

Removal of Phenol Pollutants by Modification Molecular Sieves 13X

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Abstract

Molecular sieves type 13X was modified by treatment with saturated solution of urea or thiourea and adding of sodium silicate as binder to give homogeneous admixture in approximate weight percent, 20% urea or thiourea, 30% binder, and 50% MS13X. The samples were dried and shaped in cylindrical particles of about 5mm diameter and 4-8mm length. The FTIR studies show some interaction between the added urea and thiourea with the original substrates. These are mainly hydrogen band type interactions through $-NH_2$ moiety with $-OH$ group of framework oxygen in the substrate or with adsorbed water. The urea displayed more significant interaction with MS13X than thiourea. Molecular sieve 13X and its admixtures with urea and thiourea showed good ability to remove phenol from water. The urea modified sample, which has the largest surface area, was the best adsorbent for phenol followed by thiourea treated sample. Excellent degree of phenol removal, greater than 98% was achieved by using 0.2 l/h flow rate of 10ppm phenolic solution and 56cm bed length at $30^\circ C$. The increasing of inlet phenol concentration in water affected largely the driving force and the rate of adsorption, resulted also in higher capacities. While the percentage removal of phenol was decreased by fixed other operating conditions.

Keywords: Molecular Sieves, Urea, Thiourea, Phenol Pollutant, Adsorption

أزالة ملوثات الفينول بتطوير المناخل الجزيئية 13X

الخلاصة

المناخل الجزيئية نوع 13X طورت بمعالجتها مع محلول مشبع من اليوريا والثايوريوريا، ثم إضافة سليكات الصوديوم كمادة رابطة، يتكون خليط متجانس بالنسب الوزنية، 50% مناخل جزيئية، 30% مادة رابطة، 20% مادة التحوير، يوريا أو ثايوريوريا. تم تشكيل النماذج على شكل اسطواني بقطر 5ملم و 4-8mm طول. ان تحاليل مطياف الأشعة تحت الحمراء بينت حصول تأثيرات ملحوظة لليوريا والثايوريوريا المضافة للمادة الاساس. انعكس ذلك بصورة رئيسية باتجاه ربط الهيدروجين في المادة المعززة من خلال مجاميع $-NH_2$ مع مجاميع $-OH$ لتركيب الاوكسجين في المناخل الجزيئية او من خلال الماء الممتاز. لوحظ ان اليوريا ادت الى تأثير اكثر مع المناخل الجزيئية مقارنة بالثايوريوريا. تتمتع المناخل الجزيئية نوع 13X وتحويراتها مع اليوريا والثايوريوريا بقابلية جيدة لامتزاز الفينول من الماء. حيث تعد النماذج المحسنة باليوريا والتي تتمتع بدورها باكبر مساحة سطحية، افضل النماذج امتزاز للفينول يليها تلك المعاملة بالثايوريوريا. تم تحقيق ازالة عالية للفينول اكثر من 98% باستخدام 0.2 لتر/ساعة سرعة جريان المحلول الحاوي على 10 جزء بالمليون فينول و 56 سم طول وسط الامتزاز عند $30^\circ C$ مضمن التجارب المستخدمة في البحث. يؤثر زيادة تركيز الفينول في الماء بشدة على القوة الدافعة وبالتالي على سرعة الامتزاز وتعطي ايضا سعة اكبر. بينما تنخفض نسبة الازالة للفينول عند ثبوت ظروف التشغيل الاخرى.

Introduction

The pollution of natural water resources supplied by phenolic-bearing waters is becoming an increasing serious problem in recent years.

Phenols are present in waste water from agricultural sources, oil refineries coke and phenol resins plants (1,2). It has been reported that concentration of phenols in unpolluted water are usually less than 0.02mg.L^{-1} (3).

However WHO's Guidelines for drinking water quality gives the level of phenols as 0.001mg.L^{-1} (4).

Phenols pollutants can be removed either chemically, such as by precipitation by calcium hydroxide (1) or by adsorption on zeolites (2,3). Molecular sieves are porous crystalline aluminosilicates having a large number of smaller cavities, which may be interconnected by smaller channels or pores. The dimensions of these pores are such that they accept for adsorption of molecules of certain dimensions.

The ability of molecular sieves to adsorb water and various hydrocarbons and polar compounds is well recognized (5).

Molecular sieve type X is a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio which has a greater ability to accept molecules such as organic phenolic pollutants into their internal structure (6). It is required to enhance the adsorption capabilities of molecular sieves by the use of strong adduct forming molecules.

