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Response Surface Methodology Study on Removal of Humic Acid from Aqueous Solutions Using Anionic Clay Hydrotalcite

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Abstract: Response Surface Methodology (RSM) was used in this study with the aim to evaluate the interactive effects and to obtain the optimum conditions for humic acid removal from aqueous solution using anionic clay hydrotalcite as an adsorbent. Response Surface Methodology (RSM) based on a five-level, four variable Central Composite Rotatable Design (CCRD) was used to evaluate the interactive effect of various parameters. The parameters were: time (2-6 h); temperature (30-70°C); amount of dosage (100-300 mg) and initial concentration of humic acid solution (50-100 mg L^{-1}). Batch adsorption was adopted in this study based on the experiments regarding to the Central Composite Rotatable Design (CCRD). Analysis of the data is based on three steps which are Analysis of Variance (ANOVA), regression analysis and the plotting of response surface. Simultaneously increasing adsorption time, temperature, adsorbent dose and initial concentration of humic acid increased the percentage of humic acid removal from aqueous solution. The optimum conditions derived via RSM for the removal of humic acid were adsorption time of 4.0 h, temperature 50°C, adsorbent dose of 200 mg and initial concentration of 75 mg L^{-1}. The actual experimental result for percentage removal of humic acid was 75.2% under optimum conditions, which compared well with the maximum predicted value of 73.46%.

Key words: Hydrotalcite, adsorption, adsorbent, humic acid, optimization, response surface methodology, central composite rotatable design

INTRODUCTION

The presence of humic acid has been a problem in the water industry and in environmental purification such as soil remediation. The presence of humic substances in natural waters can cause various environmental and health problems (Ibrahim *et al*., 2008). The contamination of humic substances has been known to induce a deterioration of adsorbents and a prevention of adsorption onto the adsorbents. As seen in the removal process of heavy metals contaminants in the soil remediation (Clapp *et al*., 1991) and the removal process of organic pollutants in drinking water treatment (Ellis and Korth, 1993), the humic substances often reduce the removal of the target substances through their adsorption onto adsorbents or formation of a complex with the target substances (Rav-Acha and Rebhun, 1992). The removal of the humic substances by conventional adsorbents is, however, difficult due to their water soluble formation and their wide range of distribution in molecular weight and size.

There are various methods of removing humic substances using conventional methods including coagulation and flocculation, oxidation or ozonation and membrane separation (Schulthess and Huang, 1991). However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and electrochemical oxidations and coagulation are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used and has proven successful in removing humic substances. The most common adsorbent materials are: zeolite, metal oxides and activated carbon. Activated carbon has been the most widely used adsorbent because of its high capacity for the adsorption of organics species (Juang *et al*., 1997). However, due to the difficulty and expense involved in regeneration, clays are being considered as alternative low cost adsorbents (Nassar and El-Geundi, 1991).

Hydrotalcite is a class of anionic clays with high anion exchange capacities, are effective adsorbents for removal of a variety of anionic pollutants (Amin and

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Jayson, 1996). The chemical composition of hydrotalcite can be described by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$ (1) where M^{2+} and M^{3+} are metal cations, for example Mg^{2+} and Al^{3+}, that occupy octahedral sites in the hydroxide layers, A^{n-} is an exchangeable anion and x is the ratio $M^{3+}/(M^{2+}+M^{3+})$. Carbonates are the interlayer anions in the naturally occurring mineral hydroxides, which is a member of this class of materials (Cavani *et al*., 1991). It is known that many substances in wastewater, such as humic substances, dye in the effluents carry negative charges. Species that carry negative charges account for a large part of water in the water systems. The hydrotalcite's anion exchange ability, large surface area and regeneration ability ensures that this adsorbent can be effectively utilized in wastewater purification (Vaccari, 1999).

Response Surface Methodology (RSM) is an effective statistical technique for the investigation of optimization process. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing the processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions (Ravikumar *et al*., 2007). The main objective of RSM is to determine the optimum operational conditions of the process or to determine a region that satisfies the operating specifications (Myers and Montgomery, 2001). The application of statistical experimental design in adsorption process can result in improved product yields, reduced process variability and reduced the time and overall costs than the classical method (Ravikumar *et al*., 2005). This methodology is widely used in chemical engineering, notably to optimize the adsorption process (Ricou-Hoeffer *et al*., 2001).

