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Simultaneous Coagulation-Adsorption Process Optimization for the Treatment of Real Wastewater of Complex Dyes Manufacturing Plant

A. K. SHAH[++], A. R. MEMON*, G. METLO, S. F. A. SHAH*, A. H. PEERZADA*

Chemical Engineering Department, Dawood University of Engineering and Technology, Karachi

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Abstract: This research study was carried out for the optimization of treatment efficiency of industrial dyes wastewater. Hybrid process of coagulation-adsorption was utilized for an effective reduction of wastewater pollutants concentration with the use of commercial coagulants namely Ferric chloride ($FeCl_3$), Ferrous Sulfate ($FeSO_4$) and Alum [$Al_2(SO_4)_3$] and bottom based coal ash (BBCA) as an adsorbent. An effective adsorbent was prepared from coal power plant ash waste by physico-chemical treatment in order to enhance its physical properties. The removal efficiencies of pollutants for each individual and combined process were determined keeping contact time, agitation rate, equilibrium conditions similar in each case except for the dosages of chemicals added to suit the pollutants removal rates. Adsorptive capacity and adsorption (%) of BBCA adsorbent was determined for adsorption of organic pollutants along with dosage effects. Adsorption isotherm models such as Langmuir and Freundlich were applied for the determination of adsorption suitability and their mechanism. Both processes reduced the concentration of Chemical oxygen demand (COD), coloring matter, turbidity and total suspended solids (TSS) in the range of 60-70%, whereas, hybrid process of coagulation and adsorption optimized the treatment efficiency up to 80%. The overall treatment efficiency with $FeCl_3$-BBCA, $FeSO_4$-BBCA and Alum-BBCA was observed as 80%, 78% and 73%, respectively.

Keywords: Industrial dyes wastewater, Hybrid process, Bottom based coal ash, Alum

1. INTRODUCTION

Dyes and textile industries in Pakistan are facing critical problem of the treatment of their highly toxic wastewater discharges, which are composed of high concentration of dyes, color, BOD, COD, turbidity, pH, temperature, alkali, acids, heavy metals and toxic substances (Hsu and Chiang, 1997). Discharge of dyes wastewater into receiving water bodies cause water pollution of such water bodies resulting in allergic as well as water-borne diseases as well as significantly affecting photosynthetic activity carried out by aquatic organisms due to the reduction of incidence of light (Ahamruzzaman, 2010, Gupta *et al*., 1998 and Tunay *et al*., 1996). Several physico-chemical processes such as chemical coagulation /flocculation, the Fenton reaction, ultra-filtration, nano-filtration, reverse osmosis, adsorption, oxidation and electrochemical have been used for the treatment of dye wastewater in terms of adequate removal of wastewater constituents such as COD, color, turbidity and total suspended solids (Ayoub *et al*., 2011). However, these techniques when used as an individual and sole option of the treatment, have generally been ineffective for the complete reduction of color, COD, BOD, and coloring agents. Whereas, their combinations comprising of more than one techniques have proved to be more effective for wastewater treatment, thus causing an improvement in the treatment efficiency (Chattarjee *et al*., 2001). In advanced technology, reverse osmosis is an effective method of water treatment, but regeneration and replacement cost of membrane is highly expensive. In this regard, efforts were taken for utilization of waste products into effectual engineering solution and optimization of dyes wastewater treatment efficiency via low-cost hybrid process of coagulation and adsorption. Adsorption is an effective technique for the treatment of wastewater and the reduction of dyes, color, COD, BOD and other organic substances. Adsorption capacity depends upon adsorbent porosity, chemical structure, surface area, density and particle size (Dincer *et al.*, 2007). Activated carbon has been widely used as an effective adsorbent for such treatment, but due to their high cost and regeneration factor, researchers have concentrated on alternative adsorbents for economical wastewater treatment (Swamy *et al.*, 1997). They have worked on preparation of low cost adsorbents for wastewater treatment such as fly ash, coir pith, cassava peel, cotton, orange peel, bagasse fly ash, cellulose based waste, sewage sludge, kaolinite, charfine, saw dust, wheat dust, zeolite, oil shale and olive mill waste (Dincer *et al.*, 2007). Lakhra Power Generation Company Ltd Jamshoro Pakistan is utilizing low quality lignite coal for generation of 150 MW of electric energy by use of advanced FBC technology. Lakhra coal reserves are estimated to about 1328 millions tones and generation ratio of bottom based coal ash is 16550 m^3/hr (Aziz *et al.*, 2010). Bottom based coal ash as a waste generated from coal power plants creates disposal problems causing environmental concern among the plant owners (Wang *et al.*, 2006). The dumping of coal