Urea and thiourea with their strong affinity toward phenolics are best fitted for that purpose. But due to their water solubility, they need to be supported by a suitable matrix such as zeolites (2).

The purpose of this article is to enhance the adsorption ability of

MS13X toward phenol by its modification with strong adduct forming molecules, such as urea and thiourea.

This includes preparation, characterization and adsorptive properties of the modified adsorbents.

Experiment

Molecular sieve 13X for modification was dried at 120°C , crushed and sieved to get powder of particles less than 45 micrometer. Saturated solution of urea or thiourea was prepared by dissolving of 50 g of each in 70 ml distilled water.

The required amount of pulverized MS13X and sodium silicate as binder were added to the solution at room temperature.

The mixture was mixed manually to get homogenous slurry. The admixture was shaped into cylindrical parts of 5 mm diameter and 4-8 mm length by meet machine.

The pellets were dried at room temperature and then at 120°C for two hours. The final proportion of samples was as follows, 50% MS13X, 20% urea or thiourea and 30% sodium silicate as binder.

The crystallinity of the original and modified molecular sieve 13X was determined by means of X-Ray diffraction, type 1390 Philips. While the bands and structure of adsorbents were determined by IR, type schimadzu 8400 S.

The were conducted by adsorption of N_2 using Carlo-Erba sorptomatic.

The adsorption of phenol pollutants was performed in a conventional continuous flow packed bed, as shown in figure 1. The 1.5 cm ID and 8 cm length column was insulated by fiber glass.

Aqueous solution of 10 ppm phenol was pumped at constant flow

rate for 2 hr. Samples of effluent were taken every 30 min for analysis.

High performance liquid chromatography (HPLC), type SHIMADZU LC_4A was used to determine the content of phenol in aqueous solutions using UV-Spectroscopy.

Results and Discussion Characterization

The XRD patterns of MS13X and its admixture with urea and thiourea showed the same position for the standard peaks of high intensities.

The main changes in urea and thiourea admixtures is the great difference in the intensity of crystalline level 6.2 (14.255 °A) and the appearance of some new peaks at different levels.

Thus indicate that the interance of urea and thiourea molecules in the crystalline level formation resulted in C=O and C=S respectively alumina hydroxyl and silica hydroxyl groups (2).

The infrared spectroscopy lattice vibration spectra in the 450-4000 cm^{-1} of original and modified samples show the bands resulting from a typical siliceous material, with a main band at around 980 cm^{-1} due to a symmetric Si-O-Si stretching mode (7).

The symmetric vibration of (-NH₂) which appeared at 3344 cm^{-1} in urea has no corresponding observed band in MS_U, but in MS_T.

The similar vibration, which appeared at 3270 cm^{-1} in thiourea, seems to have shifted to 3250 cm^{-1} . Interestingly the bonded (-NH₂) which give a band at 3259 cm^{-1} in urea has suffered a significant shift to 3100 cm^{-1} in MS_U, no similar band was observed in MS_T.

The characteristic MS13X bands in the region 1250 to 450 cm^{-1} seem to have hardly been affected by the presence of urea and thiourea.

Thus the very strong vibration Si-O-Si(Al) band at 978 cm^{-1} in the original MS13X appeared at almost shift to 990 cm^{-1} in MS_U, and to 985 cm^{-1} in MS_T. Taken together with the observed shifts in (-NH₂) vibration, it seems that the interaction among urea and thiourea molecules and with the matrix is mainly through (-NH₂) moiety (2).

The results of surface area measurements for MS13X and its admixtures with urea and thiourea are summarized in table.1.

An expansion in the estimated surface area for the modified sample were observed urea admixture has the largest surface area, of about 750 cm^2/g followed by MS_T of about 675 cm^2/g , compared with 600 cm^2/g for untreated MS13X.

Adsorption of Phenol

Experiments were carried out to investigate the possible use of molecular sieve 13X for the removal of phenol traces from aqueous solutions.

Modifying of molecular sieve with urea and thiourea was done, to study their ability to remove of phenol pollutant, and possible enhancement of adsorption capacity of MS13X.

The experiments were done continuously using fixed bed adsorbents to evaluate the effect of flow rate, bed length, inlet concentration and temperature on adsorption performance of phenol from water.

The breakthrough curves for phenol adsorption, as in figure 2 show a gradual increase of phenol

concentration in effluent with time toward initial concentration (10 ppm).

This observation indicates that the adsorption rate decreases with time increases, due to gradually saturation of adsorbent with operating time. Furthermore, the time dependence adsorption experiments indicated that MS13X- Urea admixture, which displayed the largest surface area, showed the greatest ability to remove phenol pollutant from water followed by thiourea admixture.

