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Preparation And Characterization Of Novel Iron (III) Hydroxide/Paper Mill Sludge Composite Adsorbent For Chromium Removal

Ali Yaraş^{*1}, Hasan Arslanoğlu²

Abstract

This work deals with the removal of Cr (III) and Cr (VI) from synthetic solutions via a novel composite adsorbent prepared by precipitating iron (III) hydroxide on paper mill sludge (PMS). To obtain Fe(OH)₃ loaded PMS, -8+16 mesh fraction of PMS was saponified with NaOH solution, then iron (III) chloride was impregnated, hydrolyzed in NaOH solution and dried. The influences of pH, time, initial concentration and temperature on removal of Cr (III) and Cr (VI) were examined and it was determined that Cr (VI) removal occurs simultaneously with a reduction reaction. Maximum removal yields for Cr (III) and Cr (VI) occurred at approximately pH = 5 and the adsorption achieved equilibrium in 90 min. Cr (VI) adsorption ratio decreases while Cr (III) removal percentage increases with raising in temperature. Experimental results are consistent with Langmuir isotherm. Adsorption capacities of Cr (III) and Cr (VI) were calculated as 8.49, 10.14, 12.62 mg/g and 7.64, 5.39 and 4.17 mg/g for 25, 40 and 55 °C, respectively. Enthalpy changes for Cr (III) and Cr (VI) were calculated as 24.67 kJ/mol and -12.46 kJ/mol, respectively. These results demonstrated that the adsorption phenomenon of Cr (III) and Cr (VI) are endothermic and exothermic.

Keywords: Hexavalent chromium, iron (III) hydroxide, paper mill sludge, adsorption, reduction.

1. INTRODUCTION

Nowadays, water pollution has become an important problem by virtue of increasing technology and human needs. The investigations indicate that a great amount of pollutants is discharged into surface waters. The pollutants such as polycyclic aromatic compounds, pesticides, radioactive substances and toxic heavy metals cause negative influence on human health, in addition they affect water adversely in terms of smell, taste and physical appearance [1].

Since chromium compounds have high toxicity, it is necessary to control the passing to water and treat chromium-containing wastewater. Chromium is

discharged from various industries; metal coating, leather, paint, textile, glass and ceramics at high concentrations. Cr is in the form of Cr⁶⁺ or Cr³⁺ in wastewater and the toxicity of Cr⁶⁺ is much higher than Cr³⁺ [1], [2].

Cr (VI) is generally first reduced to Cr (III) in the presence of various reducing agents and then removed by precipitation. Adsorption method is most preferred to remove Cr (VI) directly from the wastewater. In this context, there are numerous studies on the utilization of various industrial and agricultural wastes as adsorbents in literature [3].

A large amount of PMS is produced from the paper production plants. Storage and transportation of PMS

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material is very important in terms of reducing the waste load of environment and plants. To eliminate this problem, the storage and composting processes are generally employed [4]. However, strict environmental regulations limit the application of these methods [5], [6]. On the other hand, the incineration treatment is not preferred for PMS as it contains various components [5]. For all these reasons, the researchers focused on the utilization of PMS as an adsorbent in removal toxic and heavy metals from wastewaters [7]–[9].

Previous studies illustrated that iron (III) hydroxide is utilized as an efficient adsorbent for removal chromates from aqueous systems [10], [11]. However, iron (III) hydroxide causes application difficulties due to the colloidal properties that it forms in the aqueous medium. In the present study, we plan to produce a composite adsorbent with iron (III) hydroxide precipitated PMS and thus prevent the filtration problem by fixing iron (III) hydroxide. This situation is also probably contribute positively to the problem of swelling by the hydration reaction of PMS in the presence of aqueous solution. Therefore, in this study, adsorption characteristics of Cr (III) and Cr (VI) from synthetic solutions were studied by iron (III) hydroxide precipitated on PMS.

2. MATERIAL METHOD

2.1. Preparation of PMS

PMS was obtained from the OYKA paper factory in Çaycuma/Zonguldak in 2016. It was firstly dried by blowing air with a fan, crushed and sieved to obtain particles with -8+16 mesh ($1.2 < x < 2.4$ mm) size. The prepared sample was dried at 50°C for 12 h.

2.2. Preparation and Characterization of Iron (III) Hydroxide Precipitated PMS

It was obtained by following a process; the iron was saponified with NaOH, treatment with iron (III) chloride and hydrolyzed with NaOH [12].

