharing electrons between metal ions and adsorbents (i.e., By ion exchange and H-bonding). Hence the rate limiting step is finalized as pseudo second order which is an indicative of chemisorptions [49] due to validity of Simple Elovich and intraparticle diffusion models.

S.no	Process	Adsorbent	ΔG^o 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)	PMSC	-0.04	41.05	135.6	41.09	43.57	0.994
		APMSC	-1.55	55.70	187.6	56.84	58.22	0.966
2	Retention of Ni(II)	PMSC	-1.74	54.53	184.0	55.75	57.05	0.966
		APMSC	-1.85	63.03	214.1	64.87	65.55	0.998

Table 4: Thermodynamic parameters for the adsorption of Cr(VI) and Ni(II) ions by PMSC & APMSC.

Adsorption mechanism

The adsorption of Cr(VI) and Ni(II) ions onto PMSC and APMSC occurs as multistep process [31,32] 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 PMSC and APMSC.

The adsorption mechanisms are shown as the following equations (5-8) and scheme in Figure 6

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

$$Ar\text{-}Y^{-}\text{-}C\text{-}X^{+}H_2 + HCrO_4^{-} \qquad Ar\text{-}Y^{-}\text{-}C\text{-}HCrO_4 + H_2O + NH_3 \tag{5}$$

For Ni(II) ions : (Ion exchange)

$$2(Ar\text{-}Y^{-}\text{-}C\text{-}X^{+}) + Ni^{2+} \qquad (Ar\text{-}C\text{-}X^{+})_2Ni \tag{6}$$

$$(Ar\text{-}Y^{-}\text{-}C\text{-}X^{+}) + Ni(OH)^{+} \qquad (Ar\text{-}Ni(OH)\text{-}C\text{-}X^{+}) \tag{7}$$

(And Hydrogen bonding)

$$(Ar\text{-}Y^{-}\text{-}C\text{-}X^{+}) + Ni(OH)_2 \qquad (Ar\text{-}Y^{-}\text{-}C\text{-}X^{+})Ni(OH)_2 \tag{8}$$

Ar is the matrix of the sludge-based carbons (PMSC & APMSC) with X^{+}& Y^{-} binding centres such as -O, -N, -S,(C-H), (-C= C), (C-O),(C-N),etc.

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) ions [28]. 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 Figures 6a and 6b, 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.

Comparison of PMSC and APMSC with other adsorbents

Usually acid treated adsorbents gave best affinity towards heavy metal remediation than alkaline and any other activation method [44] because of the introduction of more extractive sites such as –O, -N, -S and –P containing groups which are responsible for adsorption. The adsorption capacity of Cr(VI) and Ni(II) onto Activated Carbons was compared with other adsorbents reported in literature and is shown in Table 6. 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. This is in keeping with the fact that the Cr(VI) get reduced to Cr(III) to large extent at pH close to 1.0.

Few raw materials that exhibited very high adsorption capacity, this could be primarily due to the initial carbon content, activation process as well as the pore development due to the basic morphology of the raw material. Compared to the reported ones, the sorption capacity of sludge based adsorbents for Cr(VI) and Ni(II) is higher than the majority of the biopolymers (treated or untreated). The high adsorption capacity is due to the activation process as well as the physical parameters selected during the preparation of adsorbent (Table 7).

Then 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 m^2/g; APMSC=284 m^2/g) on the surface of APMSC which improves the rate of diffusion of ions into the pores.

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 ion-pair formation. Hence, these 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%) and also from wastewater. Conversion of waste sludge to the cost-effective carbons synthesized from paper mill sludge which can produce comparable results for removal of contaminates from water and waste water. It is a novel and environmentally friendly process. So, the organic waste from industrial process is utilized successfully today.

Conclusion

PMSC and APMSC are effective adsorbents for the removal of Ni(II) and Cr(VI) ions from aqueous solutions. Surface morphology

S. No.	Kinetic model	Equation	Constant	Values for Cr(VI)		Values for Ni(II)	
				PMSC	APMSC	PMSC	APMSC
1	Pseudo first order	$\ln(q_e\text{-}q_t)=\ln q_e - k_1.t$	$K_1(min^{-1})$	$1.2X10^{-2}$	$3.3X10^{-2}$	$1.3X10^{-2}$	$2.9X10^{-2}$
			R^2	0.934	0.994	0.728	0.339
2	Pseudo second order	$t/q_{t=}1/K_2.q_e{}^{2+}t/q_e$ $h=k_2q_e{}^2$	K_2(g/mg.min)	$4.7X10^{-3}$	$4.8X10^{-3}$	$3.9X10^{-3}$	$3.8X10^{-3}$
			q_e(mg/g)	21.3	25.6	25	26.3
			h(mg/g.min)	2.1	3.1	2.4	2.6
			R^2	0.996	0.998	0.997	0.997
3	Simple elovich	$q_{t=}\beta\ln t+\beta\ln\alpha\beta$	α(mg/g.min)	249.5	1380	153.11	30.41
			β(g/mg)	1.75	1.84	2.12	2.63
			R^2	0.931	0.927	0.916	0.980
4	Intra Particle Diffusion	$qt=K_{id}.t^{0.5+}C$	$K_{id,1,}$ $K_{id,2}$ (mg/g.min)	0.37,0.61	0.41,0.55	0.40,0.56	0.75,0.17
			C_1,C_2	14.7,12.1	18.5,17.1	17.3,16.3	16.3,22.7
			R^2	0.99,0.99	0.94,0.84	0.97,0.92	0.97,0.77

Table 5: Summary of parameters derived for various kinetic models.

