

## **“Efficiency of hydrotropes along with soap collector in coal fines recovery”**

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### **Abstract**

Investigations on the efficiency of hydrotrope as promoter along with soap collector is presented in this paper. Madhuban Non-Coking Coal sample was used in the tests. The aim of the investigation is to achieve higher yield recoveries of cleans with lower ash percent of cleans. Flotation experiments were conducted by varying three parameters i.e hydrotrope dosage, collector dosage and kinetics. Sodium benzoate was used as hydrotrope and soap light diesel oil emulsion was used as collector in flotation test. Hydrotropes acts as in flotation. Promoters when used along with collectors results in high recoveries. The results of the flotation efficiency in terms of higher yield recoveries and low percent of concentrate were noted. From results it can be inferred that about 66% of the coal cleans were recovered when hydrotrope was used along with soap LDO emulsion with corresponding 26.95 % percent of ash. On the other hand only 20 % of cleans were recovered when diesel oil is used as collector. From Lagergren first order kinetic study the  $R^2$  value was found to be 0.458 and from pseudo second order kinetics study the  $R^2$  value was found to be 0.7457 which explains that pseudo second order kinetics shows satisfactory flotation results.

**Key words** Hydrotrope, soap light diesel oil emulsion, collector, kinetics, cleans, promoter, flotation efficiency, concentrate, yield, ash percent.

### **Introduction**

Low rank coals are known to have a low metamorphic degree, and normally a great number of oxygen-containing functional groups are present on their surface such as carboxyl, phenolic and carbonyl, which are able to bond with water readily through hydrogen bonding [1]. Furthermore, most coals are susceptible to surface oxidation by weathering, which can occur during storage or transportation of the raw coal. The result is generally the formation of surface oxygen functional groups, most commonly carboxyl, hydroxyl and carbonyl groups. These oxygen containing functional groups reduce the hydrophobicity of the coal surface and thereby make the coal difficult to float with oily collectors [2].

The flotation has been used to upgrade low-rank coal into high-quality coal resources. Froth flotation is an effective process for upgrading fine coals with a particle size of less than 0.5 mm [3]. This is a surface-based approach that relies on surface characteristics variations between target and gangue minerals. The target minerals are typically

selectively hydrophobic during the froth flotation process by adding agents called collectors at the liquid/solid interface. The hydrophobic minerals in the upper section of the flotation cell are recovered under severe stirring conditions because bubbles are pumped into the flotation cell. The hydrophobicity of the coal particle surface is one of the most critical aspects in determining the flotation impact in the fine flotation process. Low-rank coal, on the other hand, has a lot of oxygen-containing functional groups (hydroxyl, carboxyl, carbonyl, phenolic hydroxyl), which can establish a chemical connection with water molecules and cause the coal surface to be hydrophobic. Weathering can cause surface oxidation in most coals, which can happen during storage or transit of the raw coal. Surface oxygen functional groups, most often carboxyl, hydroxyl, and carbonyl groups, are formed as a result. The hydrophobicity of the coal surface is reduced by these oxygen-containing functional groups, making the coal harder to float [4].

Soaps as flotation collectors stood out due to their excellent efficiency in inducing hydrophobicity on mineral surfaces. Soaps are sodium and potassium salts of long-chain acids such as palmitic, steric, oleic, linoleic, linolenic, and ricinoleic acids, with lesser amounts of capric, caprylic, lauric, and myristic acids. The soap's straight chain carboxylic acids generate a dense adsorbed coating of fatty acid molecules on the mineral surface [5]. Soap–light diesel fuel (LDO) is used in some plants [6-7]. The use of a soap–LDO emulsion aids in the collection of coarse particles, while light diesel oil (LDO) functions as a hydrocarbon chain extender [8]. Jhamarkotra soap–LDO emulsion was found to function better [9]. In the flotation process, soap molecules perform a dual duty [10].

