

ADSORPTION OF PITCH AND STICKIES ON MAGNESIUM ALUMINUM HYDROXIDES TREATED AT DIFFERENT TEMPERATURES

Guodong Li ^{a,b} and Wenxia Liu ^{a,*}

Magnesium aluminum hydroxides (MAH) of nitrate and carbonate forms were prepared by co-precipitation, dried at different temperatures, and employed as an adsorbent for pitch and stickies in papermaking. Results indicated that MAH that had been heat-treated had higher adsorption capacity to model pitch and stickies at neutral pH. Low-temperature-dried magnesium aluminum hydroxides of nitrate form (MAH-NO₃) had higher adsorption capacity to model pitch and model stickies than those of the carbonate form (MAH-CO₃). Increasing the drying temperature of MAH reduced the difference of adsorption capacity between MAH-NO₃ and MAH-CO₃. Higher-temperature-dried magnesium aluminum hydroxides also showed higher adsorption capacity to model pitch and stickies when the drying temperature was lower than 550 °C. MAH displayed higher adsorption capacity while a lower initial adsorption rate of model stickies than of model pitch. The model pitch and stickies were adsorbed on MAH significantly by charge neutralization and distributed mainly on the surface of the platelets of magnesium aluminum hydroxides. The experimental isothermal adsorption data of model pitch and stickies on MAH dried at 500 °C fit well to the Freundlich and Dubinin–Radushkevich isotherm equations.

Keywords: Magnesium aluminum hydroxide; Pitch; Stickies; Pitch control; Adsorption

Contact information: a: Shandong Provincial Key Laboratory of Fine Chemicals, Shandong Polytechnic University, Jinan 250353, China; b: Tianjin Key Lab of Pulp & Paper, Tianjin University of Science & Technology, Tianjin 300457, China. *Corresponding author: liuwenxia@spu.edu.cn

INTRODUCTION

High yield pulps are used extensively not only in the production of newspaper, but also increasingly for paper grades of higher quality, such as printing and writing papers. In addition, in order to solve the problems of raw materials and environmental pollution, waste paper as a kind of sustainable development material has also been widely used in the papermaking industry. However, some of the substances, such as resinous wood components (pitch) in high yield pulp and tacky materials (stickies) from recovered paper, are hydrophobic in nature (Alcy et al. 2003). The thermodynamic instability of these materials in aqueous systems leads to their high inclination of agglomeration, which impairs the physical properties of paper and alters the quality of the final product due to the presence of dirt, specks, or holes and increases production costs associated with the cleanups and interruptions in production.

Chemical antidotes to combat the deposits of pitch and stickies on papermaking process are diverse. Adsorbents (Allen 1993), inorganic salts of multivalent cations

(Allen 1980; Glazer 1991), polyelectrolytes (Wågberg 2000; Leroux et al. 1997), dispersants (Hubbe et al. 2006), surfactants (Hubbe et al. 2006), and even sequestrants (Glazer 1991) have been suggested to cope with pitch and stickies problems. However, adsorbents are still one of the fundamental pitch and stickies control agents. Minerals such as talc, kaolin, and calcium carbonate, which usually are employed as fillers in paper, as well as bentonite, zeolite, etc., can take on the role of pitch adsorbents under special circumstances (Allen et al. 1993; Derrick 1994; Lamar et al. 1990). This ability is attributable to their relatively high specific surface area and affinity towards hydrophobic substances. To be more efficient, either cationic or hydrophobic modification of those minerals have been put forward as means by which further improvements in the affinity of the minerals towards negatively charged pitch and stickies can be achieved (Lamar et al. 1990; Rogan and Adams 1993; Gantenbein 2008).

Magnesium aluminum hydroxides (MAH) are positively charged, layered double hydroxides with a structure similar to hydrotalcite. The particle size of MAH may be less than a hundred nanometers (Lagaly et al. 2001; Zhang et al. 2006). The positive charges, which are balanced by various anions such as CO_3^{2-} , NO_3^- , and Cl^- , and confer anion-exchange capacity to MAH, are ascribed to the extra positive charge of aluminum ions. The positive charges, high specific surface area, and relatively weak hydrophilicity originated from the low hydration ability of anions between the layers of MAH must have made it a potential adsorbent for pitch and stickies. In fact, some authors have tried to study the applicability of MAH as a scavenger of anionic disturbing substances. The results have confirmed that properly prepared MAH can remove 100% of model pitch substances (Michalik et al. 2008). Moreover, through suitably high temperature calcinations of MAH with CO_3^{2-} or NO_3^- as associated anions, MAH may lose its bonded water, along with the associated anions, forming magnesium aluminum oxides (MAO). Thus, the specific surface area is enlarged, and as a result its adsorption capacity is enhanced.

Under certain conditions, the mixed oxides MAO can adsorb anions again and partially restore to the original layered structure, displaying a "memory effect" (Erickson et al. 2005). Taking advantage of this effect, the heat-treated material can be used as an anion adsorbent, providing more "positive charges" than MAH. Therefore, it would be interesting to know whether MAH is a more efficient scavenger for pitch and stickies after undergoing treatment at high temperatures, what the adsorption behavior of colloidal pitch and stickies is, and how fast the adsorption is. However, there has been little research aiming at the adsorption of pitch and stickies on either MAH or MAO.

The purpose of this study was to explore the adsorption mechanism and behavior of pitch and stickies on MAH that had been dried at different temperatures, and provide a scientific foundation and theoretical for the novel adsorbent of pitch and stickies. MAH of the nitrate and carbonate forms were selected, since MAH with the interlayer anions of carbonate or nitrate are easily decomposed during high-temperature drying, losing interlayer anions and water molecules, leading to the collapse of the layered structure, and then forming mixed metal oxides. In order to simplify the preparation process of MAO, the MAH compounds were directly dried at different temperatures instead of carrying out the full calcination of MAH.

EXPERIMENTAL

Materials

The water used in the experiment was distilled water prepared by an automatic double pure water distillatory. Gum rosin (WW grade) was a commercial product from Guangxi, China. Styrene-acrylate emulsion with a solid content of 52% was a commercial product, which was a conventional paper product adhesive, supplied from the local market. All the other chemicals used were analytical grade pure reagents.