[++]Corresponding author e-mail: engrakshah@yahoo.com , Cell # +923363877975
*Chemical Engineering Department, Mehran University of Engineering and Technology, Jamshoro

ash creates environmental problems caused by leaching of contaminants in the ash (Levandowski and Kalkreuth, 2009). Researchers have focused on utilization of bottom based coal ash for industrial applications due to the presence of valuable mineral constituents in it and conducive properties. It is also used along with concrete and cement for road construction and effluent treatment. It has great potential for the removal of metals (Arevalo *et al*, 2002), dyes (Gupta *et al.*, 2004) from effluent.

The aim of this research work was to optimize dyes wastewater treatment efficiency to influence reduction of pollutants in the wastewater at higher rate. A cheaper and an effective adsorbent was prepared from coal power plant ash waste, which was used along with the commercial coagulants in order to change chemical behaviour of coagulants to effect optimized reduction rate of dyes wastewater pollutants.

2. MATERIALS AND METHODS

Collection of Bottom ash and its elemental analysis

The samples of bottom based coal ash (BBCA) were collected from FBC Power plants, Lakhra Power Generation Company Limited Jamshoro Pakistan. The elemental analysis of BBCA, which was alkaline in nature, was conducted at Fuel Research Laboratory, Pakistan Council of Scientific and Industrial Research Institute, Karachi. Its elemental composition is as: Fe_2O_3 (22.34%), K_2O (0.843%), MgO (1.83%), Al_2O_3 (6.61%), SiO_2 (33.59%), Na_2O (1.2%), CaO (30.24%) and MnO_2 (0.14%), SO_3 (0.003%). The specific surface area was 1.77 m^2/g as determined by the BET-N_2 method.

Preparation of adsorbent from BBCA

BBCA adsorbent was prepared through screening, pre-treatment, washing and drying steps. The ash was grinded and sieved into fine porous size (200 mesh) on an RO-Tap Type Sieve Shaker (Model- A-871205, Heiko Seisakusho Tokyo Japan) at 290 rpm speed. This fine porous ash was washed with warm distilled water (60ºC) and 10% H_2SO_4 solution for 5 times. Pre-treated ash sample was dried in a laboratory oven (L-201C, Grieve Corporation, USA) at 110 ^{0}C temperature for 12 hr for activation of ash adsorbent, and finally cooled at room temperature (Rao *et al.*, 2006).

Morphological analysis of BBCA

The structural morphologies of raw (**Fig. 1**) and prepared adsorbent (**Fig. 2**) from BBCA samples were determined through Scanning Electron Microscope (SEM) (Wang *et al.*, 2008), (JSM-6380, JEOL Ltd, Tokyo, Japan), at Advanced Research Laboratory, Mehran University of Engineering and Technology, Jamshoro, Pakistan. There is a marked difference between the two images, which illustrates the preparedness of the sample.

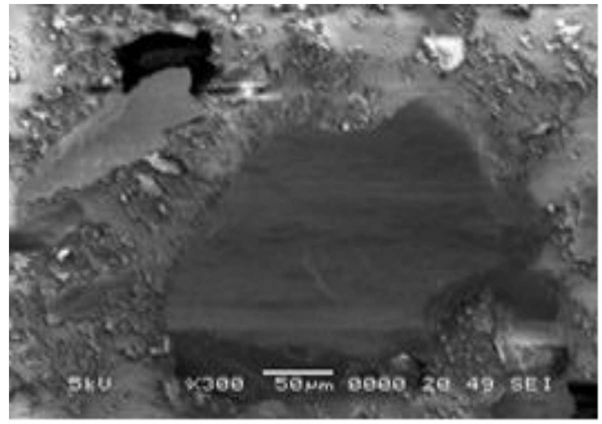

Fig.1: SEM image of raw sample of bottom based coal ash.

