Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2016







Date :27 Nov 2015 Time :16:16:59



С

Е

Figure : SEM image of all adsorbent (A)Coal dust, (B)Bentonite, (C)Fly ash, (D)Laterite soil and (E)Sodium zeolite



Figure : FTIR peak of all adsorbent

FTIR analysis of adsorbents

Figure showed the FTIR spectra of coal dust, bentonite, fly ash, laterite and zeolite respectively in the wave no range of 4000-450 cm⁻¹. In coal dust the peaks above 3500 cm⁻¹ showed the heterocyclic N-H stretching and in the range of 3300 - 2500 showed the O-H stretching of carboxyl group. The C-H stretching band of aromatic was shown in range of 3100 - 3000 cm⁻¹. The peaks at 2920 and 2850 cm⁻¹ may be due to the presence of aliphatic groups. The peaks in the range of 1700 to 1660 cm⁻¹ showed the presence of carbonyl and carboxyl groups where 1600 cm⁻¹ corresponds the presence of aromatic C=C structure. The -CH₃ group was observed at 1398 cm⁻¹ and 670 cm⁻¹ is assigned to C-S band. The peaks in the range of 900 to 700 cm⁻¹ indicate the presence of C-H aromatic out of plane bending modes [1-3]. In bentonite peaks showed in the range of 1300 to 450 cm⁻¹, represent the Si-O stretching where 466, 524, 628, 670, 686, 848, 878, 915 cm⁻¹ were attributed to Si-O-Si, Al-O-Si, Si-O-Al, Si-O-Mg, Quartz, Al-OH-Mg, Al-Fe-OH and Al-OH-Al bending. The peaks at 1645 and 3466 cm⁻¹ were assigned for OH group of water molecules. The inner hydroxyl groups between the tetrahedral and octahedral groups were present near 3620 cm⁻¹[4,5]. In flyash the peak at 3600 cm⁻¹ assigned for OH group of the Si-OH and water molecules. The peaks in the range of 2400-3400 cm⁻¹ corresponds the presence of hydrogen bonded O-H stretching of acidic groups. A broad band ranging from 1170 -1070 cm⁻¹ showed the asymmetric stretching of Si-O-Si where 1160 cm⁻¹ was attributed to the SO₄²⁻ ions. The peaks at 1103 and 656 cm⁻¹ were assigned to the Si-O and Al-O vibration bands [6-9]. In laterite soil the peak at 3680 cm⁻¹ was attributed to Al-O-H stretching. The OH group of the Fe, Al and Si were assigned in the range of 3405-3370 cm⁻¹. The peak near 1620 cm⁻¹ showed the H-O-H group of water molecules. The absorption band near 1030 cm⁻¹ corresponds to the presence of Si-O stretching. At 912 cm⁻¹, the absorption band showed Al-OH bond stretching. The band near 790 cm⁻¹ was attributed to cristobalite. The peaks ranges from 542 to 474 were assigned due to Fe-O bond stretching and Si-O-Al stretching [10]. In zeolite the peaks ranges from 3700 to 3350 cm⁻¹ were assigned to Si-OH, Si-OH-Al and OH group. The absorption bands ranges from 1200 to 450 cm⁻¹ showed the vibration of Si-O-Al, Si-O-Si, Si-O and Si-Al species and the peak at 668 cm⁻¹ was assigned to the Si-O-M functional group with Misthe exchangeable Na⁺ ion metal species [11].



Figure: XRD of Coal sample before and after adsorption

The above figure shows the XRD plot of the coal dust sample (before and after adsorption). From the figure, it is evident that no significant changes in the XRD main peaks of the coal sample (12.469°, 26.740°, 31.052° and 50.237°) occurred after adsorption, although a little decrease in intensity of the main peaks is observed. This lesser intensity of the main peaks may be due to the adsorption of S compounds on the upper surface of the adsorbent [12], but the absence of any new peak after adsorption proves that the process is physical adsorption not the chemical one [13].



Figure : NH₃-TPD curve of adsorbents

Adsorbent	Acidity (mmol/g)
Coal dust	8.22
Bentonite	5.64
Fly ash	10.65
Laterite soil	0.02
Zeolite	2.76

Table : NH₃-TPD acidity analysis of adsorbents

Table : Proximate analysis of coal

Moisture Content	Ash Content	Volatile Matter	Fixed Carbon
1.36%	17.4%	25%	56.24%

Table : Ultimate analysis of coal

Carbon	Hydrogen	Sulfur	Nitrogen
79.13%	2.23%	1.3%	1.13%







Figure : HPLC of model fuel after adsorption by coal



Figure : HPLC of model fuel after adsorption by bentonite



Figure : HPLC of model fuel after adsorption by fly ash



Figure : HPLC of model fuel after adsorption by laterite soil



Figure : HPLC of model fuel after adsorption by zeolite

Sulfur Compound	Feed	Coal	Bentonite	Fly ash	Laterite soil	Zeolite
Thiophenol	2779059	910974	853962	1308857	1149192	1221537
Benzothiophene	3975885	1368102	1569404	2111263	2086542	2071761
Di-benzothiophene	9431592	3678691	3873302	6441873	5422230	5986014