Synthesis of Magnesium Aluminum Hydroxides

Magnesium aluminum hydroxides (MAH) with either nitrate or carbonate as associated anions were prepared by a co-precipitation method (Zhang et al. 2006). For the preparation of MAH of the nitrate form (MAH-NO₃), 200 mL of nitrate solution containing 0.12 mol magnesium nitrate hexahydrate, 0.04 mol aluminum nitrate nonahydrate, and 300 mL of ammonium hydroxide solution containing 80 mL of aqueous ammonia with about 30% of NH₃ were first prepared. Then, the nitrate solution and 200 mL of the ammonium hydroxide solutions were simultaneously added dropwise to the remaining 100 mL of ammonium hydroxide solution during 2 hours at a stirring speed of 500 r/min. The resulting slurries were aged for 8h at 80 °C, washed with distilled water by multiple centrifuging, dried at a temperature between 100 and 600 °C, and milled to obtain MAH-NO₃. The MAH with carbonate associated anions (MAH-CO₃) were obtained in a similar way, except for eliminating aqueous ammonia and using Na₂CO₃ and NaOH solutions to maintain the pH at approximately 10.5 (Michalik et al. 2008).

Preparation of Model Pitch and Stickies

Model pitch was obtained by dissolving 50 g of gum rosin in 250 mL of ethanol, followed by saponifying the gum rosin using 12.5 g of 1M potassium hydroxide solution added dropwise under stirring until the saponification was completed. Then, 200 mL of ethanol was added to dissolve the model pitch (Michalik et al. 2008). The charge density of the model pitch was 183.17 µeq/L at pH 7. Model stickies were prepared by diluting 50 g of styrene-acrylate emulsion with distilled water to 500 mL. The charge density of the model stickies was 137.43 µeq/L at pH 7.

Adsorption Experiments

The model pitch and stickies were further diluted with distilled water to prepare 0.05 to 0.4 g/L dispersions, while the MAH-NO₃ or MAH-CO₃ dried at different temperatures was dispersed in distilled water to obtain 0.1 g/L slurries. The pH of the model pitch and stickies dispersions was adjusted by hydrochloric acid or sodium hydroxide to (5 to 8) ±0.01 according to predetermined protocols by using a pH meter. An adsorption test was carried out by adding 4.5 mL of either model pitch or stickies dispersions, to 1.5 mL of MAH slurries. After mixing for 60 min, the mixtures were centrifuged for 10 min at 3000 r/min (1277×g) 2 times, and the pitch or stickies concentrations of supernatants were analyzed by spectrophotometer at 350 nm according to Liu et al. (2004) and Zhao et al. (2006). A reference solution for each spectrophotometric measurement was obtained as a supernatant from a corresponding MAH sample

diluted by 4.5 mL distilled water centrifuged under the same conditions. The amount of adsorbed pitch or stickies (q) was calculated by the difference between known initial pitch or stickies concentration (C_0) and concentration (C_1) of pitch or stickies measured in the supernatant.

$$q = \frac{(C_0 - C_1) \times V}{m} \quad (1)$$

where V is the volume of the mixture of pitch or stickies dispersion and MAH slurry, and m is the mass of dried MAH in the mixture.

Characterization of Adsorbent Before and After Adsorption

The adsorption of pitch or stickies on MAH was characterized by comparing the X-ray diffraction (XRD) patterns and morphologies of MAH before and after adsorbing pitch or stickies. The XRD patterns were collected on a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using $\text{CuK}\alpha$ radiation at 40 kV and 90 mA with a scanning speed of 1 °/min. The morphologies were observed with a Tecnai 20-TWIN high-resolution transmission electron microscope (HRTEM).

RESULTS AND DISCUSSION

Adsorption Isotherms

Adsorption isotherms are fundamental to evaluate the adsorption capacity of pitch and stickies on MAH and to diagnose how the nature of adsorption depends on the experimental conditions (Donat et al. 2006). Therefore, the adsorption isotherms of model pitch and stickies on MAH were plotted. Figures 1 through 4 show the adsorption isotherms of model pitch and stickies on MAH- CO_3 and on MAH- NO_3 dried at different temperatures, respectively.

As shown in the figures, the adsorbed amounts of pitch and stickies on both MAH- CO_3 and MAH- NO_3 dried at different temperature increased with the increase of the concentration of pitch and stickies. The saturation points of both pitch and stickies on MAH- CO_3 and MAH- NO_3 were not reached under the current pitch and stickies concentrations, although the adsorption amounts were as large as 400 to 900 mg/g for model pitch and 500 to 1300 mg/g for model stickies, implying a much higher adsorption capacity of the two MAHs to both model pitch and model stickies.

Increasing the drying temperature of both MAH- CO_3 and MAH- NO_3 from 100 °C to 550 °C significantly increased the adsorptions of pitch and stickies. However, when the drying temperature exceeded 550 °C, further increase of the drying temperature impaired the adsorptions of pitch and stickies on the two MAHs. This may be attributed to the alteration of the structures of the MAH- CO_3 and MAH- NO_3 at high temperatures. It is well known that when MAH with carbonate or nitrate as interlayer anions are dried at a temperature between 400 to 500 °C they undergo decomposition with the losses of interlayer anions, yet the layered crystal structure of MAH is not completely lost. When the drying temperature reaches and exceeds 500 °C, the laminates of MAH collapse

completely, losing the layered crystal structure, but still maintaining the laminates of MAH, showing a "memory" effect (Erickson et al. 2005). Thus, when it is dispersed in aqueous solutions the high temperature, dried MAH will restore its MAH structure by absorbing anions into its interlayer.