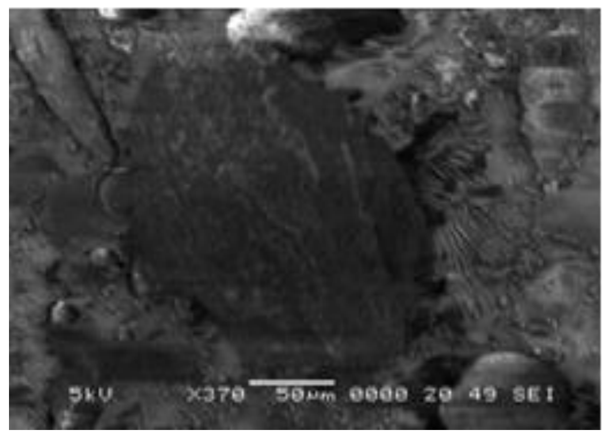

Fig.2: SEM image of prepared adsorbent of bottom based coal ash.

Treatment of industrial dyes wastewater through chemical coagulation- adsorption process

The collected industrial dyes wastewater was the multifarious assortment of various effluents of dyes, pigments, textile chemicals and binder emulsion processing plants. These wastewater samples were gathered from the effluent disposal point of dyes manufacturing plant, Clariant Pakistan Limited, Jamshoro. The commercial coagulants were purchased from Al-Mehran Chemicals Ltd, Karachi. All the research work in this regard was done at Effluent Treatment Laboratory of dyes manufacturing plant, Pakistan. The wastewater analysis was conducted according to the standard laboratory protocols. Various effluent quality parameters such as Total dissolved solids (TDS), electrical conductivity, pH, chemical oxygen demand (COD), color, turbidity and total suspended solids (TSS) were analyzed for performance evaluation of the process. pH of the samples was directly measured using pH meter (Hach, USA). COD was determined via dichromate COD method using standard COD vials in DR-2000 Spectrophotometer (Hach, USA). The samples were diluted for 10 times with double distilled water, and then 2 ml of the diluted sample was poured into COD vial, inverted for 30 seconds and placed in COD Reactor (TR-320, Merck, USA) at 148^0C for 2 hr for digestion of the prepared sample. COD, Color, turbidity and TSS of effluent samples were measured through absorptometric method using DR-2000 Spectrophotometer at their specific wavelengths of 620, 455, 450 and 810 nm, respectively. The samples were treated via coagulation process using $FeCl_3$, $FeSO_4$, and Alum at a fixed dose of 1.68g/l. Calcium hydroxide or lime (0.8 g/lit) was used as a flocculant with the above-mentioned coagulants for proper floc formation and pH maintenance.

The coagulation process was conducted though Jar test method by maintaining parameters such as agitation speed (150 rpm), temperature (27ºC), agitation time (5 minutes) and settling time (1 hour). The sample was filtered through whatman filter paper 42 (125 µm, What man manufacturing limited, USA). Coagulated samples were analyzed according to Lab protocols and compared. In order to optimize wastewater treatment efficiency, adsorption process was utilized using prepared adsorbent of bottom based coal ash (BBCA). Different dose ratios of BBCA adsorbent were mixed with wastewater samples in Jar test system. The process parameters in this case were maintained at 150 rpm for agitation speed for agitation time of 3 min and optimum contact time of 30 min. For adsorption equilibrium condition, treated water samples were filtered for elimination of ash through vacuum filtration system and analyzed (Mane *et al*., 2007).

Adsorptive capacity and adsorption (%) of BBCA adsorbent for dyes wastewater pollutants removal

The adsorption study for effluent pollutants was conducted with the use of BBCA, which was used as an adsorbent with variant doses and contact time and at fixed agitation speed. The adsorption % of effluent pollutants on ash adsorbent was calculated as under:

$$\% \text{ Sorption} = (C_i - C_f) *100/ C_f \qquad (1)$$

Where C_i and C_f are the initial and final concentrations in mg/l of effluent pollutants before and after adsorption process, respectively (Solangi *et al*., 2010). In the same way, the adsorption capacity (mg/g) was calculated by the following equation:

$$qe=(C_i-C_f)V/m \qquad (2)$$

Where qe is the adsorption capacity (mg/g), C_i and C_f are the initial and final concentration (mg/l) of pollutants in dyes effluent, respectively, V is the volume (mL) of effluent and m is the mass (g) of fly ash adsorbent (Memon *et al*., 2011).