100 g of PMS was stirred with 0.1 M NaOH solution for 1 h and filtered. The filtrate PMS was washed with purified water until the pH=8 and dried at 50°C for 12 h. Then, it was then stirred in 0.5 M FeCl₃ solution for 1 h using a magnetic stirrer, waited for 12 h, filtered and the filtrate was dried at 50°C for 24 h. Lastly, it was hydrolyzed in 0.1 M NaOH solution by stirring, waited for 12 h, then filtered and washed the washing water was until pH 8 was reached. The prepared sample was

dried at 50°C for 24 h. As presented in Table 1, some features of the Fe(OH)₃-loaded PMS adsorbent prepared are given.

Table 1. Some features of the Fe(OH)₃-loaded PMS adsorbent prepared

Characteristics	Value
Bulk density (g/cm ³)	1.36
BET surface area (m ² /g)	4.5
Langmuir surface area (m ² /g)	7.8
Methylene blue sorption capacity (mg/g)	63.6
Mass yield (% w/w)	78.9
Iron content (% w/w)	1.77
Ash content (% w/w)	5.86
Swelling capacity (ml/g)	1.1
Water retention (g/g)	3.42
COD (mg/g)	19.7

Figure 1 and Figure 2 depicts SEM image and EDX spectra analysis of the prepared adsorbent, respectively. EDX spectra results demonstrates the quantitative elemental analysis in weight %; oxygen 55.9, carbon 19.0, iron 17.8, chlorine 6.7 and sodium 0.6. In the light of these findings, it is pointed out that the presence of Fe in the structure is clearly seen.

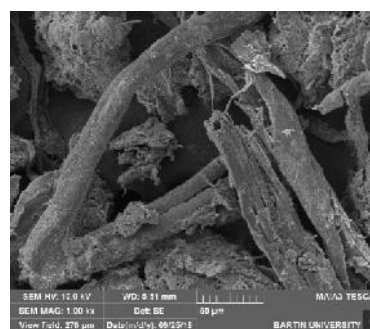
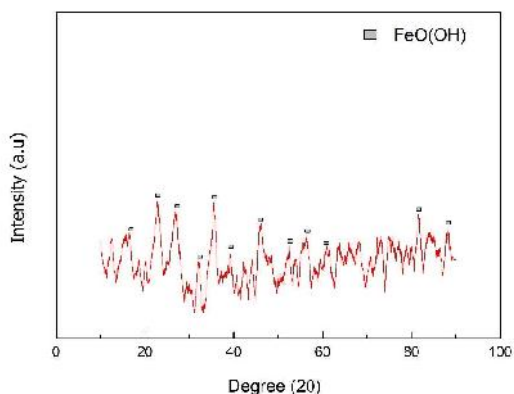
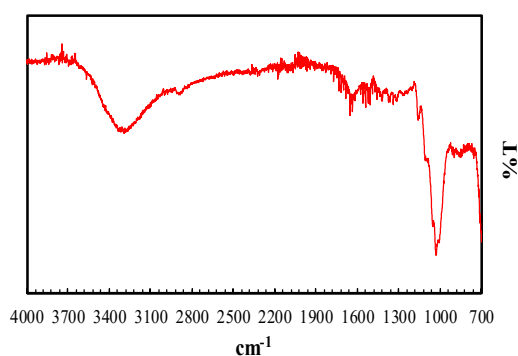


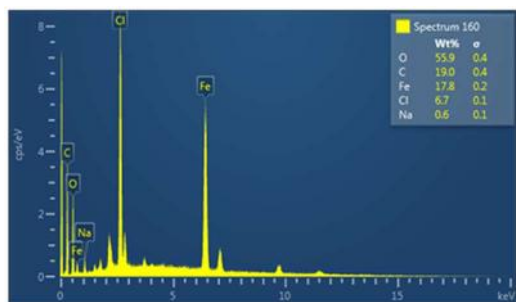
Figure 1. SEM image of Fe(OH)₃ loaded PMS

Figure 2. EDX results of Fe(OH)₃ loaded PMSFigure 3. XRD patterns of Fe(OH)₃ loaded PMS

The presence of the peaks in Figure 3 clearly demonstrates that the FeO(OH) particles are loaded into the PMS. On the other hand, broad band at 3400 cm⁻¹ in Figure 4 pertain to the stretching -OH of cellulose. The weak peak (about 1630 cm⁻¹) was related to deformation vibration of -OH group. The strong peak at 1050 cm⁻¹ was attributed to the presence of Fe-OH bonds.