Hydrotropes are a class of chemicals that improve the solubility of sparingly soluble solutes by several orders of magnitude under normal conditions. Hydrotropy is a molecular phenomenon in which the addition of a second solute (the hydrotrope) causes the aqueous solubility of weakly soluble solutes to increase. Hydrotropes are anionic molecules with an aromatic ring replaced by a sulphate, sulfonate, or carboxylate group; sodium xylene sulfonate (SXS) and sodium benzoate are two examples of hydrotropes. Later on, the concept was expanded to include cationic and neutral aromatic compounds [11].

### **Reagents**

Commercial grade reagents used in the plant are used in flotation experiments. Light Diesel oil was supplied by Indian oil . Diesel oil and sodium benzoate which are used in experimentation are procured from the plant store, CMIFR, Digwadih, Jharkhand.

### **Materials and Methods**

Laboratory flotation tests were carried out in a 2 litre Denver type sub-aeration cell. In the same cell, the ore pulp was conditioned at 25% solids. The collector (Soap-light diesel oil emulsion @ 2.5 kg per tonne of ore) was added to the pulp for 2 minutes, followed by the conditioning of hydrotrope at a concentration of 2.3 kg/t for another 2 minutes, as necessary for the various experiments in this study. Throughout the test, the

impeller in the flotation cell was set at 1500 r/min to ensure that the pulp was completely disseminated but that no surplus pulp flowed into the froth. The froth was scraped for 30 seconds after air was added to the cell at a flow rate of 200ml/min. Filtration was done on both the concentrate and the tailing.

**Results and Discussions**

**A) Effect of sodium benzoate (hydrotrope) dosage to recover clean Madhuban coal**

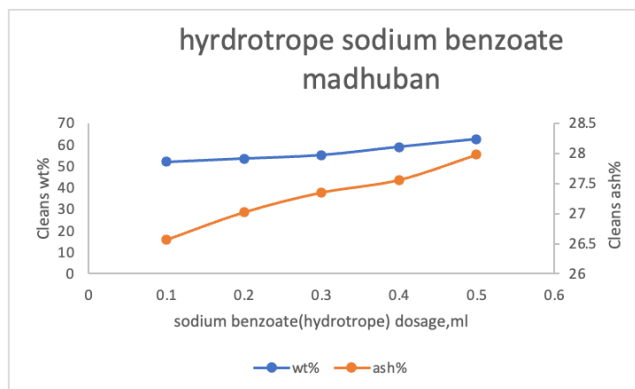
In present experimentation sodium benzoate (hydrotrope) was used as promoter. Since sodium benzoate proved to be a best recover to recover fine particles, it was selected for flotation of Madhuban Non-coking coals. The sodium benzoate dosage was varied in the range from 0.1 to 0.5ml per 250 grams of coal sample .

Table 1 Effect of hydrotrope dosage to recover cleans

Sl.no	Conditioning		Cleans		Rejects		Feed	combustible	Non-combustible	Efficiency
	Promoter	Promoter dosage ml	Wt%	Ash%	Wt%	Ash%	Ash%	Recovery	Recovery	Index
1	Sodium benzoate(hydrotrope)	0.1	52	26.56	48.0	46.0	35.9	59.6	38.5	21.1
2		0.2	53.6	27.02	46.4	52.1	38.7	63.8	37.5	26.3
3		0.3	55.2	27.35	44.8	63.6	43.6	71.1	34.6	36.5
4		0.4	59	27.56	41.0	52.3	37.7	68.6	43.1	25.5
5		0.5	62.6	27.98	37.4	63.3	41.2	76.7	42.5	34.1