RSM comprising a five level-four-factor Central Composite Rotatable Design (CCRD) was used in our work to evaluate the interactive effects and to obtain the optimum conditions for humic acid removal from aqueous solution using anion clay hydrotalcite as an adsorbent.

MATERIALS AND METHODS

Preparation and characterization of hydrotalcite: The work reported in this study was conducted between February 2009 and December 2009. All chemicals and reagents used in this study were of high purity and were used without further purification. Hydrotalcite was prepared in our laboratory from magnesium sulphate hydrate $[Al_2(SO_4)_3.16H_2O]$, aluminium sulphate hydrate $[Mg(SO_4).7H_2O]$ and sodium carbonate at moderate conditions following Reichle's procedures (Reichle, 1985). X-ray diffraction (XRD) pattern of the sample powder was recorded on a Siemen diffractometer D500 with Ni filtered, CuKα radiation at 40 Kv and 20 mA. The sample was mounted on a glass slides and scans at 2°-65° 2θ min^{-1} at 0.003° steps. The basal spacing was determined via powder technique.

Experimental design: A five-level-four-factor CCRD was employed in this study, requiring 21 experiments (Cohran and Cox, 2002). The fractional factorial design consisted of 8 factorial points, 8 axial points and 5 center points. The variable and their levels selected for the removal of humic acid were: time (2-6 h); temperature (30-70°C); amount of dosage (100-300 mg) and initial concentration of humic acid solution (50-100 mg L^{-1}). The data obtained were fitted to second order polynomial equation:

$$Y = \beta_0+\sum 4\beta_i x_i + \sum 4\beta_{ii}x_i^{2} + \sum 3 \sum 4\ \beta_{ij}x_{ij} \quad (1)$$

where, Y is percentage of humic acid removal; β_0, $\beta_i^{i=1,}$ $\beta_{ii}^{j=i}$, β_{ij}^{+1} are constant coefficients and x_i the uncoded independent variables.

Batch adsorption and analysis: Humic acid purchased from Merck was used for the adsorption experiment. Stock solutions of humic acid were prepared in deionized water and were diluted according to the working concentration. Humic acid concentration was measured using Lambda 20 UV-visible spectrophotometer. 0.25 g of synthesized compounds was put into 25 mL of 50-100 mg L^{-1} solutions of the humic acid solutions. Twenty five milliliters of humic acid solution in 250 mL conical flask was contacted with 0.25 g hydrotalcite and was agitated using water batch shaker operating at 120 rpm. Experiments were performed according to the Central Composite Rotatable Design (CCRD) as given in Table 1. The response was expressed as percentage of humic acid removal, calculated as:

$$\frac{C_0-C_t}{C_0}\times 100$$

Data analysis: The data from the experiments performed are analyzed using design expert 6.06 version and then interpreted. Three main analytical steps; Analysis of Variance (ANOVA), a regression analysis and the plotting of response surface were performed to establish an optimum condition for the removal of humic acid.

RESULTS AND DISCUSSION

Characterization of hydrotalcite: The XRD pattern of original hydrotalcite synthesized at different ratio are presented in Fig. 1 and show original hydrotalcite indicate fairly good crystallinity, with d-spacing 7.9Å which is demonstrated general features of hydrotalcite (Ibrahim and Lwin, 2010). The d-spacing show the characteristic values for trigonal structures with symmetrical peaks assigned to the (003) and (006) planes, respectively. The interlayer spacing of the sample corresponding to the 006 plane was found to be 4.5 Å. The result is similar to the study reported previously, in which the XRD pattern of this white powder corresponds to that of hydrotalcite; the peaks are sharp signifying high crystallinity (Hussein *et al*., 1996). Hydrotalcite at ratio 4 (Mg/Al) was subsequently used as adsorbent for removal of humic acid in this study.

