Exploitation of Low Cost Coal Fly Ash Adsorbent with Coagulants for the Treatment of Industrial Complex Nature Dyes Wastewater

Abdul Karim Shah, Zeenat M. Ali, Abdul Rehman Memon, A. Jabbar Laghari, Moina Akhtar Mughal, Syed Farman Ali Shah, Hussain Saleem

Abstract:

Dyes manufacturing industries are disposing of 100 tons of toxic dyes into water per annum which generates highly toxic wastewater, which harm the marine and aquatic life. Present research study was conducted to optimize the pollutant reduction rate of dyes wastewater using hybrid process of chemical coagulation and adsorption. Low cost and prepared an adsorbent which was more effective from coal of Lakhra Power Plant Jamshoro's waste through physical and chemical treatment and was utilized in conjunction with commercial coagulants such as Ferric Chloride ($FeCl_3$), Ferrous Sulfate ($FeSO_4$) and Alum. Treatment efficiency of individual and combined process was analyzed for the reduction of turbidity, Chemical Oxygen Demand (COD), Color and total suspended solids (TSS) from dyes wastewater. Overall treatment efficiency of $FeCl_3$, $FeSO_4$, Alum and Ash adsorbent was determined by 57%, 20%, 63% and 58% respectively. Hybrid process of $FeCl_3$-CFA, $FeSO_4$-CFA and Alum-CFA have reduced the concentration of pollutants by approximately 73%, 60% and 68% respectively. The adsorptive capacity and adsorption percent of Ash adsorbent was determined. The adsorptive capacity of adsorbent declined on the ever-increasing adsorbent quantity. The adsorption behavior of Ash adsorbent in dyes wastewater pollutants removal was measured using Langmuir and Freundlich isotherm models. Freundlich model with isotherms found appropriate for the effluent pollutants adsorption.

Keywords: Dyes Wastewater, Coagulation-Adsorption, pollutant

1. INTRODUCTION

Manufacturing of dyes and industries mainly textiles are one of the main users of municipal water along with chemicals during processing and manufacturing of textiles and dyes. These industries are major problematic groups because these are continuously disposing about 100 tons of poisonous dyes annually into wastewater streams (Sun et al., 2010)**.** Recent studies suggest that 10,000 dyes of different nature produced and consumed annually are multiplied up to $7*10^5$ tons (Kamboh et al., 2011). Utilization of water by such industries during cleaning and processing generate poisonous effluents thereby pollute river and sea waters (Namsivayam et al., 2001). Textile and dye industries require it mandatory to treat such polluted effluents before discharging them into estuaries, because these effluents possess high degree of contaminants such as; intense color, pH, Biochemical oxygen demand (BOD), alkaline substances, Chemical oxygen demand (COD), temperatures, turbidity, heavy metals, acids, and toxic substances (Hsu and Chiang, 1997). The complex dyes wastewater is the mixture of dyes, raw chemicals, binder, pigments, textile chemicals and other many toxic chemicals used in the manufacturing of dyes and textile chemicals. The simple process is ineffective in the degradation of dyes and phenolic compounds. The treatment efficiency of individual process varies according to the nature, rate of pollution load and chemical composition. The industries also focusing on the process efficiency, recovery of raw material losses, installation, operation and maintenance cost of treatment process. In this fact, chemical coagulation is most practiced process in industries used for the general treatment of wastewater. This process is cost effective and gives good performance. But in case of complex dyes wastewater this process efficiency declined due to its complexity. The adsorption technique is considered as good treatment process for the adsorption of pollutants of wastewater, but regeneration cost of adsorbent is critical problem. From the literature survey it has been reported that fly ash has good tendency in adsorption of dyes and break up of phenolic compounds. Worldwide production of coal fly ash is 600 million tons annually. Coal reserves at

Lakhra for power generation are 1328 million tons. Current coal fly ash generation by Khanote FBC power plant is estimated at 55680 m^3/hr (Aziz et al., 2010).

In this regards, the coal fly ash waste of power plant was considered for the preparation of low cost adsorbent in order to reduce pollution load of coal power plant and make it useful for industrial wastewater treatment at low cost. The prepared adsorbent was combined the commercial coagulants in order to optimize the effluent pollutants reduction rate and treatment process efficiency.

2. MATERIALS AND METHODS

2.1. Collection of Industrial Wastewater Samples

The complex dyes wastewater was generated from various manufacturing plants of dyes, textile chemicals, pigments, pharmaceuticals and binder emulsion during chemical reactions, washing and cleaning of reactors, vessels and other equipments. This wastewater was the complex mixture of variety of toxic dyes, textile chemicals, pigments, monomers, polymers, plasticizers, lubricants, catalysts, pharma chemicals and many other used chemicals. These plants's wastewater was assorted and stored in the effluent treatment pond for treatment purpose through coagulation and biological aeration process. These samples were collected before and after treatment for analysis and research work. These samples were sampled and stored at room temperature according to the laboratory protocols.