2.3. Preparation of Synthetic Cr Solutions

Synthetic Cr (III) and Cr (VI) solutions were prepared from Cr₄(SO₄)₅(OH)₂ and Na₂Cr₂O₇ salts. Firstly, the the stock Cr solutions were prepared (1000 ppm) and it was diluted with distilled water. Its pH adjustments were carried out with H₂SO₄ and NaOH solutions.

Figure 4. FTIR analysis of Fe(OH)₃ loaded PMS

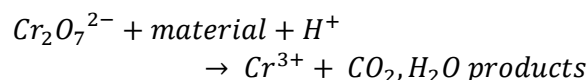
2.4. Adsorption study

All adsorption tests were performed in a 300 ml flask using shaker incubator (Zhcheng ZHWY-200D) with adjustable stirring speed and temperature and samples were taken at the end of the desired times. Cr (VI) amount in supernatant were performed spectrophotometrically by diphenyl carbazide method [13]. Cr (III) and iron analyses were determined by atomic absorption spectrophotometer.

3. RESULT AND DISCUSSION

Figure 5 was demonstrated the impact of pH on removal Cr (III), Cr (VI), total Cr and Fe using Fe(OH)₃ loaded PMS. Cr (III) removal is considerably high in varied range from pH=5 to pH=8 and the highest Cr (III) removal value (98.7%) was reached at pH =7. This is due to the tendency of Cr (III) to precipitate by hydrolysis in this pH region. In other words, it can be said that the Cr (III) removal mechanism for this pH range takes place by precipitation. On the other hand, Cr (III) removal is occurred by adsorption process due to Cr (III) concentration values are above 100 mg/l at around pH 4. This result shows that the precipitation of Cr (III) in hydroxide form on depends pH [3]. Above pH=9 values, the removal efficiency decreases and up to 30% at around pH=12. This situation may be attributed to the adsorbent surface being negatively at high pH, the amphoteric properties of Cr (III) and its high tendency to form complexes [14]. In terms of the amount of Fe passing to the solution, as 3.1 mg/l concentration of Fe was passing to the solution at around pH 1.8, this amount decreases to 0.1 mg/l with increasing pH. The pH value was chosen as 4 for subsequent experiments since the removal efficiency is high and Fe concentration passing through the solution is negligible.

The results in Figure 5 indicate that Cr (VI) removal ratio is close to 100% at acidic pH (1-3.5) because of the adsorption comes with the reduction reaction. It is known that Cr (VI) is reduced to Cr (III) using organic material according to the following reaction;



With increasing pH, the removal values of Cr (VI) and total Cr are approaching each other. Maximum removal percentages for total Cr and Cr (VI) were achieved at 88.85% and 95.55% at pH 4, respectively. This suggests that Cr (VI) is partially reduced and adsorbed

together with Cr (III) because the maximum adsorption of Cr (III) occurs at pH=4.

Based on the results in Figure 6, the removal efficiency increases for both Cr species with increasing of time and the adsorption of Cr (III), Cr (VI) and total Cr reaches the equilibrium after 90 min. At the end of 240 min, 87% of total Cr is removed while the amount of Cr (VI) removed is about 96%.