3. RESULTS AND DISCUSSIONS

Elemental analysis of bottom based coal ash

The adsorption is a surface phenomena, the rate and degree of sorption is specific for given sorbent that is influenced by its physico-chemical properties such as surface area, pore size, surface area and composition (Kamboh *et al*., 2009). Material composition showed that bottom based coal ash (BBCA) have suitable chemical composition. Oxides of alumina, silica and iron in ash behaved also as good coagulants for the reduction of effluent pollutant's concentration. Due to high surface area, porosity and adsorption capacity, ash waste could work like activated carbon adsorbent. The percentage of oxides of iron and alumina was high in material composition of bottom ash. BBCA chemical behaviour proved highly effective for the treatment of industrial effluent as it has high surface area and less porosity. The sorption rate was affected much more by the particle size of adsorbent because bottom ash was not a high porous material. The smaller particle size of adsorbent results in higher specific surface area, which promotes external surface adsorption (Ugurlu, 2011). From SEM analysis of bottom coal ash, it was found that physico-chemical treatment enhanced the adsorption capacity, surface area and porosity of bottom ash. Adsorption capacity was mainly due to their structural characteristics and their porous texture, which gives them a large surface area, and because of their chemical nature, which can easily be modified by chemical treatment in order to increase their adsorptive properties. Effective effluent treatment via adsorption depends upon porosity, chemical structure, particle size, surface area and adsorption capacity of ash adsorbent. Low surface area (1.77 m^2/g) of BBCA adsorbent showed upon its analysis that the ash particles did not have too many micro pores (Dincer *et al*., 2007).

Determination of adsorptive capacity of BBCA

Adsorptive capacity of prepared material allowed the removal from dyes wastewater of either the color or soluble and suspended organic pollutants. The bottom ash was found to have good settling capacity, which enabled it to remove suspended solids by behaving as a settling aid. Industrial dyes effluent sample (100 ml) was treated via adsorption process using prepared BBCA adsorbent with different doses to effect the removal of effluent pollutants. From adsorption study, it was concluded that BBCA has high potential for adsorption of effluent pollutants. From experimental study, it was found that all BBCA showed higher adsorptive capacity at lowest dosage (2g/100ml). On increasing adsorbent dosage, less adsorption rate was found in all used fly ashes **(Table 1 and Fig.3)**. This suggests that with 2 g or higher of the adsorbent dosage did not improve adsorption efficiency. This may be due to the availability of more adsorbent surfaces for effluent pollutants to be adsorbed (Kamboh *et al*., 2011).

Table 1: Bottom based coal ash adsorbent dosage effect on the adsorptive capacity for industrial effluent pollutants removal

Adsorbent Dosage (g/ 100ml)	COD Removal (mg/g)	Color Reduction (mg/g)	Turbidity Removal (mg/g)	Total Suspended Solids Removal (mg/g)
2	17	111	22	16
4	7	49	10	8
6	5	40	7	5
8	4	32	6	4

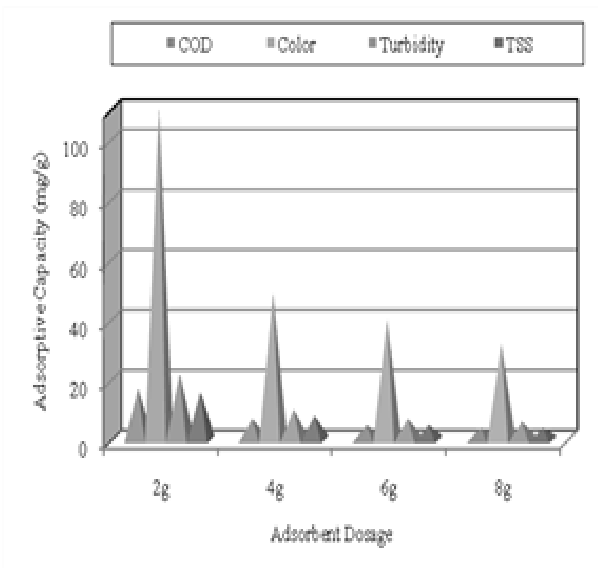

Fig. 3: Adsorptive capacity (qe) of bottom based coal ash adsorbent at dose variations in treatment of industrial dyes wastewater.