Model fitting and ANOVA: Experimental data for removal of humic acid using anion clay hydrotalcite are given in Table 1, the predicted values were obtained from model fitting technique using the software design expert version 6.06 and were seen to be sufficiently correlated to the observed values. Fitting of the data to various models (linear, two factorial, quadratic and cubic) and their subsequent ANOVA showed that removal of humic acid from aqueous solution using hydrotalcite were mostly suited with quadratic polynomial model. From the design expert, the quadratic polynomial model is given below:

$$\text{Removal (\%)} = 73.46 + 17.24\,A + 19.32\,B + 2.39\,C + 13.08\,D - 7.64\,A^2 - 8.17\,B^2 - 1.98\,C^2 - 4.81\,D^2 \qquad (2)$$

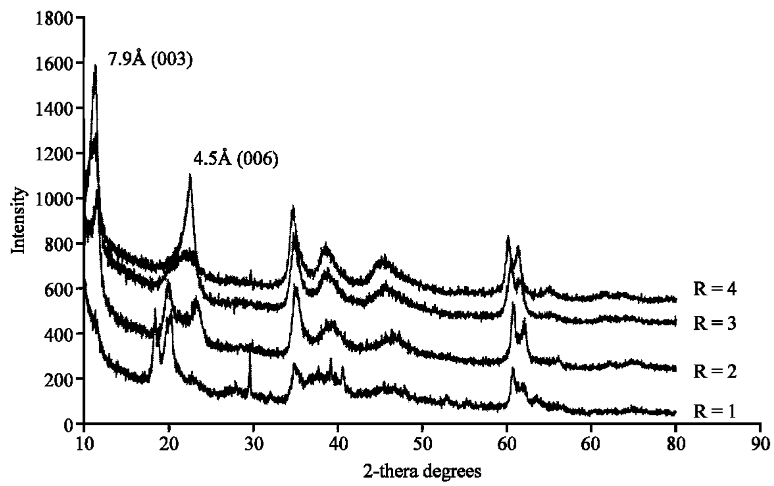

Fig. 1: XRD pattern of synthesized hydrotalcite

Table 1: Central composite rotatable quadratic polynomial model, experimental data, actual and predicted values for five-level-four factor response surface analysis

Treatment	Time (h)	Concentration (mg L^{-1})	Temperature (°C)	Dosage (mg)	Actual removal (%)	Predicted removal (%)
1	4.00	75.00	50.0	200.0	70	70.50
2	6.00	50.00	30.0	300.0	70	65.47
3	6.00	50.00	70.0	300.0	35	35.50
4	4.00	32.96	50.0	200.0	78	73.47
5	4.00	75.00	50.0	200.0	35	30.47
6	4.00	75.00	50.0	200.0	27	27.50
7	2.00	100.00	70.0	300.0	79	79.50
8	2.00	50.00	70.0	100.0	29	24.47
9	4.00	75.00	50.0	200.0	20	22.85
10	2.00	100.00	30.0	300.0	78	80.85
11	6.00	100.00	70.0	100.0	15	17.85
12	4.00	75.00	83.64	200.0	80	82.85
13	4.00	75.00	16.36	200.0	55	63.83
14	4.00	75.00	50.0	368.18	75	71.87
15	2.00	50.00	30.0	100.0	35	37.85
16	7.36	75.00	50.0	200.0	79	81.85
17	4.00	75.00	50.0	31.82	75	73.46
18	6.00	100.00	30.0	100.0	75	73.46
19	4.00	117.04	50.0	200.0	75	73.46
20	4.00	75.00	50.0	200.0	75	73.46
21	0.64	75	50.0	200.0	74	73.46

Table 2: ANOVA for joint test

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob>F
Model	10604.23	14	757.45	19.80	0.0007
Time (A)	1682.0	1	1682.0	43.96	0.0006
Concentration (B)	2112.50	1	2112.50	55.21	0.0003
Temperature (C)	77.99	1	77.99	2.04	0.2033
Dosage (D)	968.0	1	968.0	25.30	0.0024
A^2	872.30	1	872.30	22.80	0.0031
B^2	997.61	1	997.61	26.07	0.0022
C^2	58.78	1	58.78	1.54	0.2615
D^2	345.99	1	345.99	9.04	0.0238
AB	280.86	1	280.86	7.34	0.0351
AC	0.13	1	0.13	0.00033	0.9563
AD	13.93	1	13.93	0.36	0.5683
BC	1.13	1	1.13	0.029	0.8695
BD	1028.61	1	1028.61	26.88	0.0020
CD	1.13	1	1.13	0.029	0.8695
Residual	229.57	6	38.26		
Lack of fit	228.77	2	114.39	571.94	<0.0001
Pure error	0.80	4	0.20		
Cor total	10833.81	20			