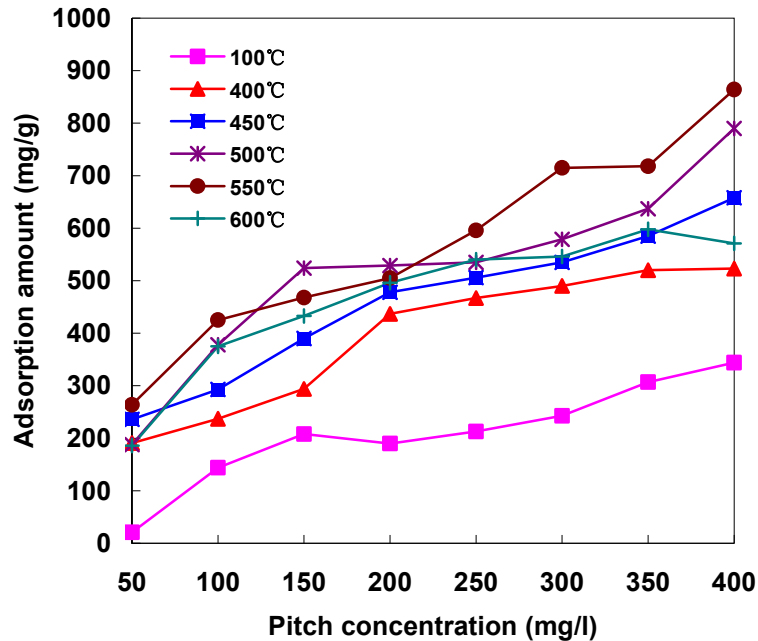


Fig. 1. Adsorption isotherms of model pitch on MAH-CO₃ at pH 7

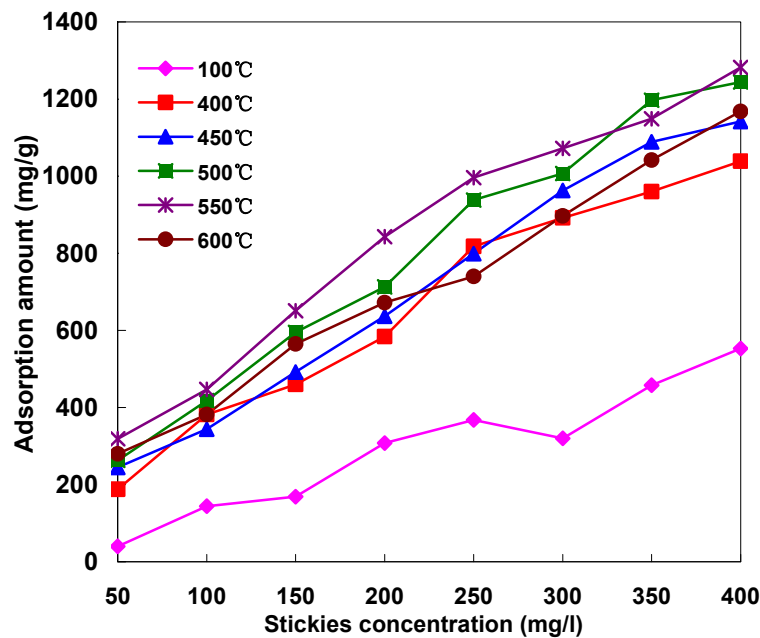


Fig. 2. Adsorption isotherms of model stickies on MAH-CO₃ at pH 7

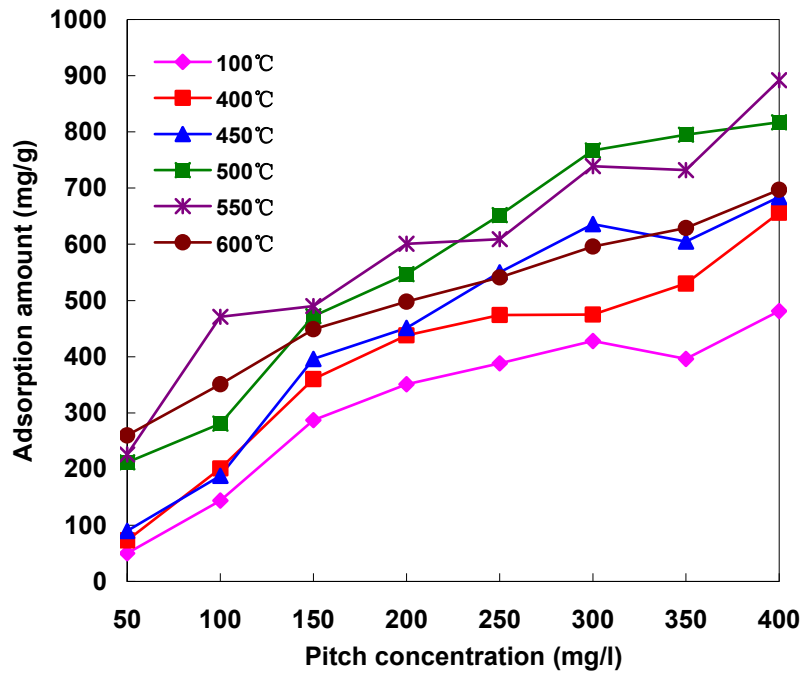


Fig. 3. Adsorption isotherms of model pitch on MAH-NO₃ at pH 7

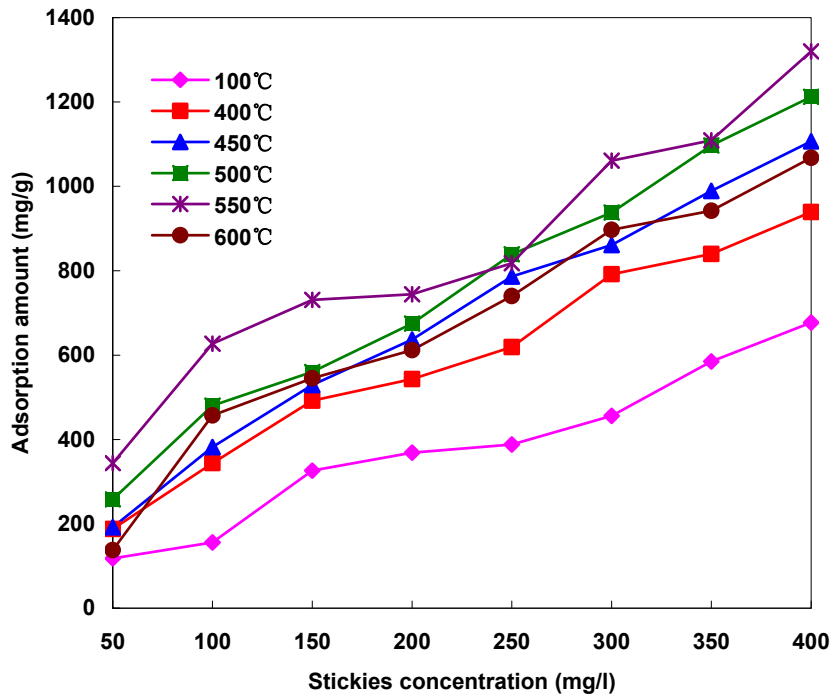


Fig. 4. Adsorption isotherms of model stickies on MAH-NO₃ at pH 7

When the drying temperature exceeds 600 °C, a new crystalline phase forms, and part of the structure cannot be restored (Shen et al. 2006). Although drying at a temperature between 400 and 600 °C must be different from a true calcination, at least part of the MAH may undergo similar changes, which has been confirmed by XRD analysis presented later. Therefore, the enhanced adsorption with drying temperature may be explained by means of the structural variations of the two MAHs. That is, at the drying temperature of 400 to 550 °C, either the decrease of spatial resistance to anions resulting from the incomplete loss of the laminates of the MAH or the memory effect originating from the complete loss of the laminates of the MAH leads to higher adsorption of model pitch and stickies, since the former can accommodate larger amounts of negatively charged pitch or stickies, while the latter can double its anionic charge demands. The formation of a new crystalline phase at a drying temperature higher than 550 °C may result in the reduction of attractive force of the MAH to the model pitch and stickies.