Adsorption isotherm models study

Sorption isotherms are used for measuring the concentration of the sorbate in the medium before and after sorption, at constant temperature (27 ^{0}C). These isotherm models are used to study of liquid/solid phase sorption behaviour, sorption capacity, structure of sorbed layer and interaction between sorbate and sorbent (Kamboh *et al*., 2011). Isotherms of Freundlich and Langmuir were very prominent to explain the nature of sorption (Memon *et al*., 2011). Langmuir isotherm model assumes monolayer coverage of the adsorbate on a homogeneous surface of adsorbent. Freundlich isotherm model suggests the heterogeneity of the adsorbent surface and multilayer (Kamboh *et al*., 2011). A multilayer sorption involves the distribution of active sites that is the characteristic of heterogeneous surfaces. Monolayer adsorption involve the sorption take place on fixed number of sorption sites confined to monolayer with no transfer of sorbate on the plane of surface (Memon *et al*., 2011). The experimental data was analyzed by using the linear forms of Langmuir and freundlich isotherm models in the following way:

$$(Ce/Cad) = (1/Qb) + (Ce/Q) \quad (3)$$
$$\ln Cad = \ln A + (1/n)\ln Ce \quad (4)$$

Where Cads is the amount of sorbate (mg/g) at the sorbent surface and Ce is the amount of sorbate in the liquid phase at equilibrium (mg/l). 1/n is sorption intensity, b is Langmuir constant (l/mg), Q is monolayer sorption capacity (mg/g). The value of sorption intensity ($1<n<10$) indicates that sorption is favourable. The magnitude of sorption isotherm constants, gives an indication of favourability and unavoidability of sorption process (Memon *et al*., 2011). The value of Langmuir constant b was calculated from the slope and intercept of the plot of Ce/Cads vs. Ce (Kamboh *et al*., 2011). For understanding interactive behaviour of the ash adsorbent and adsorbate, two adsorption isotherm models such as Langmuir and Freundlich models were used. Adsorption correlation co-efficient (R^2) of bottom based coal ash was determined for adsorption of dyes effluent pollutants such as COD, color, turbidity and TSS as shown in **(Table 2)**.

Table 2: Langmuir and Freundlich constants for adsorption of dyes wastewater pollutants

Langmuir Equation			Freundlich Equation			
	b L/mg	R^2	A mg/g	n	1/n	R^2
COD	-121.3	0.962	$1.2*10^{90}$	0.0734	13.62	0.970
Color	15.86	0.918	$5.2*10^{-8}$	0.544	1.838	0.844
Turbidity	11.53	0.781	$8.7*10^{-8}$	0.5431	1.84	0.934
TSS	1.032	0.762	$3.990*10^{-3}$	0.544	1.838	0.939

Treatment of industrial dyes wastewater through adsorption process

In initial phase, treatment of industrial dyes wastewater was performed by adsorption via the effect of using bottom coal ash as adsorbent. It was observed that higher wastewater pollutants removal rate was achieved at optimum dose (8g/100 ml) of adsorbent. On increasing further dose, small increase in removal rate was observed. Optimum dosage and contact time (30 minutes) gave good results in adsorption rates and adsorption reached in equilibrium state. On increasing adsorbent dosage helped in high adsorption of effluent pollutants but at specific limit. Reduction rate of COD (43%), color (55%), turbidity (53%) and total suspended solids (87%) was observed at optimum dosage (8g/100 ml) of adsorbent. These pollutants got interacted with the ash adsorbent pores on its surface area and thus were captured in the pores until equilibrium condition was achieved. Turbid material of the effluent was also captured in the pores of ash adsorbent. High porosity also reduced high concentration rate of turbidity. When adsorption equilibrium occurred, maximum contact time did not reduce pollutants concentration rate of effluent and thus it stopped the adsorption process **(Fig. 4)**. Dincer *et al*. reduced COD of coking wastewater and paper making wastewater by 45% and 40.6% respectively with the use of bottom ash. They also obtained the color reduction rate from 45-76% by decreasing particle sizes of bottom ash, ranging from 2–6 mm to <0.074 mm (Dincer *et al*., 2007).