The below fig 1 is drawn against the sodium benzoate (hydrotrope) dosage(ml) by cleans wt% and ash%. From the below fig it is observed as the dosage of sodium benzoate increases the recovery of the clean coal increased. An optimum dosage of sodium benzoate i.e 0.4ml for 250 gm of coal (collection time of 30sec, RPM-1500, Conditioning of pulp 5min, pH-7) about 59% of cleans were recovered with an ash percent of 27.56. However the recovery of coal in Cleans increased from 37.6% when diesel oil was used to (diesel oil-0.33ml, MIBC-30 ml, RPM-1500, Pulp density-250grams for one liter of water) 59% (sodium benzoate=0.4ml for 250 grams of sample, frother dosage(MIBC)=0 lit/ton of ore, collection time= 30 seconds, RPM-1500, Pulp density-250grams for one liter of water) with corresponding 27.56 percent of ash. However increasing the dosage further produced only a slight difference in the recovery of cleans. The amount of ash percent increased linearly as the collector dosage increased. The technical reason might be due to the ability of sodium benzoate exhibit the phenomena to hydrotropy which is nothing

but that hydrotropes influence the formation and structure of micelles and micro emulsions [12].



**Fig 1 Effect of sodium benzoate (hydrotrope) dosage to recover clean coal(Madhuban)**

**B ) Effect of collector dosage (sodium benzoate+ soap light diesel oil emulsion) to recover clean Madhuban coal and ash percent**

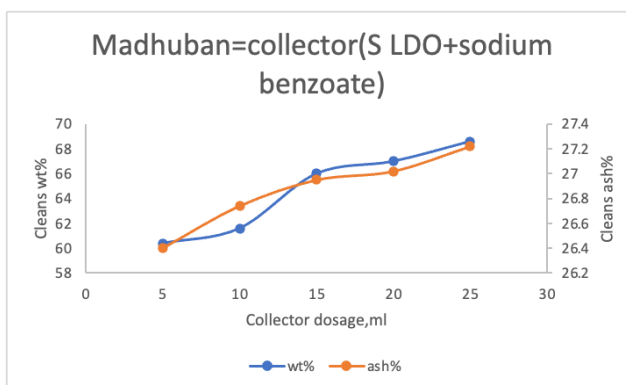
In present experimentation sodium benzoate (hydrotrope) along with soap-light diesel oil emulsion is used as collector.

Table 2 Effect of Collector dosage to recover coal fines

Sl.no	Conditioning		Cleans		Rejects		Feed	combustible	Non-combustible	Efficiency
	Sodium benzoate (hydrotrope) dosage ml	Collector + Sodium benzoate (hydrotrope) ml	Wt%	Ash%	Wt%	Ash%	Ash%	Recovery	Recovery	Index
01	0.4	5	60.4	26.4	39.6	46.0	34.2	67.5	46.7	20.8
02		10	61.6	26.74	38.4	52.1	36.5	71.0	45.2	25.9
03		15	66	26.95	34.0	63.6	39.4	79.6	45.1	34.4
04		20	67	27.02	33.0	52.3	35.4	75.6	51.2	24.5
05		25	68.6	27.22	31.4	63.3	38.5	81.2	48.4	32.8

The below fig 2 is drawn against the collector dosage(ml) by cleans wt% and ash%. From the below fig it is observed as the dosage of collector increases the recovery of the clean coal increased. At An optimum dosage of collector( sodium benzoate - 0.3ml +soap light diesel oil emulsion-15ml) for 250 gm of coal(collection time of 30sec,RPM-1500,Conditioning of pulp 5min,pH-7) about 66% of cleans were recovered with an ash percent of 26.95. However the recovery of coal in Cleans increased from 59% when sodium benzoate alone was used to (sodium benzoate-0.37ml,MIBC-30 ml,RPM-1500, collection time-30 sec,Pulp

density-250grams for one liter of water) 66% when sodium benzoate is used along with soap-light diesel oil emulsion(sodium benzoate=0.4ml+soap-light diesel oil-20ml, frother dosage(MIBC)=0 lit/ton of ore,collection time= 30 seconds, RPM-1500,Pulp density-250grams for one liter of water) with corresponding 26.95 percent of ash.However increasing the dosage further produced only a slight difference in the recovery of cleans. The amount of ash percent increased linearly as the collector dosage increased.The technical reason might be due to the ability of soap-light diesel oil to improve oil dispersion when used along with sodium benzoate(hydrotrope).Improved oil dispersion produces finer and finer droplets which increase the probability of collisions between particles and oil droplets which in turn increases recovery[13].