Table: HPLC Instrumental analysis of peak area

Table : Efficiency of adsorbents on real fuel

Name of adsorbent	Sulfur removal in Gasoline	Sulfur removal in LGO	
	(%)	(%)	
Coal Dust	82	36	
Bentonite powder	80	35	
Fly ash	79	34	
Laterite soil	75	32.6	
Zeolite	70	28.9	

Property	Before adsorptio	n	After Adsorption			
		Coal	Bentonite	Fly ash	Laterite	
ASTM Distillation						
IBP(⁰ C)	102	101	102	103	102	
FBP(⁰ C)	143	140	141	142	144	
Specific Gravity	0.75	0.749	0.748	0.749	0.748	
API	57.16	57.41	57.67	57.41	57.67	
RVP (psi)	1	1	1	1	1	
Flash Point (⁰ C)	62	65	64	63	61	
Fire Point (⁰ C)	68	70	69	68	68	
Gum Content (mg/	ml) 0.2738	0.272	0.273	0.2725	0.2735	
Oxygen Content (w	/t %) 1.6	1.4	1.45	1.5	1.51	

Table :Property of straight run gasoline fuel before and after adsorption

*API:- American Petroleum Institute

**IBP & FBP:- Initial & Final boiling point

***RVP:- Reid Vapour pressure

Property	Before adsorption	After Adsorption			
		Coal	Bentonite	Fly ash	Laterite
ASTM Distillation	n				
IBP(⁰ C)	170	168	169	168	167
FBP(⁰ C)	336	332	331	334	335
Specific Gravity	0.843	0.841	0.842	0.841	0.842
API	36.35	36.75	36.55	36.75	36.55
Viscosity (CS)	6.19	5.9	6.0	6.1	5.98
Cloud Point (⁰ C)	15	12	13	14	12
Pour Point (⁰ C)	-15	-12	-13	-13	-14
Cetane No	55.11	56.08	56	55.57	55.86

Table : Property of light gas oil before and after adsorption

*API:- American Petroleum Institute

**IBP & FBP:- Initial & Final boiling point

*** CS:- Centistoke

Name of adsorbent	Nitrogen removal in Gasoline	Nitrogen removal in Diesel	
	(%)	(%)	
Coal Dust	53	40	
Bentonite powder	43	35	
Fly ash	24	30	
Laterite soil	18	25	
Zeolite	14	20	

Table. Efficiency of adsorbents on nitrogen compound removal from real fuel

Reference

[1] D. Nag, P. Biswas, V. K. Chandaliya and P. K. Banerjee, International Journal of Coal Preparation and Utilization, 2011, 31(1), 1-8.

[2] M. Balachandran, American Journal of Analytical Chemistry, 2014, 5, 367-72

[3] B.H. Stuart, Infrared Spectroscopy: Fundamental and Application, 2004, 71-93

[4] M.H. Ashtiani, Part. Part. Syst. Charact., 2011, 28, 71-6

[5] F.G. Alabarse, R.V. Conceicao, N.M. Balzaretti, F. Schenato and A.M. Xavier, Applied Clay Science, 2011, 51, 202–08

[6] O. Celik, E. Damc and S. Piskin, Indian Journal of Engineering & Materials Sciences, 2008, 15, 433-40.

[7] S. Katara, S. Kabra, A. Sharma, R. Hada and Ashu Rani, International Research Journal of Pure & Applied Chemistry, 2013, 3(4), 299-307

[8] R. Shawabkeh, M.J. Khan, A.A.A. Juhani, H.I.A.A.Wahhab and I.A. Hussein, 3rd International conference on industrial and hazardous waste management, 2012, 1-8

[9] D. Jain, R. Hada and A. Rani, Journal of catalysts, http://dx.doi.org/10.1155/2013/723957

[10] V.K. Rathore, D.K. Dohare and P. Mondal, Journal of Environmental Chemical Engineering, 2016, 4, 2417–30

[11] S. Hashemian, S.H. Hosseini, H. Salehifar and K. Salari, American Journal of Analytical Chemistry, 2013, 4, 123-6.

[12] V. Balakrishnan, S. Arivoli, A.S. Begum and A.J. Ahamed, J. Chem. Pharm. Res., 2010, 2(6),176-90.

[13] A. Ravikumar, S.M.M.N. Khan, Iranica Journal of Energy and Environment, 2015, 6(4), 316-22.