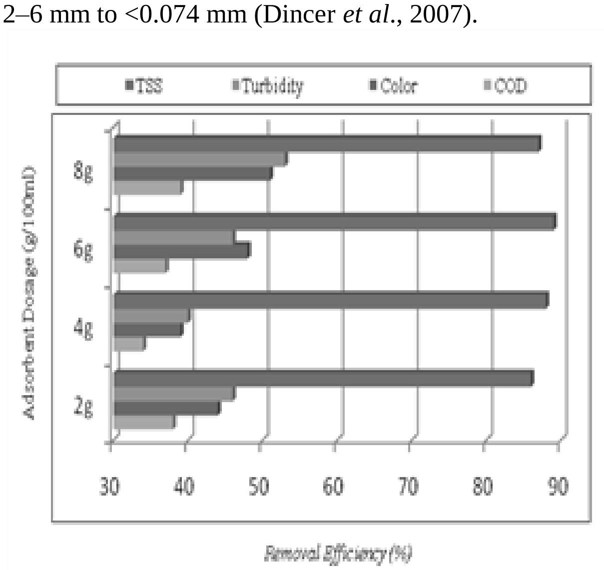

Fig.4: Treatment of industrial dyes wastewater through bottom based Coal ash with variant doses.

Treatment of industrial dyes wastewater through hybrid process of coagulation-adsorption.

Treatment with ferric Chloride-lime and BBCA adsorbent.

The industrial dyes wastewater was treated by use of hybrid process of chemical coagulation and adsorption. Wastewater sample was treated by ferric chloride-lime at specific parameters. After coagulation treatment, same sample was treated through adsorption technique by use of prepared adsorbent of bottom based coal ash at dose variations. From experimental study, it was concluded that $FeCl_3$-lime treatment could reduce COD (49%), color (73%), turbidity (75%) and TSS (93%) of dyes wastewater. When coagulated samples were treated through adsorbent at dose variations, it was found that higher rate of wastewater pollutant removal could be achieved at adsorbent dose of 4g/100 ml. It caused reduction in COD, color, turbidity and TSS by 61%, 82%, 84% and 95% respectively **(Fig. 5)**. Simultaneous process of coagulation-adsorption enhanced the pollutants removal rate. This prepared adsorbent showed good performance in industrial wastewater treatment due to its physical properties and chemical behaviour. Higher dosing of adsorbent than 4 g did not show better results in terms of reduction in pollutants' concentration as steady state condition was observed with higher dosing of adsorbent. The complex mixture of coagulants and bottom ash adsorbent behaved effectively in the complex nature of dyes and helped in higher reduction of wastewater pollutants. Joo *et al*., reduced the concentration of turbidity (80.5%) and COD (86%) of textile wastewater at $FeCl_3$-Powdered activated carbon (PAC) dose (40mg/l-20mg/l) respectively (Joo *et al*., 2007).

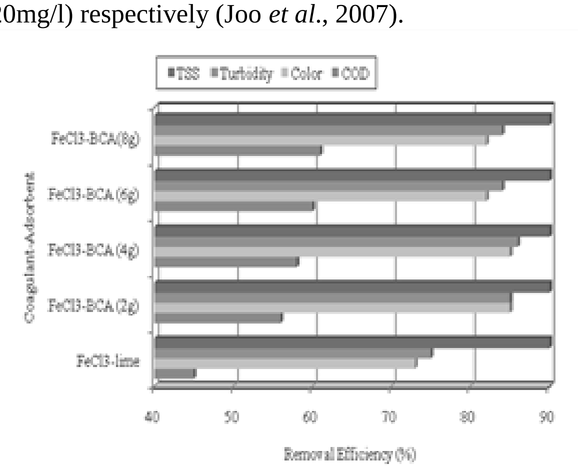

Fig.5: Treatment of industrial dyes wastewater using $FeCl_3$-Lime and BBCA adsorbent at dose variations.