Furthermore, a gradual increase of accumulative phenol adsorption with increasing contact time was observed, noticeably for modified adsorbents, as shown figure 3.

The adsorbent useful capacity is usually fixed by the actual amount available to hold phenol and its required outlet concentration.

Two bed lengths were chosen to investigate the effect of adsorbent amount on removal of minor amount of phenol. Those were 30 cm and 56 cm. the results are given in table 2 at a solution flow rate of 0.2 l/h for the three adsorbents.

Furthermore, the effect of bed length on adsorption ability of admixture with urea is illustrated in figure 4 at different contact time.

The results show, that the amount of phenol adsorbed from water increases with increase of bed length, due to increase the actual amount of surface available to hold phenol.

Figure 4 indicates clearly, that about a complete removal of phenol pollutant is achieved by using 56 cm bed length of urea modified sample at the mentioned conditions.

This indicate that the amount of adsorbent has a predominate roll on removal of phenol from aqueous media (8).

The effect of solution flow rate on adsorption efficiency if the considered adsorbents is given in table 2 as comparison by using a low flow rate, 0.2 l/h and a high flow rate, 1.0 l/h at constant other conditions.

It is noticed that the removal of phenol from aqueous solutions decreases as flow rate increases, as its expected (8). This could be attributed to the fact that the low flow rate increases the contact time of phenol within the bed, leading to more adsorption affinity than high flow rates.

This effect is clearly demonstrated for urea modified adsorbent in figure 5 as an example. The results show that at flow rate 0.2 l/h, the outlet aqueous solution contains less than 0.2 ppm phenol, while it is about 2 ppm at 1.0 l/h, both are for the first sample collection at 30 min.

Experiments were conducted to investigate the inlet concentration dependent on removal of phenol by adsorption.

The remaining concentration of phenol in effluent should give an indication about the adsorption ability of adsorbents toward phenol, as shown in figure 6.

From this figure, it can be noticed a progressive increase of phenol quantity in outlet, as the inlet concentration increases for all adsorbent.

Furthermore, table 3 shows that the phenol adsorbed from water increase with increase of inlet concentration. This may be attributed to the fact that the driving force is affected noticeably the adsorption rate at the increasing of phenol in the inlet solutions (8).

It must also be observed that high removal of phenol for high inlet concentrations required more amount

of adsorbent (higher bed length) or low flow rates.

Figure 7 shows the effect of temperature on adsorption ability of phenol for all studied adsorbents. Three temperatures were chosen for this purpose, 303, 313, and 323°K.

Temperature increases leads in a noticeable decrease in removal of phenol. This can be attributed to the fact that the adsorption is usually a reversible and exothermic process.

Thus, the extent of phenol adsorption is increased with decreasing the temperature it is noticed also that the temperature dependence is approximately the same for all considered adsorbents.

Conclusions

The XRD patterns show that the modifying molecular sieve 13X with urea and thiourea had resulted in some changes in the silica and alumina structure which may be attributed to the solubilization of both silica and alumina in the presence of urea and thiourea.

The FTIR studies show hydrogen-bond type interactions of urea and thiourea molecules through their $-NH_2$ moiety with $-OH$ or oxygen in the substrate.

The largest surface area MS_U adsorbent showed the greatest ability to remove phenol traces from water than MS_T sample, and the latter is greater than the original MS_{13X} .

The percentage removal of phenol onto MS_{13X} , MS_T , and MS_U increased with increasing bed length, low flow rates and decreasing with temperature increase.

Nomenclature

°A	Angstrom, standard unit for measuring small distances.
FTIR	Infrared Diffraction.
MS	Molecular sieves.
ppm	Part Per million.
X	Zeolite type X, also referred as 13X.
1 13X	Zeolite type X, the number referred to sodium as the main cation.
XRD	X-Ray Diffraction.
WHO	World Health Organization.
Q	flow rate.