Comparing the adsorption isotherms of model pitch in Figs.1 and 3 with that of model stickies in Figs. 2 and 4, it is easily discovered that the two MAHs dried at different temperatures all showed higher adsorption capacities to model stickies than to model pitch. This may be explained by the differences of the charge density of the model pitch and stickies. The model stickies carried less negative charges than the model pitch, which would be expected to allow more model stickies to directly adsorb on positively charged MAH by charge neutralization.

It can also be found by comparing Fig. 1 with Fig. 3 and Fig. 2 with Fig. 4 that the MAH-NO₃ dried at low temperature had higher adsorption capacity to the model pitch and stickies than carbonate MAH dried at the same temperature. However, with the increase of drying temperature the differences of the adsorption capacity between MAH-NO₃ and MAH-CO₃ were diminished, implying that a loss of nitrate or carbonate results in the formation of the same magnesium aluminum oxide.

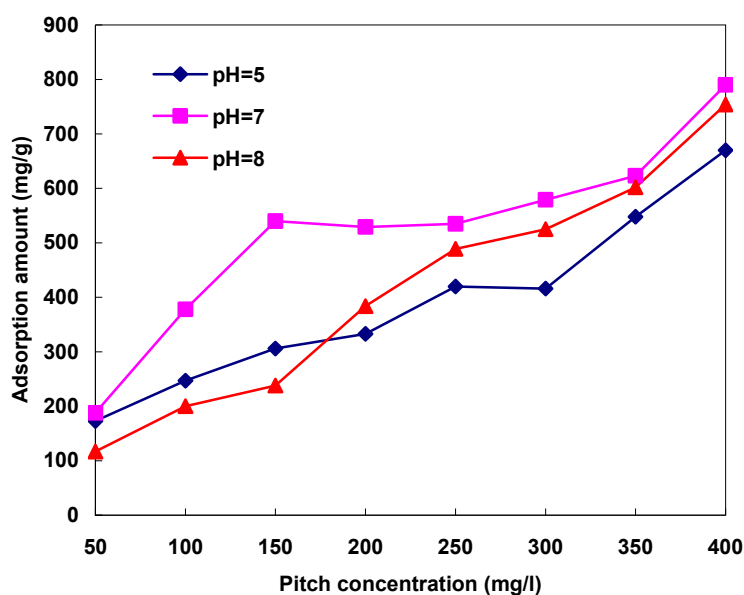


Fig. 5. Adsorption isotherms of model pitch with different pH on MAH-NO₃ dried at 500 °C

Since pH influences the dissociation of the hydrophilic groups of model pitch and stickies, it may affect the adsorption isotherms of model pitch and stickies on MAH. The adsorption isotherms of pitch and stickies with different pH on MAH-NO₃ are also plotted as shown in Figs. 5 and 6, respectively.

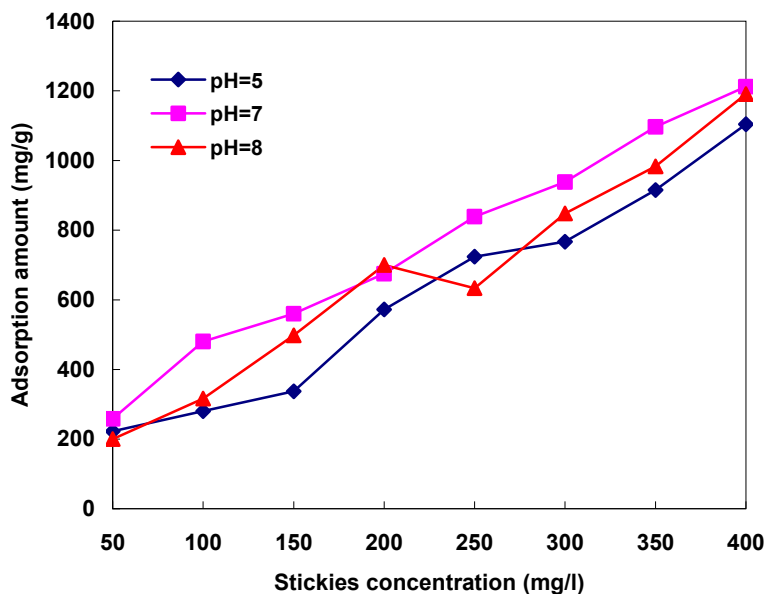


Fig. 6. Adsorption isotherms of model stickies with different pH on MAH-NO₃ dried at 500 °C

It can be seen from Figs. 5 and 6 that with the increase of the initial pH from 5 to 7 the adsorption capacities of model pitch and model stickies on MAH-NO₃ were increased at all the experimental concentrations of model pitch and stickies. However, when the dispersions of model pitch and stickies became alkaline at pH 8, the adsorption decreased. The reason is as follows: the MAH dried at 500 °C includes part of magnesium aluminum oxides, which will be partially dissolved under acidic conditions such as pH 5, resulting in the loss of adsorbent. On the other hand, while more acidic groups of model pitch and stickies dissociate at alkaline pH, the model pitch and stickies carry more negative charges, exhibiting higher charge demand relative to the positively charged MAH at pH 8 than that at pH 7.

MAH dried at high temperature has a certain buffering effect to an aqueous dispersion, since when the initial pH is low, the partial dissolution of the MAH consumes some of hydrogen ions. At the same time, the magnesium aluminum oxides in the MAH dried at high temperature adsorb the anions of pitch and restructure with water molecules, releasing hydrogen ions, which makes the equilibrium pH value relatively high and stable within a certain range. Therefore, as an adsorbent, MAH dried at high temperature can simplify the processes, reduce costs, and effectively control the pitch trouble with its pH-buffering effect (Li et al. 2007). The neutral and alkaline system in pulp and papermaking is more appropriate for the adsorption of pitch and stickies on MAH dried at high temperatures.

Fitting of Adsorption Isotherms

In order to clarify the adsorption characteristics of model pitch and stickies on MAH dried at high temperature, the Langmuir (Langmuir 1918), Freundlich (Freundlich 1907), and Dubinin-Radushkevich (Dubinin and Radushkevich 1947) isotherms were fitted to the adsorption data of model pitch and stickies on MAH-NO₃ dried at 500 °C. The pH of both the model pitch dispersion and the model stickies dispersion was 7.

The Langmuir isotherm assumes that metal ions are chemically adsorbed at a fixed number of well-defined sites; each site can hold only one ion; all sites are energetically equivalent; and there is no interaction between ions (Langmuir 1918).