Treatment with Ferrous Sulfate-lime and BBCA adsorbent

Industrial dyes wastewater was treated through simultaneous process of coagulation-adsorption by the use of ferrous sulfate coagulant and bottom based coal ash adsorbent. In this coagulation process lime was used as flocculant as well as pH maintaining agent. The combinations of $FeSO_4$ and lime in coagulation process did not prove effective for the reduction of pollutants, because, neither there was any proper formation of sludge nor proper flocculation. In this case, removal rate remained lower than 10%. Dyes wastewater components probably did not behave with this coagulant and remained ineffective in treatment area. When coagulated samples were further treated with prepared adsorbent at dose variations, higher removal efficiency was analyzed due to complex chemical behaviour of coagulant, adsorbent and presence of chemical compounds. Adsorbent showed good performance due to surface area, porosity and chemical composition. This combined process showed an effective treatment. At optimum adsorbent dose (4g/100 ml), resulted in the reduction of COD (61%), color (93%), turbidity (93%) and TSS (95%). It was concluded from experimental work that ferrous sulfate coagulant was ineffective in dyes wastewater treatment, but its further treatment efficiency was enhanced by the use of bottom based coal ash adsorbent. In this treatment process, higher dosage did not give better results than 4g. As a result, small variations in pollutants reduction were found as illustrated in **(Fig. 6)**. Dincer *et al*. reported the removal of organic compounds from paper making and coking wastewater, but they could reduce maximum COD by 27.8% and 45.8% respectively at dosing 12.5g/ 100ml of bottom based coal ash (Dincer *et al.*, 2007).

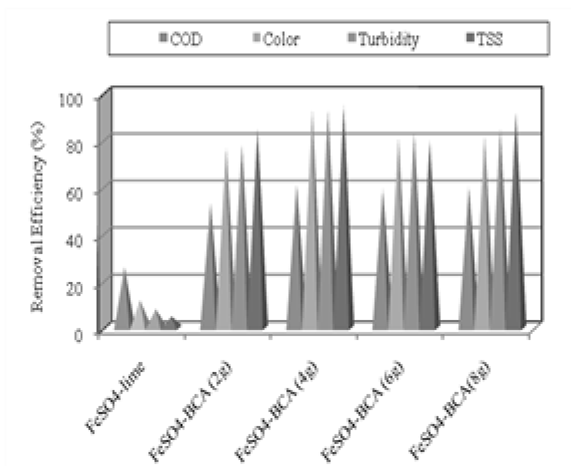

Fig. 6: Treatment of industrial dyes wastewater using FeSO4-lime and BBCA adsorbent with variant doses .

Treatment with Alum-lime and with bottom based coal ash adsorbent

In this coagulation run, alum-lime coagulants were tested for wastewater pollutants reduction. From the experimental work, it was found that Alum coagulant could reduce higher rate of pollutants effectively because it was reacted with dyes compounds and formed sludge due to formation of solids precipitates. All organic dyes compounds were captured in sludge. Lime was also used as flocculants and pH maintaining agent. Alum and other coagulants reduced pH of wastewater in acidic form, which is highly prohibited in disposal regulations. Acidic nature of wastewater declined treatment efficiency of coagulation process. Alum-lime coagulation abridged the wastewater pollutants by COD (41%), color (57%), turbidity (60%) and TSS (93%). This coagulated sample was further treated through adsorption technique via the use of coal ash adsorbent. The effect of adsorbent dosage was analyzed in pollutant reduction. It was concluded from experimental work that higher removal rate was achieved at optimum dose of 8g/100ml. It reduced COD (60%), color (77%), turbidity (79%) and TSS (93%) effectively. An increase in adsorbent dosage, the removal rate was increased to some extent as small variations in reduction rates were analyzed **(Fig. 7)**. Maximum contact time between adsorbent and water sample reduced higher rates of pollutants until adsorption equilibrium occurred.