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Table.1 Surface Area of Adsorbent Samples

Adsorbents	m ² /g
MS13X	600
MS _T	675
MS _U	730

Table(2) Percentage Removal of Phenol at Different Flow Rate and bed Hight
Time = 30 min, C₀= 10 ppm, and T=30°C

Adsorbent	Q (l/h)	h (cm)	% removal	Ppm phenol in effluent
MS13X	0.2	56	92.9	0.71
MS _T	0.2	56	94.6	0.54
MS _U	0.2	56	98.8	0.12
MS13X	1.0	56	75.7	2.43
MS _T	1.0	56	77.8	2.22
MS _U	1.0	56	79.7	2.03
MS13X	0.2	30	65.8	3.42
MS _T	0.2	30	68.7	3.13
MS _U	0.2	30	70.5	2.95

Table.3 Removal of Phenol at Different inlet
Concentrations

Q=0.2 l/h, h= 56 cm, and T=30°C

Inlet, ppm	Phenol adsorbed, ppm and (%)		
	MS13X	MS _T	MS _U
10	9.30 (93)	9.46 (95)	9.88 (99)
50	33.0 (66)	34.5 (69)	36 (72)
100	58 (58)	62 (62)	68 (68)
150	72 (48)	80 (53)	84 (56)

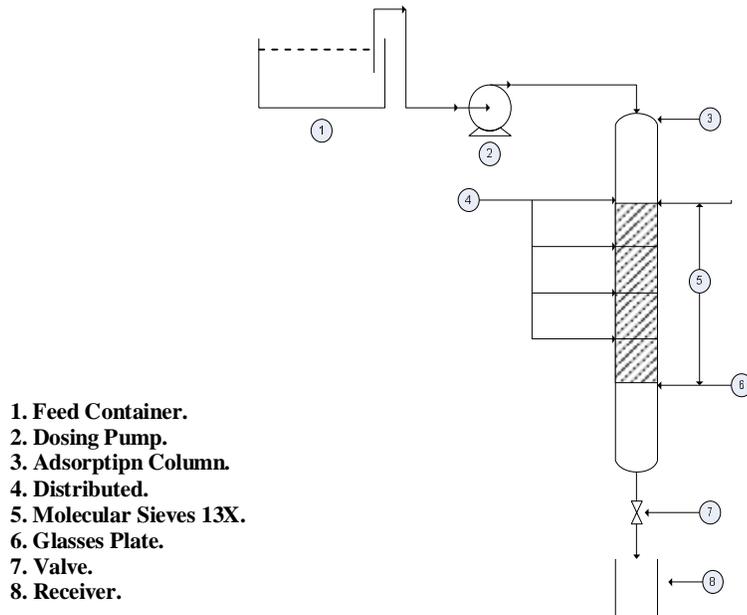


Figure (1) Flow Sheet Diagram of
Experimental Equipment

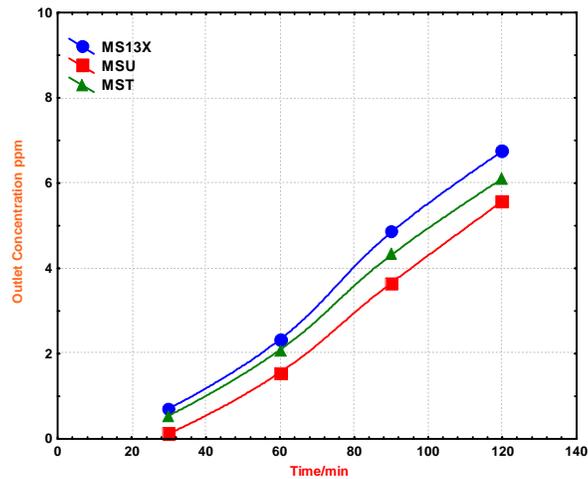


Fig.2 Breakthrough Curves for Adsorption of Phenol
Q=0.2 l/h, h=56 cm, and T= 30°C

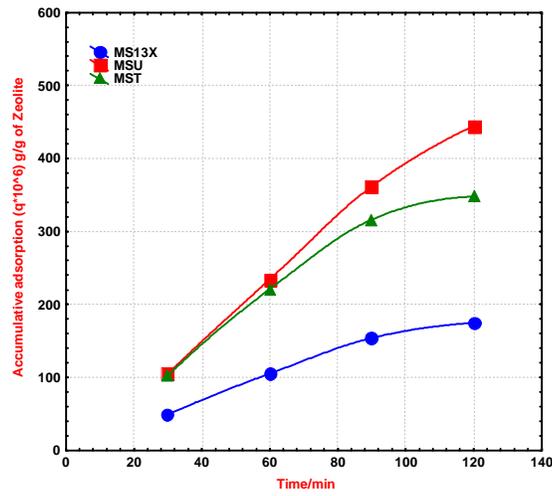


Fig.3 Accumulative Adsorption of Phenol at Different Time
O=1.0 l/h, h=56 cm, and T= 30°C