The Langmuir isotherm represents the equilibrium distribution of adsorbate between the solid and liquid phases, and the linearized form can be used for linearization of experimental data by plotting C/q versus C , which is often expressed as:

$$C/q = 1/K_L q_m + C/q_m \quad (2)$$

In the adsorption of model pitch and stickies on MAH, C represents the equilibrium concentration of pitch or stickies in aqueous dispersion, mg/L; q is the adsorbed amount of pitch or stickies on unit mass of MAH at the equilibrium concentration C , mg/g; q_m is the maximum adsorption amount of monolayer of pitch or stickies on unit mass of MAH, mg / g; and K_L , with units of L/mg, is the Langmuir isotherm constant, which is related to the adsorption energy.

The Freundlich isotherm is regarded as empirical. Attempts have been made to obtain information about surface heterogeneity from the empirical Freundlich constants. It often describes the adsorption intensity of the adsorbent towards the adsorbate and is conveniently used in the linearized form by taking the logarithm of both sides as,

$$\log q = \log K_f + 1/n \log C \quad (3)$$

where K_f and n are the Freundlich isotherm empirical constants, which are related to the adsorption capacity and adsorption strength, respectively (Freundlich 1907).

The Dubinin-Radushkevich (D-R) isotherm was also selected to estimate the adsorption energy of model pitch and stickies on MAH dried at 500 °C, distinguishing between physical and chemical adsorption. The D-R isotherm equation has the following linearized form (Dubinin and Radushkevich 1947),

$$\ln q = \ln q_{mx} - \beta \varepsilon^2 \quad (4)$$

$$\varepsilon = RT \ln(1+1/C) \quad (5)$$

where q_{mx} is the maximum adsorbed amount of pitch or stickies on a unit mass of the MAH under optimum experimental conditions (mg/g); β is related to the free energy of adsorption per mole of the adsorbate as it migrates to the surface of the adsorbent from an infinite distance in the solution (mol²/kJ²); ε is the Polanyi potential, expressed as equation (5); R is the gas constant in kJ.K⁻¹.mol⁻¹; T is the absolute temperature in Kelvin, and C is the equilibrium concentration of pitch or stickies in dispersions.

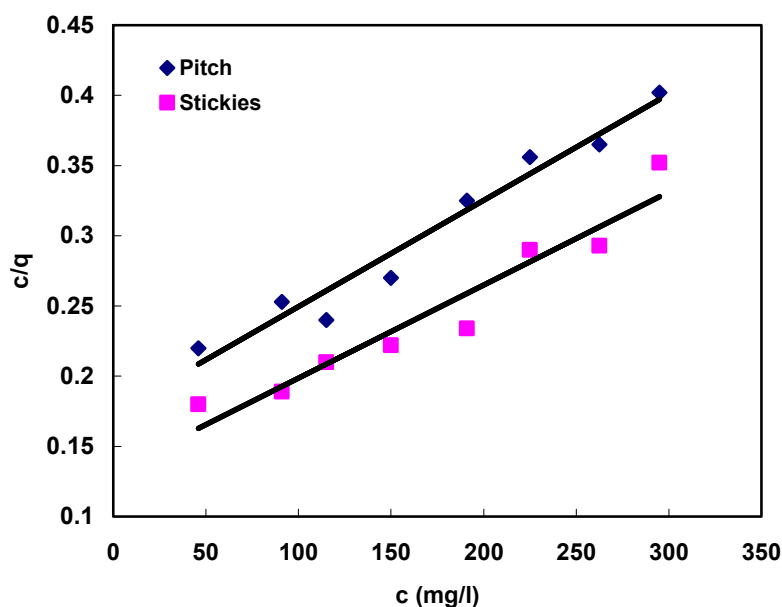


Fig. 7. Langmuir adsorption isotherm of model pitch and stickies on MAH-NO₃ dried at 500 °C

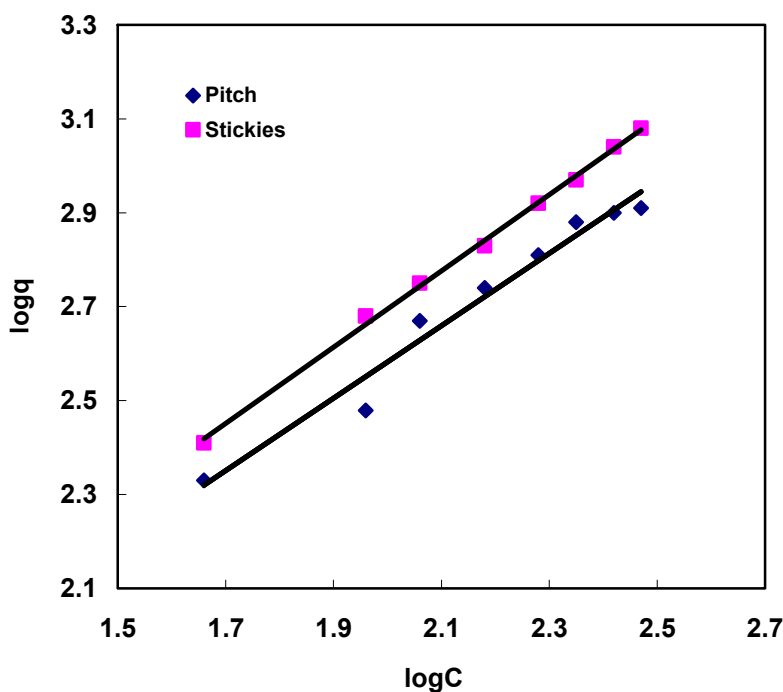


Fig. 8. Freundlich adsorption isotherm of model pitch and stickies on MAH-NO₃ dried at 500 °C

By linear plotting C/q versus C , $\log q$ versus $\log C$, as well as $\ln q$ versus ε^2 , the Langmuir, Freundlich, and D-R equations were fitted as shown in Figs. 7, 8, and 9, respectively. From the slopes and intercepts of the Langmuir, Freundlich, and D-R isotherms, the isotherm constants K_L , K_f , n , β , the Langmuir monolayer saturation

capacity q_m , and the D-R maximum adsorption capacity q_{mx} can be calculated and are presented in Table 1. The apparent adsorption energy E was calculated from β using Equation (6), and the results also are listed in Table 1.