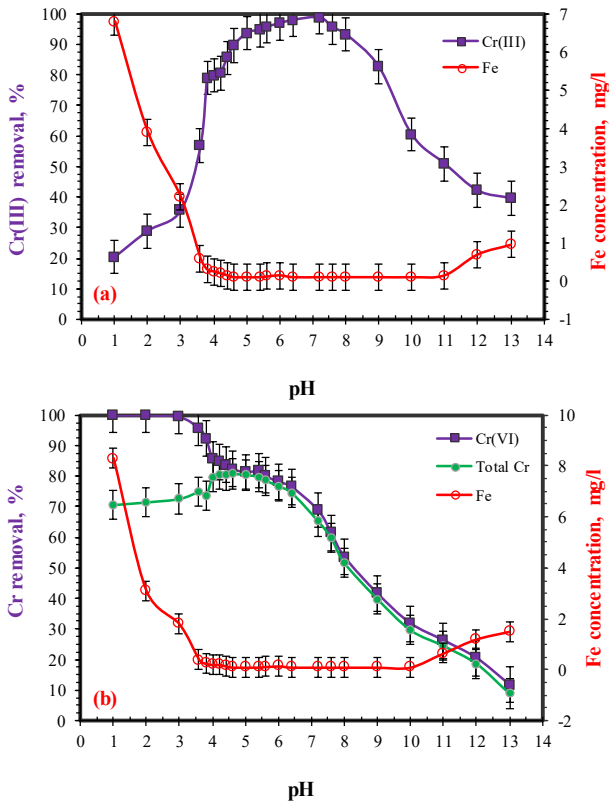


Figure 5. Influence of pH on removal of Cr (III), Cr (VI), total Cr and Fe

To calculate the adsorption kinetics, experimental data were applied to the following Lagergren equation (1) [15];

t is the contact time (min.), k is adsorption rate constant (min^{-1}), q_t and q_e are amount of substance adsorbed at any time and equilibrium time (mg/g). According to Figure 7, it is seen that the experimental data is good agreement with Lagergren equation for both Cr types. Adsorption rate constants for Cr (III) and Cr (VI) were found to be 0.0456 and 0.0234 min^{-1} , respectively. It can be said that this result is reasonable due to Cr (VI) and Cr (III) are cationic and anionic complex structure in the aqueous solution, respectively. As seen from Figure 8, while Cr (III) removal percentage increases with increase temperature, Cr (VI) removal efficiency decreases. According to the classification by Sposito (1989) [16], above aforementioned nonlinear

equilibrium curves correspond to the L type for Cr (III) and Cr (VI).

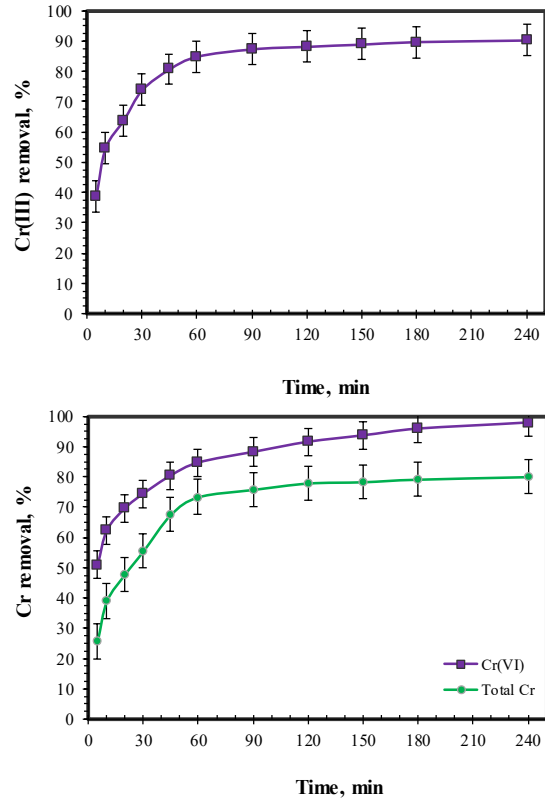


Figure 6. Influence of time on removal of Cr (III), Cr (VI) and total Cr

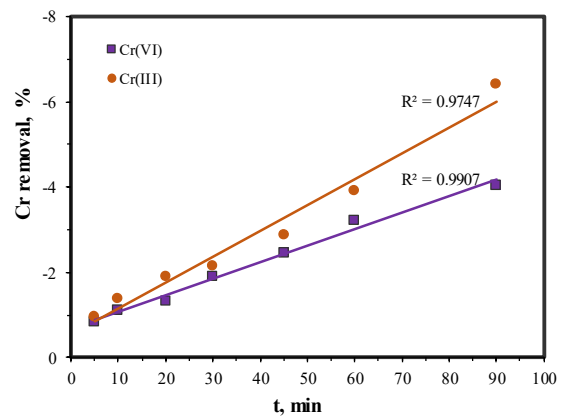


Figure 7. Lagergren graph for adsorption process of Cr (III) and Cr (VI)

$$\ln(q_e - q_t) = \ln q_e - kt \quad (1)$$

Table 2. Langmuir isotherm constants

Cr type	Temperature, °C	q _{max} (mg/g)	b
Cr (III)	25	8.49	2.65
	40	10.14	1.68
	55	12.62	1.16
Cr (VI)	25	7.64	9.89
	40	5.39	12.28
	55	4.17	17.30