**Fig 2 Effect of collector dosage (sodium benzoate+ soap light diesel oil emulsion) to recover clean Madhuban coal and ash percent**

**C) Flotation kinetics studies Madhuban coal**

**Table 3 flotation Kinetics**

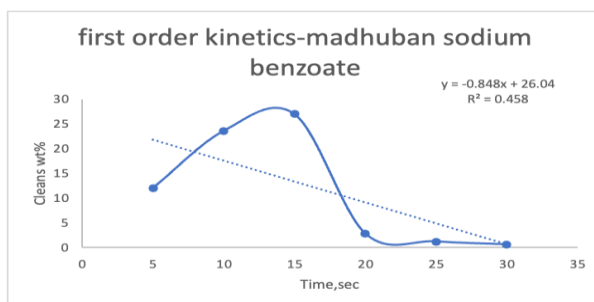
Sl.no	Conditioning			cleans		Rejects		Feed	combustible	Non-combustible	Efficiency
	Sodium benzoate (hydrotrope) ml	Collector (Soap LDO) ml	Time sec	Wt %	Ash %	Wt %	Ash %	Ash %	Recovery	Recovery	Index
01	0.4	20	5	12	27	88.0	46.0	43.7	15.6	7.4	8.2
02			10	23.6	26.6	76.4	52.1	46.1	32.1	13.6	18.5

03			15	27	25	73.0	63.6	53.2	43.2	12.7	30.6
04			20	2.8	29	97.2	52.3	51.6	4.1	1.6	2.5
05			25	2	34	98.0	63.3	62.7	3.5	1.1	2.5
06			30	0.6	37	99.4	78.6	78.4	1.7	0.3	1.5

**(i) Lagergren first order**

Lagergren plot and pseudo second order kinetics plot for flotation of Madhuban coking coal are drawn in figs. 4.4.2.3(a) &4.4.3.3(b). Table-5.2 summarizes the rate constant values for first and second order rate equations[14-15]. It is noted that first order rate equation does not explain flotation satisfactorily on the other hand second order rate equations explain the flotation interactions satisfactorily

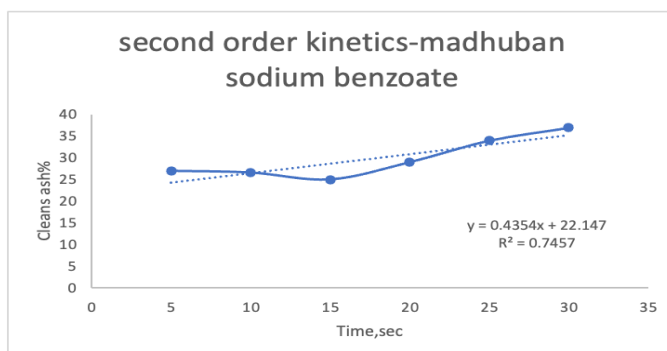
$$Wt\% = -0.848t + 26.04, R^2 = 0.458$$



**Fig 4.4.2.3(a) Lagergren first order for flotation of Madhuban coal**

**4.4.2.3 (b) pseudo second order**

second order rate equations explain the flotation interactions satisfactorily [16-17]. The rate constant values for second order rate equations  
 $Ash \% = 0.4354t + 22.147, R^2 = 0.7457$



**Fig 4.4.2.3 (b) pseudo second order for flotation of Madhuban coal**

**Table 4 Equation and rate constants**

Order	equation	R <sup>2</sup>
Lagergren first order	Wt% = -0.848t + 26.04	R <sup>2</sup> = 0.458
pseudo second order	Ash % = 0.4354t + 22.147	R <sup>2</sup> = 0.7457

**Conclusions**

It can be concluded that hydrotropes when used along soap collector clearly influenced the efficiency of the flotation. From results it can be inferred that about 66% of the coal cleans were recovered when hydrotrope was used along with soap LDO emulsion with corresponding 26.95 percent of ash. On the other hand only 20% of cleans were recovered when diesel oil is used as collector. From Lagergren first order kinetic study the R<sup>2</sup> value was found to be 0.458 and from pseudo second order kinetics study the R<sup>2</sup> value was found to be 0.7457 which explains that only pseudo second order kinetics showed satisfactory flotation results.