S. No.	Adsorbent	Retention Efficiency (mg/g) or %		References
		Cr(VI)	Ni(II)	
1	Chitosan flakes	22.09	-	Aydin et al. (2009)
2	Fe-Cross-linked Chitosan complex	295	-	Zimmermann et al. (2010)
3	Acid treated OPSC Chitosan coated OPSC Acid treated-Chitosan coated OPSC	44.68 52.68 60.25	- - -	Nomanbhay et al. (2005)
4(a) 4(b)	Agricultural wastes agri-waste biomass	(a) high affinity for heavy metal remediation (b)- 79%		Sud et al. (2008) Garg et al. (2008)
5	Peanut hulls (a) aqueous solution (b) nickel plating effluent	- -	80% quantitative removal	Oliveira et al. (2010) Periasamy et al. (1995)
6	Hazelnut Shell	-	effective removal at pH 5.0	Demirbas et al. (2002)
7	Activated Carbon from coir pith (a) aqueous solution (b) electro plating effluent	- quantitative removal	62.5 at pH 5.0 -	Kadirvelu et al. (2001) Suksabye et al. (2008)
8	apple waste	effective removal with treated bed		Maranon et al. (1991)
9	palm flower (i) raw (ii) acid treated	Cr(III)6.24/Cr (VI)4.9 Cr(III)1.41/Cr (VI)7.13	- -	Elangovan et al. (2008)
10(a)	sugarcane bagasse	Effective removal at pH2.0 & 200rpm -	-	Garg et al. (2009)
10(b)	Pretreated bagasse with NaOH and acetic acid	90%	67%	Rao et al. (2002)
11	Neem leaf powder	62.97	-	Gupta et al. (2008)
12	treated Tamarind wood carbon	90% efficiency optimized by RSM	-	Sahu et al. (2009)
13	neem sawdust mango sawdust	58.82 37.73	- -	Vinodhini et al. (2010)
14	treated rubberwood sawdust	44.05	-	Karthikeyan et al. (2005)
15	treated sawdust of sal tree	9.35	-	Baral et al. (2006)
16	treated sawdust of Indian rosewood	10	-	Garg et al. (2004)
17	role of sawdust	remove contaminants from wastewater		Shukla et al. (2002)
18	pyrolysed sawdust	removal increases with increase in temperature		Hamadi et al. (2001)
19	(i) phosphate treated rice husk (ii) rice milling by products	- -	(i) two or three times higher affinity than raw rice husk (ii) effective removal	Mohan et al. (2008) Marshall et al. (1995)
20	activated coconut husk	acid treated more effective than base treated		Olayinka et al. (2009)
21	Sludge based activated carbon PMSC APMSC	52.6 90.1	90.9 128.2	Present Study

Table 6: Comparison of PMSC & APMSC with other adsorbents.

100 mg/L	PMSC-Ni(II) –Effect of contact time	100 mg/L	APMSC-Ni(II)-effect of contact time
0	0	0	0
20	19.573	20	19.25
40	20.852	40	19.83688
60	22.518	60	20.3125
90	23.173	90	21.3125
120	24.488	120	22.3125
150	24.911	150	23.375
180	24.908	180	23.675

Table 7: Effect of contact time of PMSC and APMS.

study reveals that they are mesoporous carbons since pore size is 11.821 nm and the BET surface area is 73 m^2/g for PMSC and 284 m^2/g for APMSC. The adsorbents seem to be rough and protrusions. APMSC has greater efficiency for the removal of Cr(VI) and Ni(II) ions than PMSC. The FTIR spectra of PMSC and APMSC confirm the presence of polar poly-functionality. The Introduction of heteroatom by activation is responsible for stretching and bending vibrations. The activation process increases the development of new tunable surface functionality. Adsorption of Ni(II) ions onto PMSC and APMSC is more effective at pH 5 and for Cr(VI) at pH 2. At pH 5.0, the adsorption of Ni(II) ions occurs through ion-exchange along with H-bonding due to the existence of ionic and non-ionic active species, so the adsorption capacity is maximum. At pH 2.0, the adsorption of Cr(VI) ions occurs through ion-exchange process because of the existence ionic active species only. Equilibrium isotherm for both Ni (II) and Cr(VI) ions removal is best represented by Freundlich isotherm based on r^2

and x^2, which reveals the multilayer ion exchange sorption via weak electrostatic forces. But rate of sorption follows the pseudo second order kinetics for both Ni(II) and Cr(VI) ions. These chemisorptions are also confirmed by the validity of simple Elovich and intraparticle diffusion models. The thermodynamic study further reveals the endothermic, randomness and feasibly spontaneous nature of the adsorption processes. Regeneration of PMSC and APMSC are possible and the acid–base reactions are effective upto six cycles. These results suggest that mesoporous carbons (PMSC & APMSC) are feasibly a good substitute for other commercially available activated carbons produced from natural resources. It is a novel and environmentally friendly process.

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