$$E = \frac{1}{\sqrt{2\beta}} \quad (6)$$

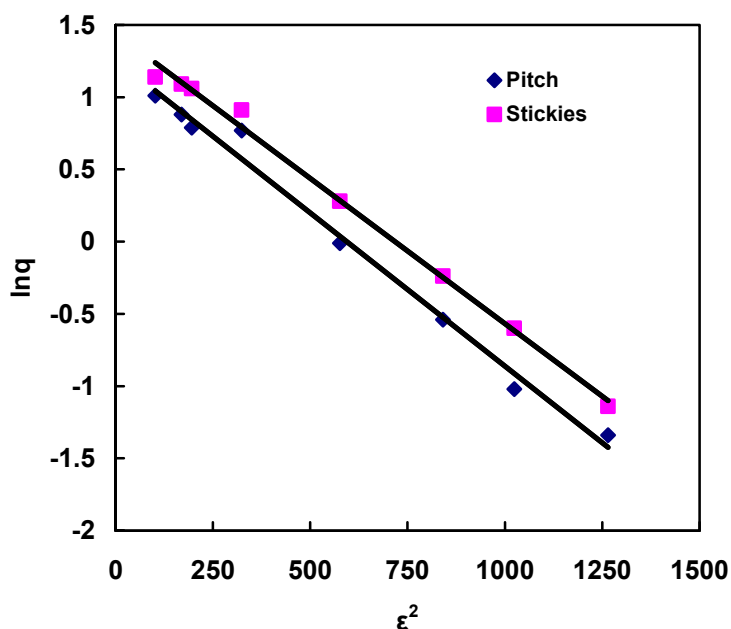


Fig. 9. D–R adsorption isotherm of model pitch and stickies on MAH dried at 500 °C

From the figures and the table it can be seen that the adsorption processes of both model pitch and model stickies on MAH-NO₃ dried at 500 °C were more in line with the Freundlich isotherm, where the correlation coefficients, R^2 , of model pitch and stickies were 0.970 and 0.998, respectively. Therefore, the pitch and stickies adsorptions on the MAH can be attributed mainly to surface adsorption. Since the slopes $1/n$ of the Freundlich adsorption isotherms of the model pitch and stickies were quite close to 1, the adsorbed pitch and stickies on unit mass of the MAH did not change significantly with equilibrium concentrations, revealing a high affinity between the pitch or stickies with the MAH at various equilibrium concentrations.

Table 1. Parameters of Langmuir, Freundlich, and Dubinin–Radushkevich Equations

Model	Langmuir			Freundlich			Dubinin–Radushkevich			
	q_m (mg.g ⁻¹)	K_L (l/mg)	R^2	n	K_f (mg.g ⁻¹)	R^2	q_{mx} (mg/g)	β (mol ² /kJ ²)	R^2	E (kJ/mol)
Pitch	1250.0	0.0046	0.961	1.30	10.94	0.970	1065.94	0.0021	0.989	15.38
Stickies	1428.6	0.0053	0.926	1.23	11.76	0.998	1280.26	0.0020	0.995	15.82

From Table 1 it can also be found that the maximum adsorption capacities of model pitch and stickies on MAH-NO₃ dried at 500 °C calculated by D-R isotherm were 1065.94 mg/g and 1280.26 mg/g, respectively, which are quite high, indicating that MAH dried at high temperature is an efficient adsorbent for the model pitch and stickies. The apparent adsorption energy of the model pitch and the model stickies on the MAH-NO₃ dried at 500 °C were 15.38 kJ·mol⁻¹ and 15.82 kJ·mol⁻¹, respectively. The value of apparent adsorption energy in the range of 1 to 8 kJ·mol⁻¹ and 8 to 16 kJ·mol⁻¹ predict physical adsorption and chemical adsorption, respectively (Helfferich 1962). The adsorption energy of both the model pitch and the model stickies on the MAH were in the range of 8 to 16 kJ·mol⁻¹, indicating a chemisorption or ion exchange. Hence, it is very likely that the model pitch and model stickies are adsorbed on MAH dried at high temperature, predominantly by chemical adsorption.

Characterization of High Temperature Treatment of Adsorbent

According to the above fitted results, the adsorption of model pitch on MAH dried at 500 °C may be due to chemical forces, such as ion-exchange, while MAH generally has a layered structure similar to hydrotalcite. High temperature treatment and the adsorption of negatively charged model pitch may bring some changes to the crystal structure of MAH, which can be characterized by XRD and HRTEM. The XRD patterns and HRTEM micrographs of MAH-NO₃ dried at 100 °C, MAH-NO₃ dried at 500 °C and MAH-NO₃ dried at 500 °C and adsorbed with model pitch are shown in Fig. 10.

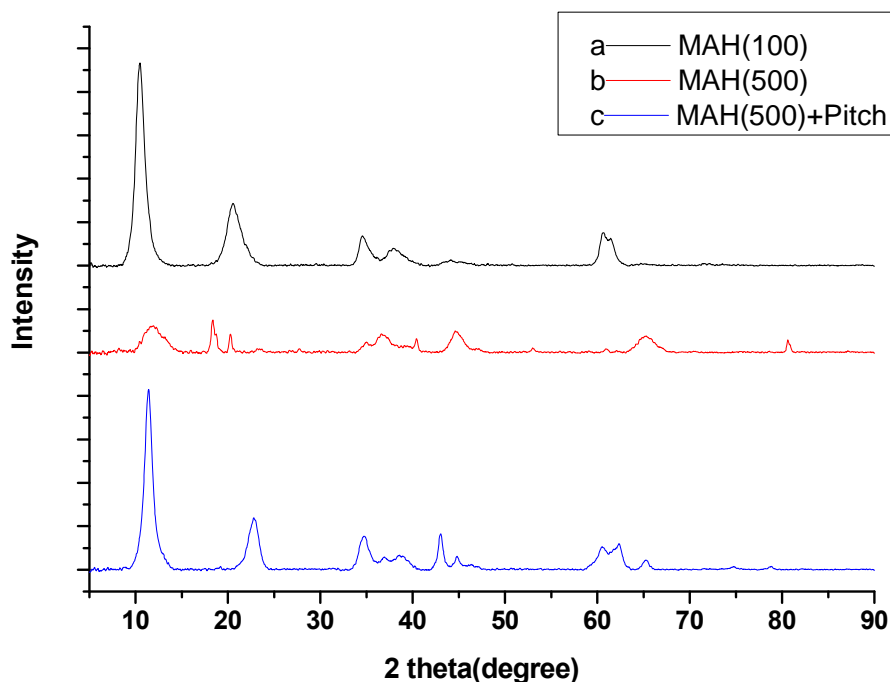


Fig. 10. XRD patterns of MAH-NO₃: (a) dried at 100 °C, (b) dried at 500 °C, (c) dried at 500 °C and adsorbed with model pitch

As shown in Fig.10, the XRD pattern of MAH-NO₃ dried at 100 °C had diffraction peaks at $2\theta = 11.59^\circ$, 23.34° , and 34.99° , corresponding to (003), (006), and (012) reflections, which are typical diffraction peaks of a layered hydrotalcite-like compound.