Table 3. Thermodynamic parameters

Cr type	Temperature, °C	ΔG (kJ/mol)	ΔS (kJ/molK)	ΔH (kJ/mol)
Cr (III)	25	-2.415	0.091	
	40	-1.350	0.083	24.67
	55	-0.405	0.076	
Cr (VI)	25	-5.680	-0.023	
	40	-6.531	-0.019	-12.46
	55	-7.774	-0.014	

Experimental results were applied to linear Langmuir isotherm equation (2) following as [11];

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{2}$$

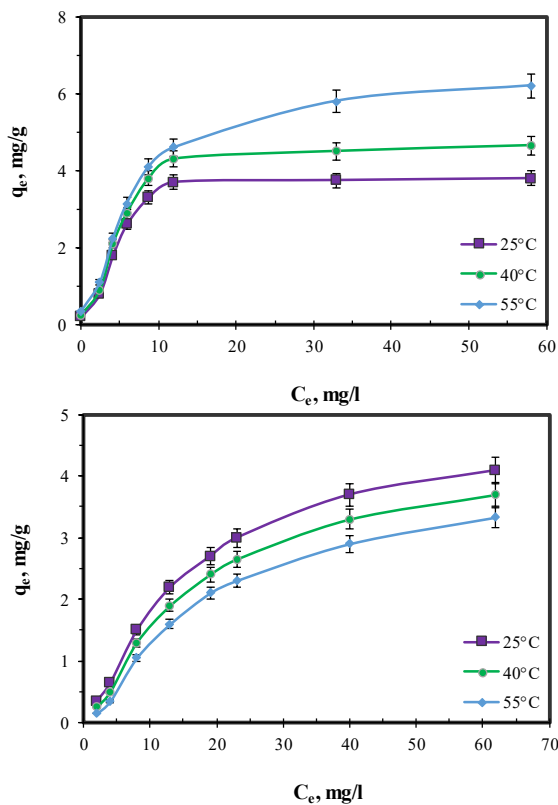


Figure 8. Non-linear adsorption isotherms

C_e is total Cr concentration at equilibrium (mg/l), q_e is amount of Cr adsorbed per unit adsorbent weight, q_{max} is maximum adsorption capacity (mg/g), b is a constant (mg⁻¹). Langmuir isotherms and the calculated coefficients for Cr (III) and Cr (VI) are illustrated in Figure 9 and Table 2.

The changes of free energy, enthalpy and entropy for adsorption process can be calculated by following equations (3), (4) and (5) [12];

$$\ln b = \ln b^I - \frac{\Delta H}{RT} \tag{3}$$

$$\ln(1/b) = \frac{\Delta G}{RT} \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

ΔG is free energy (kJ/mol), T is ambient temperature (K), R is universal gas constant (8.314 J/molK), ΔH is enthalpy (kJ/mol) and ΔS is entropy (kJ/molK).

Enthalpy changes for Cr (III) and Cr (VI) were calculated as 24.67 kJ/mol and -12.46 kJ/mol from the slope of the curves in Figure 10, respectively. These results indicated that adsorption phenomenon of Cr (III) and Cr (VI) are endothermic and exothermic, respectively. Free energy and entropy changes of process are given in Table 3. Based on these results, it is seen that Cr (III) adsorption is spontaneously at high temperatures.