Significant at Prob>F less than 0.05, insignificant at Prob>F more than 0.05

where, A is the time; B the concentration; C the temperature and D is the amount of adsorbent dosage.

The computed model F-value of 19.80 was higher than tabular value of F = 12.97, implying the model are significant at 1% confidence level. The model also showed a very low value of pure error of 0.8 which indicate good reproducibility of the data obtained. The high coefficient of determination (R^2 = 0.9788) and a very small p-value (0.0001) from the analysis of ANOVA showed that, quadratic polynomial was highly significant and sufficient to represent the actual relationship between the response (%removal) and the significant variables. From Table 2, the variables of time, concentration and dosage of hydrotalcite are the most significant in adsorption of humic acid from aqueous solution using hydrotalcite. This result indicated that time, concentration and dosage of hydrotalcite were the important variables.

Response surface plots: The quadratic polynomial equation was then used to facilitate plotting of response surfaces. Two parameters were plotted at any one time on the x_1 and x_2 axes, respectively, with the other two remaining parameters set at their centre points values (coded level:0). Figure 2 shows the profile of time and initial concentration of humic acid solution on the removal of humic acid using anionic clay hydrotalcite. As expected, increase in both time and initial concentration of humic acid solution will increase in percentage removal of humic acid from aqueous solution. This indicates that higher the contact time between humic acid and hydrotalcite, higher the removal efficiency till the equilibrium time is reached. The same trend of adsorption was reported (Ravikumar *et al*., 2005) for dyes removal on novel adsorbent. As shown in the Fig. 2, humic acid removal is increasing with increasing humic acid concentration. The adsorption is fast at early stages and will approach equilibrium after 4 h. The same trend of adsorption was reported (Wang *et al*., 2008) in the removal of humic acid using fly ash. Adsorption with high concentration of humic acid and longer contact time between humic acid and hydrotalcite favored maximal percentage removal of humic acid (Wang *et al*., 2008).

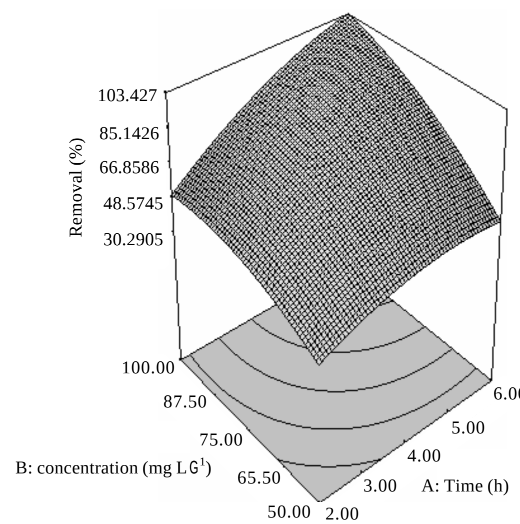

Fig. 2: Response surface plot showing the effect of time and concentration and their mutual effect on removal of humic acid using anionic clay hydrotalcite

Response surface predicted for interaction of time and temperature of adsorption is illustrated in Fig. 3. The effects of temperature can be appointed to its effects on adsorbate solubility as well as its direct influences on the

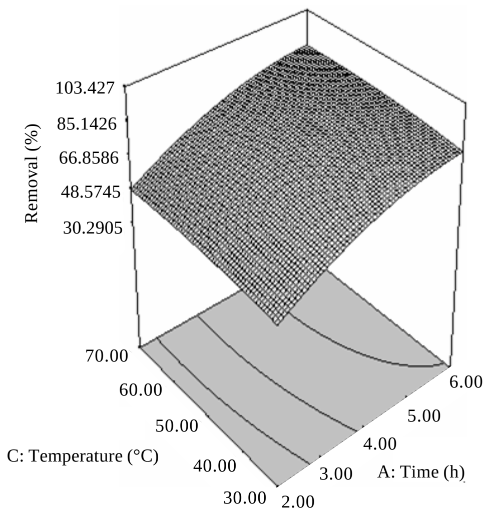

Fig. 3: Response surface plot showing the effect of time and temperature and their mutual effect on removal of humic acid using anionic clay hydrotalcite