The diffraction peaks of (003) and (006) were sharp and symmetrical in comparison to the (012) peak, indicating that the MAH-NO₃ had a good crystallinity and high degree of orientational uniformity. These characteristics are in a good agreement with the results previously reported in the literature for well crystallized hydrotalcite-like structure with a Mg/Al molar ratio of 3:1 (Anbarasan et al. 2005).

For the XRD pattern of the MAH dried at 500 °C, one still could observe hydrotalcite's characteristic diffraction peaks of (003) and (006) reflections. However, the peaks were much weaker and broader, and the d_{003} spacing was reduced from 0.847 nm to 0.776 nm, suggesting that the layer structure of part of the MAH was collapsed and destroyed.

Furthermore, new diffraction peaks at (2θ) 44.60° and 65.26° attributable to metal oxide had appeared, which indicates that along with the structural collapse of the original mineral structure, MgO and Al₂O₃ mixed oxides were formed. After adsorbing model pitch, the XRD pattern of MAH dried at 500 °C showed sharp diffraction peaks of hydrotalcite-like compound again, indicating the recovery of the layered structure by re-hydration.

However, the diffraction peaks of MgO and Al₂O₃ mixed oxides still occurred in the pattern. Also, some new peaks appeared due to the adsorbed pitch. The value of d_{003} spacing was 0.751 nm, which is even smaller than that of the MAH dried at 100 °C, suggesting that it is the anions of external model pitch solution but not the model pitch itself that entered into the laminates, resulting in recovery of the layered structure. The decrease of peak intensity suggests that the degree of crystallinity of the sample declined and only parts of the layer structure was recovered.

From the HRTEM micrographs shown in Fig. 11, it can be further discovered that the MAH-NO₃ dried at 100 °C had a well-defined thin platelet morphology with plate diameter less than 50 nm.

By treating at 500 °C for 4 h, most of the platelets of the MAH became curled and collapsed, losing their laminate structure. The curled and collapsed platelets agglomerated together, forming an amorphous and porous structure. However, intact platelets of MAH still were present.

After being dispersed in a model pitch dispersion, the re-hydration of the high-temperature-treated MAH-NO₃ recovered most of the platelet structure and allowed adsorption of the model pitch on the platelet surface. Before carrying out the electron microscopy experiments, the investigated samples were air-dried and re-dispersed with alcohol, thus it is manifested that the pitch colloidal particles were homodispersed and uniformly adsorbed on the particle surface of the recovered MAH.

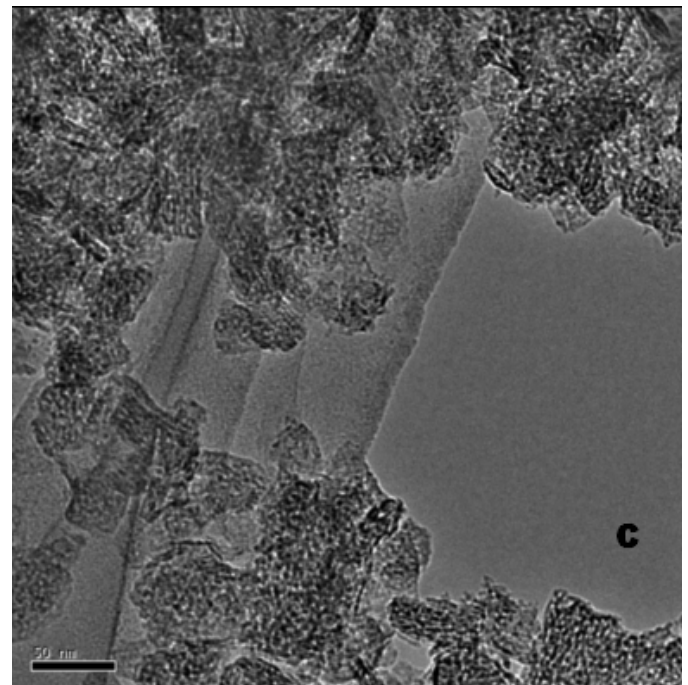
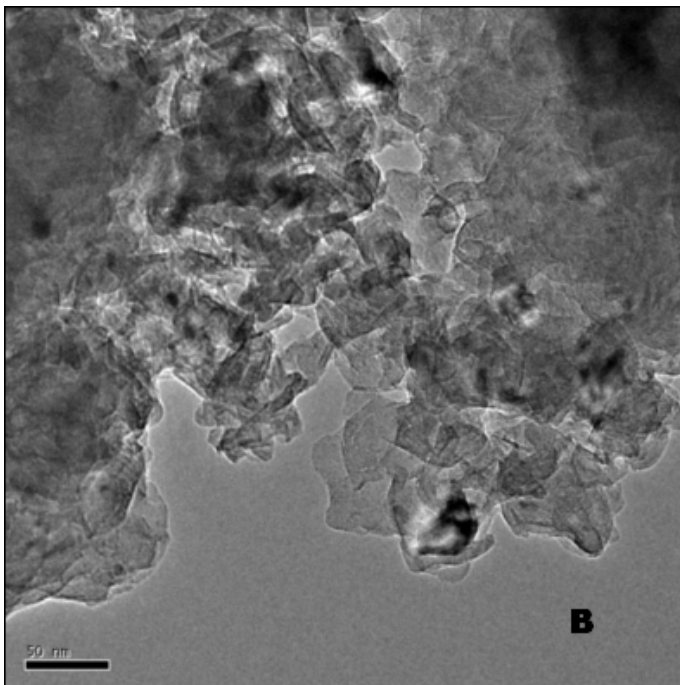
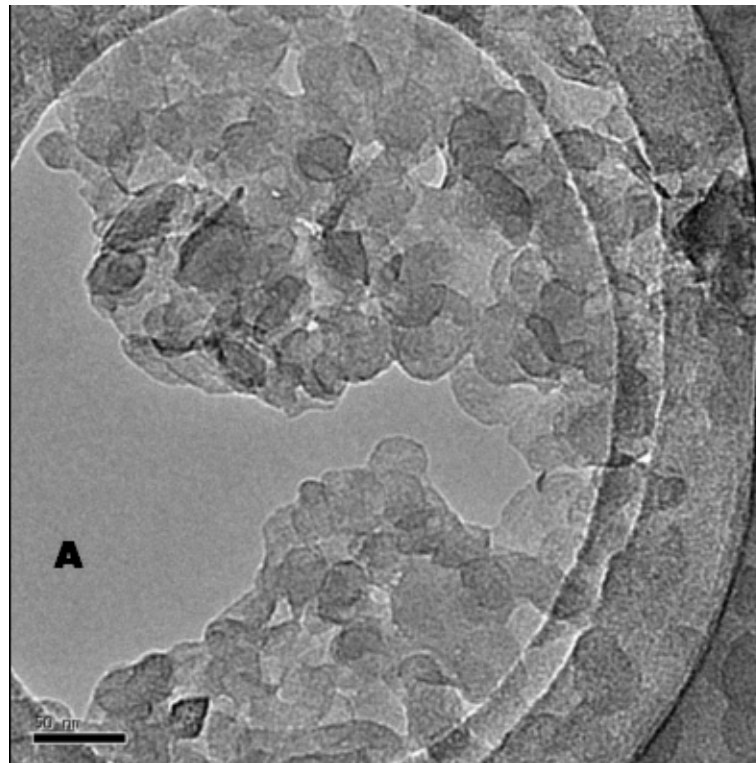