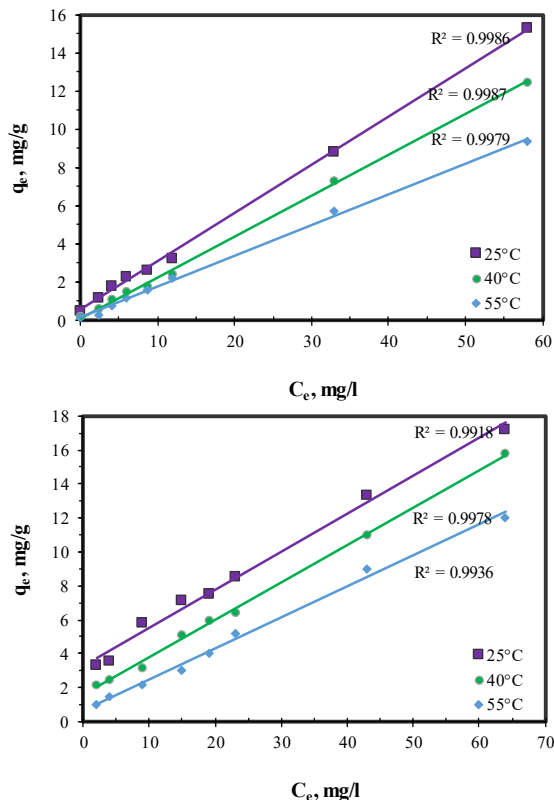


Figure 9. Langmuir isotherms

A slight decrease in entropy change with increasing temperature for Cr (III) indicates that irregularity also decreases with increased adsorption efficiency. This situation is contrary for Cr (VI). Finally, sorption capacities related to chromium reduction via different adsorbents in literature are presented in Table 4. The chromium removal capacity of the Fe(OH)₃ loaded PMS was found to be 12.6 mg/g. Therefore, it can be used effectively for removal chromium from synthetic aqueous solutions.

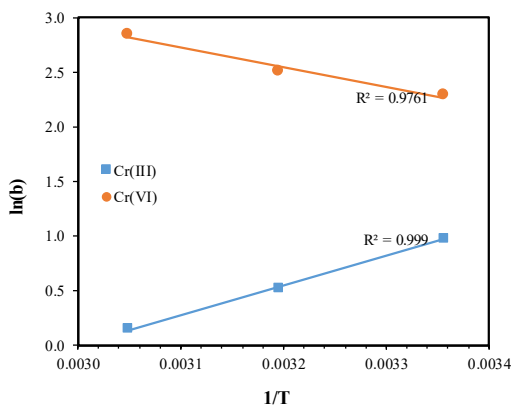


Figure 10. 1/T against ln(b)

Table 4. Sorption capacities related to chromium reduction with various sorbents in literature

Sorbents	Sorption capacities (mg/g)	Ref.
Grass (<i>Onopordom Heteracanthom</i>)	37.3	[17]
Magnetic Chitosan Hydrogel	27.3	[18]
Magnetic activated carbon	51.7	[19]
Walnut shell pyrolysis product	49.8	[20]
Grapefruit shell	39.1	[21]
Carbon / AlOOH composite	32.6	[22]
Biomass waste	53.4	[23]
A kind of flower (<i>Eupatorium adenophorum</i>)	89.2	[24]
Activated carbon modified with nitric acid	16.1	[25]
Coconut shell activated carbon	10.9	[26]
Terminalia arjuna nuts activated carbon	28.4	[27]
Peanut shell activated carbon	16.3	[28]
Modified coconut commercial activated carbon	20	[29]
Fe(OH) ₃ -loaded PMS	12.6	This work

4. CONCLUSIONS

Experimental findings demonstrate that the removal of Cr (III) and Cr (VI) using Fe(OH)₃ loaded PMS is depending on pH value. It was determined that Cr (III) was removed with a high efficiency at neutral pH and the optimum pH was 4 for Cr (III) adsorption. Cr (III) removal efficiency reached 89% under process conditions; 10 mg/l initial concentration, 10 g/l dosage, 25°C temperature and 120 min. Cr (VI) was substantially removed at acidic pH, and removal efficiencies of Cr (VI) and total Cr were obtained 95%

and 87% under the same conditions at pH 4, respectively.

The results indicate that the adsorption yield increases with increasing time for both Cr species and the process reaches equilibrium in 90 min. Based on Lagergen equation, adsorption rate constants were found as 0.0456 and 0.0234 min⁻¹ for Cr (III) and Cr (VI), respectively. Experimental data were determined to be in good agreement with the Langmuir isotherm and adsorption capacities of Cr (III) and Cr (VI) were obtained to be 8.49, 10.14, 12.62 mg/g and 7.64, 5.39 and 4.17 mg/g for 25, 40 and 55°C, respectively.

Enthalpy changes for Cr (III) and Cr (VI) were calculated to be 24.67 and -12.46 kJ/mol and these results indicated that the adsorption phenomenon of Cr (III) and Cr (VI) are endothermic and exothermic, respectively. The entropy value for Cr (III) was found to decrease with temperature while it increased with temperature for Cr (VI). In addition, it is possible to remove Cr (III) and Cr (VI) from synthetic solutions with Fe(OH)₃ loaded PMS, but the removal mechanisms for two types of chromium are quite a change from each other. Consequently, PMS can be economically evaluated in the preparation of a composite adsorbent with this proposed process. It means to reduce of PMS load in terms of the environmental and paper production plant. The removal of toxic dyes and heavy metals from wastewater by using PMS or modified PMS can be studied for further study.

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