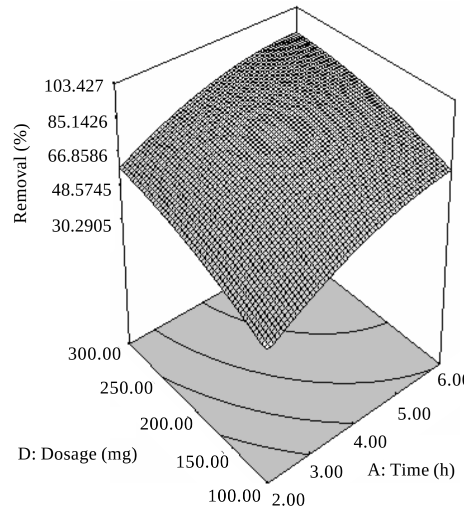

Fig. 4: Response surface plot showing the effect of time and dosage and their mutual effect on removal of humic acid using anionic clay hydrotalcite

adsorption using hydrotalcite. On increasing reaction temperature, adsorbate solubility is improved reducing mass transfer limitations and making the adsorbate more available to the hydrotalcite (Zakaria *et al*., 2007). Higher reaction temperatures also promote collisions between molecules to result in accelerated rates of reaction. As shown in the Fig. 3, adsorption with highest temperature and highest contact time favored maximal percentage adsorption. The results are in contrast with the study reported by some authors in the adsorption of different types of dyes and other organic compounds over several adsorbents (Mckay *et al*., 1983; Asfour *et al*., 1985). The increase of efficiency in humic acid removal with the increase of the temperature suggested that anion-exchange mechanism may occur during the adsorption (Vreysen and Maes, 2008).

Figure 4 depicts the response surface plot showing the effect of time and amount of adsorbent dosage on the removal of humic acid using hydrotalcite. As shown in Fig. 3, at any given amount of adsorbent dosage from 100 to 300 mg and increased in contact time of adsorbent and humic acid solution led to higher percentage of removal. As expected, adsorption rate increase with increase in adsorbent dosage. This is due to the fact that, increase in adsorbent dosage increase area available for adsorption. The result is similar to the study reported previously, in which the percentage removal of humic acid increased with increased in adsorbent dosage (Zakaria *et al*., 2007). Figure 5 and 6 depict the response surface plots as a function of concentration versus temperature and concentration versus amount of adsorbent dosage respectively. As expected, adsorption with highest concentration of humic acid and highest temperature favored maximum percentage of adsorption.

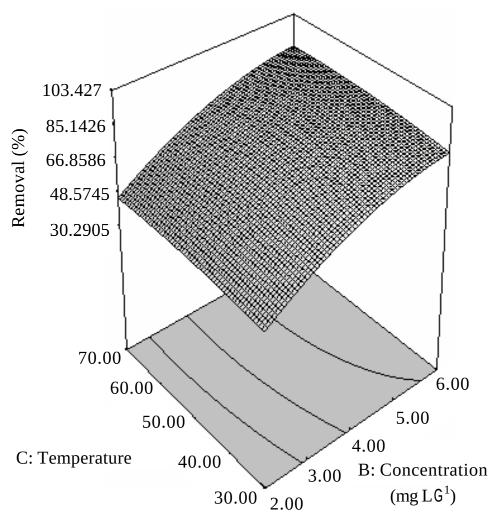

Fig. 5: Response surface plot showing the effect of concentration and temperature and their mutual effect on removal of humic acid using anionic clay hydrotalcite

Table 3: Solutions of optimum conditions

Experiment	Time (h)	Concentration (mg L^{-1})	Temperature (°C)	Dosage (mg)	Actual removal (%)	Predicted removal (%)
1	4.00	75	50	200	75.20	73.46
2	2.00	50	30	100	63.25	66.98
3	6.00	100	70	300	82.40	79.94