Fig. 11. HRTEM micrographs of MAH-NO₃: (a) dried at 100 °C, (b) dried at 500 °C, (c) dried at 500 °C and adsorbed with model pitch.

CONCLUSIONS

1. Magnesium aluminum hydroxides show high adsorption capacity to model pitch and stickies at neutral pH. Low temperature dried magnesium aluminum hydroxides of nitrate form have higher adsorption capacity to model pitch and model stickies than that of carbonate form. Increasing the drying temperature of magnesium aluminum hydroxides from 100 °C to 550 °C gradually improves their adsorption capacity to model pitch and stickies and reduces the difference of the adsorption capacity between the magnesium aluminum hydroxides of nitrate form vs. those of the carbonate form.
2. Magnesium aluminum hydroxides display higher adsorption capacities while lower initial adsorption rate to model stickies than to model pitch. The model pitch and stickies are adsorbed on magnesium aluminum hydroxides significantly by charge neutralization and distributed mainly on the surface of the platelets of magnesium aluminum hydroxides.
3. The experimental isothermal adsorption data of model pitch and stickies on magnesium aluminum hydroxides dried at 500 °C fit well to the Freundlich and Dubinin–Radushkevich isotherm models.

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REFERENCES CITED

- Alcy, D., Troy, W., and Przemyslaw, P. (2003). "Total approach to deposit control on newsprint machine using TMP and DIP pulp mix from specialized fixation of individual pulps to retention," *the 57th Appita Annual Conference and Exhibition*, 5-7.
- Allen, L. H. (1980). "Mechanisms and control of pitch deposition in newsprint mills," *Tappi J.* 63(2), 81-85.
- Allen, L. H., Cavanagh, W. A., Holton, J. E., and Williams, G. R. (1993). "New understanding of talc addition may help improve control of pitch," *Pulp Paper*, 67(13), 89-91.
- Anbarasan, R., Lee, W., and Im, S. (2005). "Adsorption and intercalation of anionic surfactants onto layered double hydroxides—XRD study," *Bull. Mater. Sci.* 28(2), 145-149.
- Derrick, A. P. (1994). "Method for controlling pitch," *US Patent* 5368692, Nov. 29.
- Dubinin, M. M., and Radushkevich, L.V. (1947). "Equation of the characteristic curve of activated charcoal," *Proc. Acad. Sci. U.S.S.R, Chem. Sect.* 55, 331-333.

- Erickson, K. L., Bostrom, T. E., and Frost, R. L. (2005). "A study of structural memory effects in synthetic hydrotalcites using environmental SEM," *Materials Letters*. 59(2-3), 226-229.
- Freundlich, H. (1907). "Ueber die Adsorption in Loesungen," *Z. Physic.Chem.* 57, 385-470.
- Gantenbein, D., Schölkopf, J., and Gane, P. A. C. (2008). "Process for the control of pitch", *WO. Patent* 1,138,39, Sept. 25.
- Glazer, J. A. (1991). "Overview of deposit control," *Tappi J.* 74(7), 72-74.
- Helfferrich, F. (1962). *Exchange*, McGraw-Hill, New York, 335-360.
- Hubbe, M. A., Rojas, O. J., and Venditti, R. A. (2006). "Control of tacky deposits on paper machines – A review," *Nordic Pulp Paper Res. J.* 21(2), 164-171.
- Lagaly, G., Mecking, O., and Penner, P. (2001). "Colloidal magnesium aluminum hydroxide and heterocoagulation with clay minerals. I Properties of colloidal magnesium aluminum hydroxide," *Colloid Polym. Sci.* 279, 1090-1096.
- Lamar, R. S., Pratt, W. E., Weber, K. E., and Roeder, R. E. (1990). "Method of reducing pitch in pulping and papermaking operations," *U.S. Patent* 4964955, Oct. 23.
- Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica and platinum," *J. Am. Chem. Soc.* 40(9), 1361-1403.
- Li, D., Wang, H., Wang, L., and Zhao, Z. (2007). "Removal of sulfate from aqueous solution by adsorption of it on layered double hydroxides," *Acta Miner. Sinica* 27(12), 109-114.
- Michalik, A., Serwicka, E.M., Bahranowski, K., Gawel, A., Tokarz, M., and Nilsson, J. (2008). "Mg,Al-hydrotalcite-like compounds as traps for contaminants of paper furnishes," *J. Appl. Clay Sci.* 39, 86-97.
- Ramos-Ramirez, E., Ortega, N. L. G., Soto, C. A. C., and Gutierrez, M. T. O. (2009). "Adsorption isotherm studies of chromium (VI) from aqueous solutions using sol-gel hydrotalcite-like compounds," *J. Hazard. Mater.* 172(2-3), 1527-1531.
- Rogan, K.R., and Adams, J. M. (1993). "Pitch control using clay coated with inorganic gel," *U.S. Patent* 5,221,436, Jun. 22.
- Shen, Z., Tang, X., Liu, C., and Xu, C. (2006). "Experimental study of treating anion dyestuff containing wastewater by calcined layered double hydroxides," *J. Environ. Sci. Technol.* 29(3), 89-91.
- Wågberg, L. (2000). "Polyelectrolyte adsorption onto cellulose fibers – A review," *Nordic Pulp Paper Res. J.* 15(5), 586-597.
- Zhang, K., Liu, W., and Chen, Z. (2006). "Preparation and characterization of hydrotalcite based cationic microparticulate retention aid," *Paper Chemicals* .18(2), 9-12.
- Zhao, L., Liu, W., and He, B. (2006). "Organic modification of mineral clay and improvement of its adsorption ability," *China Pulp Paper* 25(12), 15-18.

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