Table:1 Characteristics of industrial dyes wastewater

Effluent Pollutants	
Total Dissolved Solids	2400 mg/lit
Electrical Conductivity	3750 µS/cm
pH	8-10
COD	1164 mg/lit
Color	6560 ptco
Turbidity	1280 FTU
Total Suspended Solids	349 mg/lit

2.2. Collection of Coagulants and Low Cost Adsorbent

To carry out the research work, the commercial coagulants were collected from the effluent treatment laboratory of Clariant limited Pakistan, Jamshoro. Coal fly ash as waste of coal power plant was collected from the electrostatic precipitator of fluidized bed combustion (FBC) technology at *Lakhra Power* Generation Company Limited, Jamshoro, Pakistan.

2.3. Material Analysis of Low Cost Adsorbent

For the determination of elemental composition of coal fly ash, sealed packed ash samples were proceed to Fuel Research Laboratory Pakistan Council of Scientific and Research (PCSIR) Karachi for the material analysis of ash. Its composition (w/v) is reported as: Lithium oxide (LiO) (14.48%), Silica Oxide (SiO_2) (23.61%), Aluminum tri-oxide (Al_2O_3) (14.09%), ferric oxide (Fe_2O_3) (9.15%), Calcium oxide (CaO) (22.89%), Magnesium oxide (MgO) (2.71%), Silica tri-oxide (SO_3) (13.13%) (Aziz et al., 2010).

2.4. Preparation of Low Cost Adsorbent from Power Plant Waste

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Preparation of fly ash adsorbent consists of sieving, pretreatment, washing and drying steps. Coal fly ash (FA) screened at 290 rpm speed by RO-Tap Type Sieve shaker (A-871205, Heiko Seisakusho Tokyo Japan). Fine fly ash (mesh 200, Aperture 25 um, wires dia 25µm) obtained from Sieve (IIDA Model, Japan) was used as adsorbent. Vacuum filtration system with porcelain Buchner funnel having Whatman 42 filter paper (Ash less grade (Ash 0.007%, UK) was used for ash sample filtration at 60 ^{o}C for five times and dried. Then ash sample was washed with 10% diluted sulfuric acid and at last washed with deionized water to remove sulfuric acid. The ash sample heated in oven (Lo-201C, USA) at 110 ^{0}C temperature for 24 hours for activation of ash as adsorbent. The samples thus prepared were cooled at ambient temperature and sieved, if needed (Rao, 2006).

2.5 Determination of Microstructure and Surface Morphology of Coal Fly Ash

Microstructure and surface morphology of raw and adsorbent coal fly ash samples were characterized by Scanning Electron Microscope (SEM) **(**JEOL 6490 LV – SEM by JAPAN) with accelerating voltage of 25.0 kV at a magnification x250 to x2500 Fig [ ] that of raw coal material and x1000 to x4000 for adsorbent coal sample Fig. [ ] (Wang et al., 2008) with courtesy of Centre for Pure and Applied Geology, University of Sindh, Jamshoro, Pakistan.