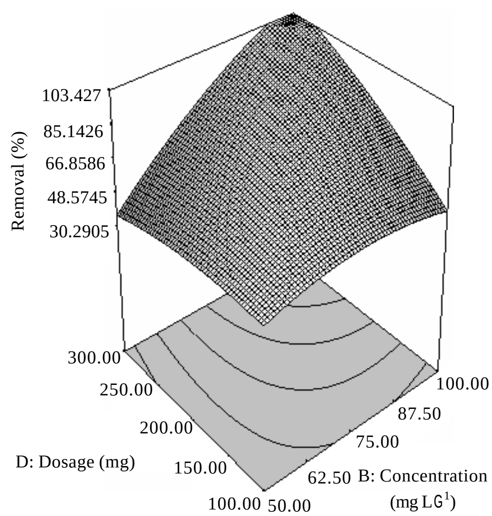

Fig. 6: Response surface plot showing the effect of concentration and dosage and their mutual effect on removal of humic acid using anionic clay hydrotalcite

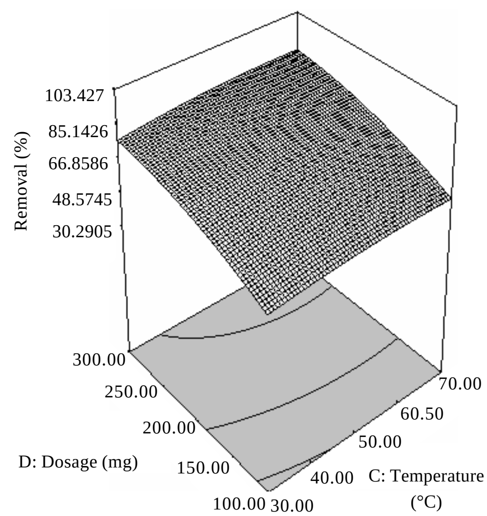

Fig. 7: Response surface plot showing the effect of temperature and dosage and their mutual effect on removal of humic acid using anionic clay hydrotalcite

Figure 6 represents the effect of varying concentration and amount of dosage of hydrotalcite. At low amount of dosage and low concentration of humic acid, the percentage removal of humic acid was lower. High percentage of removal was recorded when high amount of hydrotalcite and high concentration of humic acid were used. Presence of larger amount of adsorbate generally increases the availability of adsorbate to adsorbent. This relationship holds when there are no limiting factors such as presence of activators or inhibitors or mass transfer effect. Figure 7 represents the effect of varying the temperature and the amount of dosage of hydrotalcite. As shown in Fig. 7, percentage removal increased with increasing temperature and amount of dosage. It may be noted that, at low amount of dosage and temperature, the percentage removal of humic acid was lower.

Optimization of adsorption: Within the experimental range studied, optimum conditions for removal of humic acid using anionic clay hydrotalcite were predicted using the optimization function of the Design Expert. These are presented in Table 3 along with their predicted and actual values. The analysis indicated that maximum percentage removal of humic acid was at adsorption time of 4.0 h, temperature 50°C, adsorbent dose of 200 mg and initial concentration of 75 ppm. The response behavior of time and initial concentration of humic acid (Fig. 3) were followed while holding the other reaction parameter constant at suggested point. Therefore the reaction conditions (adsorption time 4.0 h, temperature 50°C, adsorbent dose 200 mg and initial concentration 75 ppm) were recommended as optimal for removal of humic acid using anionic clay hydrotalcite. Comparison of predicted and experimental values revealed good correspondence between them, implying that empirical models derived from the RSM could be used to adequately describe the relationship between the factors and response in removal of humic acid using anionic clay hydrotalcite.

CONCLUSION

The adequacy of the predicted model was examined by additional independent experiments under the suggested optimal removal conditions. From the data obtained, the observed values were statistically near the predicted values and the generated model adequately predicted the percentage removal. Thus, the removal of humic acid using anionic clay Hydrotalcite was successfully developed by fractional factorial design of RSM.

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