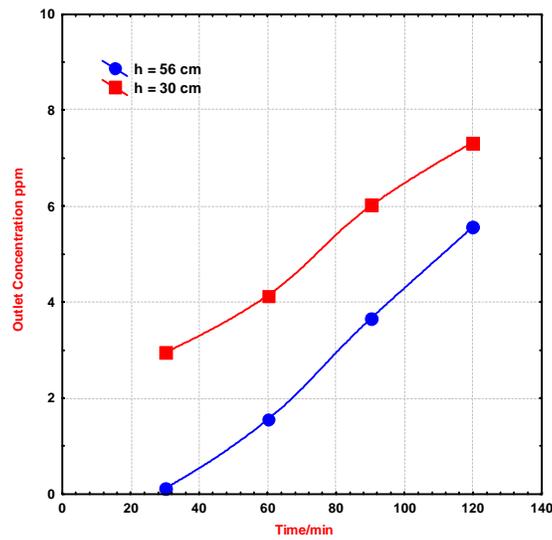


Fig.4 Adsorption of Phenol at Different Bed Hight of Z_{UREA} Modified
Q=0.2 l/h, and T= 30°C

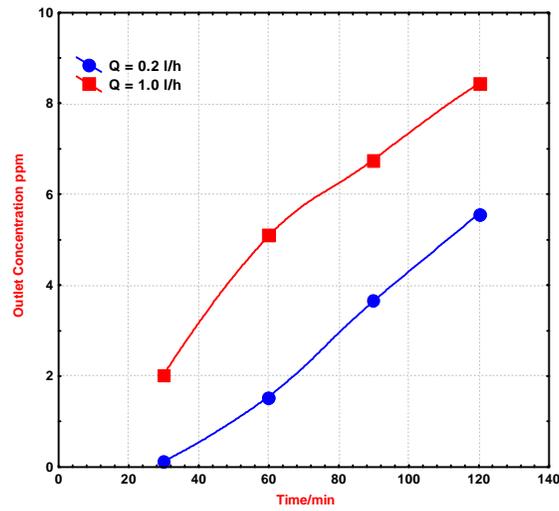


Fig.5 Effect of Flow Rate on Adsorption Phenol by Using Urea MS13X
h=56 cm, and T= 30°C

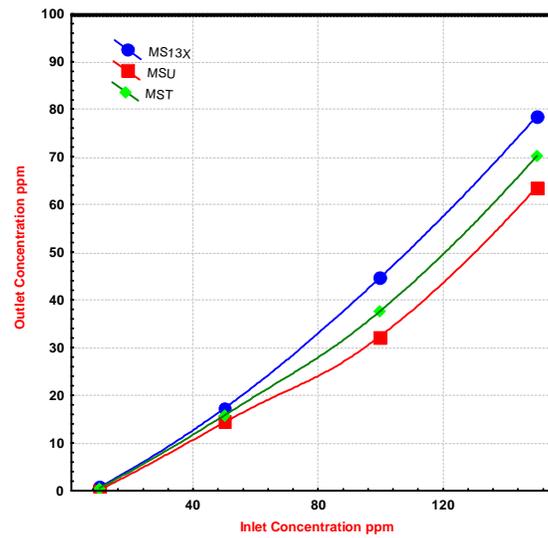


Fig.6 Adsorption of Phenol at Different inlet Concentrations
Q=0.2 l/h, h= 56 cm, and T=30°C

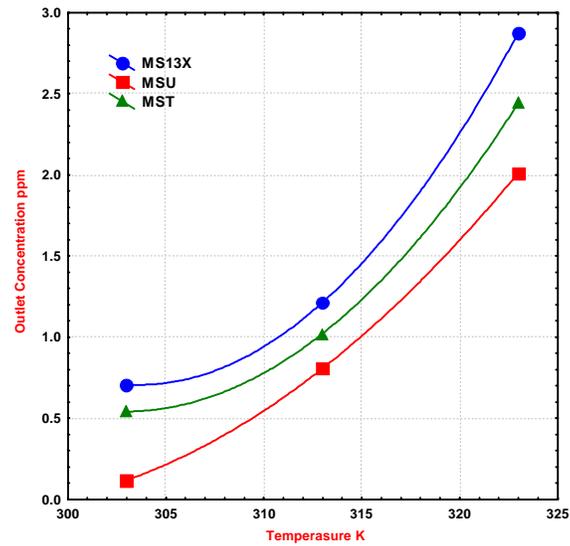


Fig.7 Adsorption of Phenol at Different Temperature
Q=0.2 l/h, t=30 min, and h= 56 cm