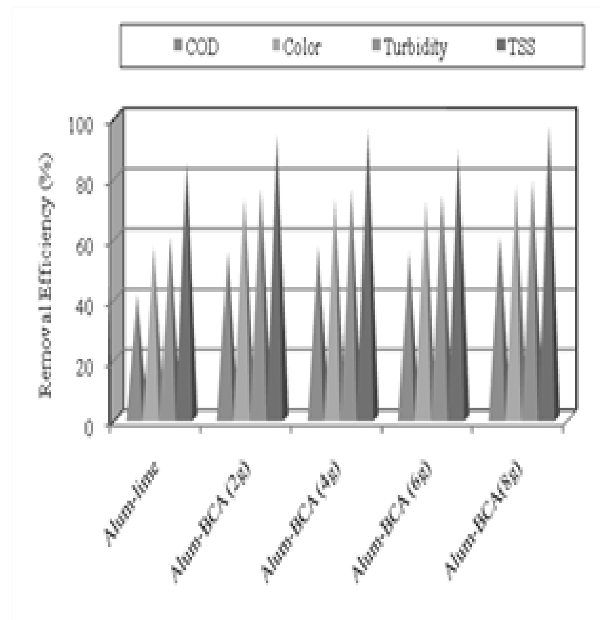

Fig.7: Treatment of industrial dyes wastewater using Alum-lime and BBCA- adsorbent at dose variations.

Comparative study for hybrid process of coagulation-adsorption

Comparative study of the hybrid processes was done for analyzing the most effective combinations of coagulants and adsorbent. From experimental work, it was concluded that FeCl3-lime, FeSO4-lime, Alum-lime and bottom based coal ash adsorbent reduced overall pollutants percent as 70%, 15%, 63% and 54% respectively. When these coagulants and ash adsorbent were used simultaneously, the pollutants reduction rate was increased. The combinations of FeCl3-BBCA, FeSO4-BBCA and Alum-BBCA could reduce overall pollutants by 80%, 78% and 73% respectively. These results suggested that combination of FeCl3-BBCA was the most effective for reduction of pollutants from highly concentrated dyes wastewater. Though FeSO4-lime treatment yielded lower results than other coagulants, but their combination with the adsorbent resulted in increased removal efficiency, which was even higher than other combinations **(Fig. 8)**.

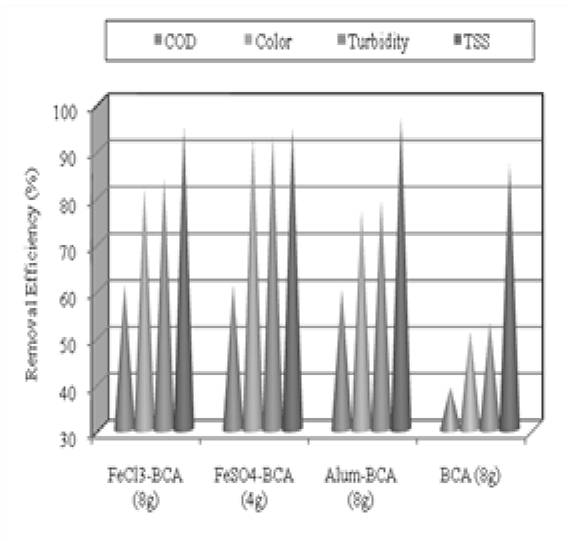

Fig.8: Comparative treatment efficiency of combined coagulants and adsorbent for industrial wastewater pollutants removal.

4. CONCLUSION

From this research work, it was concluded that single coagulation or adsorption was unsuitable for industrial dyes wastewater treatment as their treatment efficiency varied form 15-60%. However, hybrid process of coagulation and adsorption optimized treatment efficiency up to 80%. The treatment efficiency of $FeCl_3$-BBCA, $FeSO_4$-BBCA and Alum-BBCA was observed as 80%, 78% and 73% respectively. These results suggest that bottom based coal ash can be used as an adsorbent instead of powdered activated carbon with suitable commercial coagulants due to its higher adsorption rate and economical cost for dyes wastewater treatment.

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