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**References**

1. Atesok G, Boylu F, Celik MS. Carrier flotation for desulfurization and deashing of difficult-to-float coals. *Miner Eng* , 14(6), 661–70, 2001.
2. G. H. HARRIS et al” Coal flotation with non-ionic surfactants”,*Coal Preparation*,16,135-147,1995.
- 3.Cebeci, Y. “The investigation of the floatability improvement of Yozgat AyrÄa dam lignite using various collectors”. *Fuel*, 81, 281–289, 2000.
- 4.Foucaud, Y.; Badawi, M.; Filippov, L.; Filippova, I.; Lebègue, S. “A review of atomistic simulation methods for surface physical-chemistry phenomena applied to froth flotation”. *Miner. Eng.* 143, 106020 ,2019.
- 5.Ch. A.I. Raju et al “Hydrotropes in soap flotation:a critical review”.*Emerging trends in chemical engineering*, 5(2), 1-6, 2018.
- 6.Sekhar DMR, Ranga Rajan VS, Ramanamurthy SV, et al. Processing Low Grade Silica based Rock Phosphate Ore. *Fertiliser News*.31, 6,1986.

7. Sekhar DMR, Jain CL. Reengineering the Jhamarkotra phosphate concentrator. Proceedings of the XXIII International Mineral Processing Congress; Istanbul, Turkey, Sep 3, 2006.
8. D.M. Mihir, R. Padmasree”Soap Flotation: A Brief Review”, Journal of Modern Chemistry & Chemical Technology, 7(2), 5-8, 2016.
9. Srinivas K, Sekhar DMR. Comparative Study of Jhamarkotra Soap Emulsion and Tall Oil Soap Emulsion as Flotation Collectors. Indian Chemical Engineer, 52(3), 248–53, 2010.
10. 17.Srinivas K, Sekhar DMR, Chauhan YK. Soap Flotation of dolomite. Proceedings of the National Seminar on Indian Mineral Processing Advances; 1996 Apr 18–19; Puri, India. Available from: <https://www.researchgate.net/publication/2>.
11. Stig E. Friberg , Robert V. Lochhead , Irena Blute & Torbjörn Wårnheim, Hydrotropes—Performance Chemicals, Journal of Dispersion Science and Technology, 25(3), 243-251, 2004.
12. Maheshwari Rajesh Kumar, Mathur Vineet, Satrawala Yamini, Rajput Mithun Singh. Ecofriendly spectrophotometric estimation of diclofenac sodium in tablets using N, N-dimethyl urea as a hydrotropic solubilizing agent, International research journal of pharmacy.1 (1) ,157-160,2010.
13. Ji Young Kim, Sungwon Kim, Michelle Papp, Kinam Park, Rodolfo Pinal, Hydrotropic Solubilization of Poorly Water-Soluble Drugs, Journal of pharmaceutical sciences. 99(9) , 3953-3965, 2010.
14. P Vijay Kumar et al,” Tri sodium citrate as promoter in the soap flotation of phosphate minerals”, XXVI INTERNATIONAL MINERAL PROCESSING CONGRESS(IMPC) 2012 PROCEEDINGS / NEW DELHI, INDIA , 24 - 28, SEPTEMBER 2012.
15. Jenkins, B., O’Brien, G., Beath, H. and Esterle, J. Automated Image Analysis System for Coal Petrographic Characterization. Exploration & Mining Report 809. ACARP PROJECT C8056, 1-58, 2001.
16. X.M. Makukule et al “The usefulness of petrographic information for the coal industry”.CIMERA, Department Of Geology, University of Johannesburg, Johannesburg, South Africa, 1-13, 2001.
17. Chen-LinChou et al “Sulfur in coals: A review of geochemistry and origins”.International journal of coal geology,1,1-13, 2012.