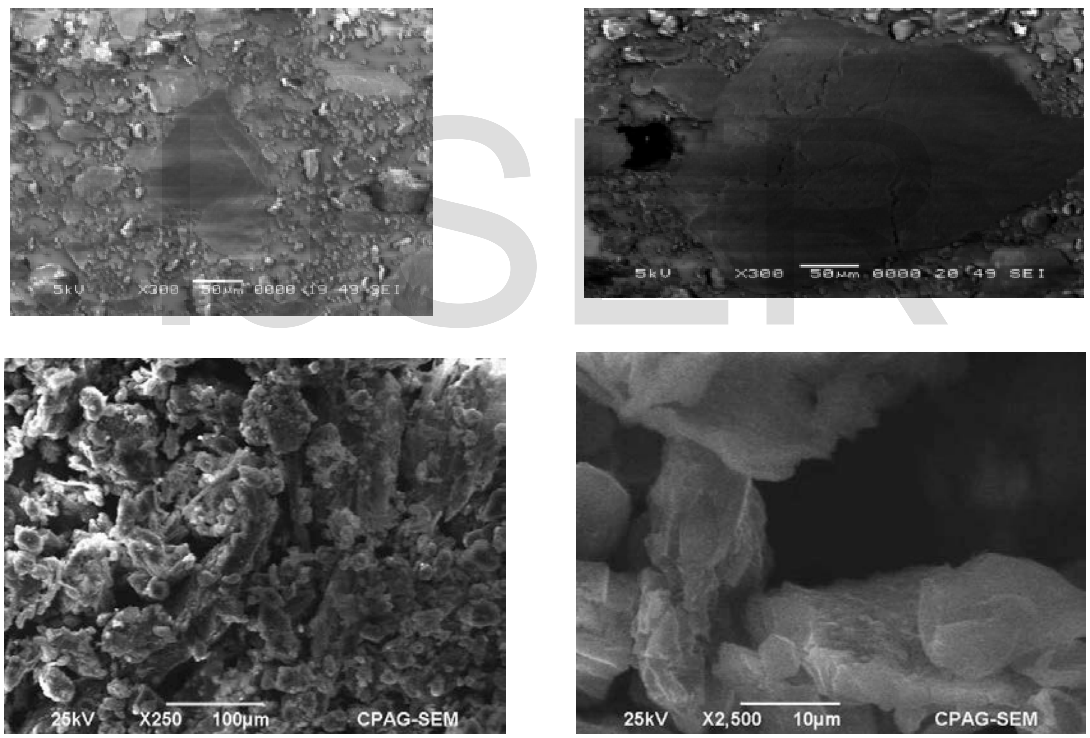

Fig. (a) RAW Coal (Untreated) (b)

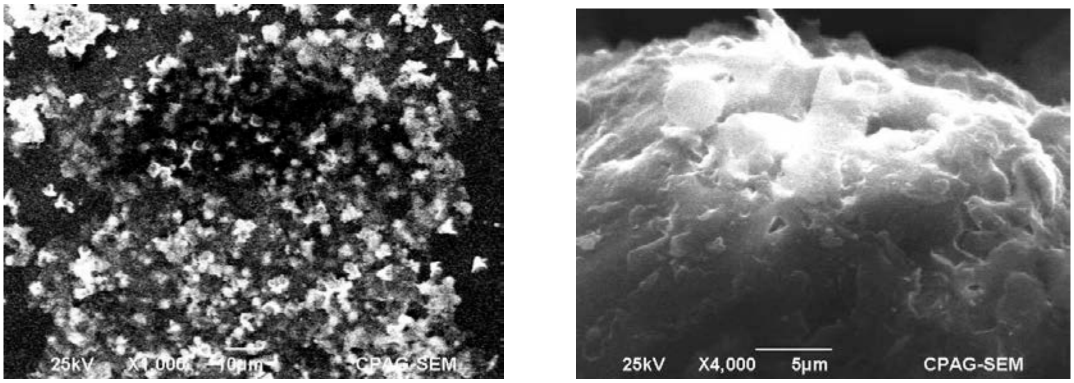

Fig. (a) Adsorbent Coal (Treated) (b)

Fig. 1. SEM images of raw and treated fly ash

2.6 Analysis of Complex Nature Dyes Wastewater

pH of the wastewater sample was measured by pre-calibrated pH meter (Dincer et al., 2008) (SENSION 378, Model No. 5475012, Company Limited, Hach, Loveland, Colorado. USA). Total dissolved solids (TDS) of the wastewater samples were measured using laboratory Conductivity meter (Sension 378, Model No. 5475017, Hach Company, and Loveland, Colorado, USA). Chemical Oxygen Demand (COD) of wastewater was determined by conventional COD technique, measuring COD with treatment of sulfuric acid, potassium dichromate and mercury(II) sulfate (E. Merck, Germany) in proportionate ratios in vials. COD vials containing ash samples were heated for 2 hrs in COD heater (TR-320, Merck, USA) at 148 ^{0}C for completion of reaction, cooled for 30 minutes and observed COD on spectrophotometer (DR-2000, Hach, USA), at 620nm wavelength, wastewater Color at 455nm wavelength, wastewater total suspended solids (TSS) at 810nm wavelength, turbidity at 450nm wavelength (Devi et al, 2008).

2.8 Treatment of Wastewater by Individual and Hybrid Process

The collected wastewater samples were treated in the 500 ml beaker by addition of ferric chloride, ferrous sulfate, alum and calcium hydroxide individually at dose of 1.2 grams/250ml. The coagulation process was carried out at room temperature by maintaining agitation speed (150 rpm) for 5 minutes and was then settle down for 1 hour for formation of precipitates in order to remove pollutants. The coagulated samples were filtered through whatmann filter paper (125 µm, Whatman manufacturing Co. Ltd, UK) and then were pre-analyzed. These coagulated samples were further treated through adsorption process using prepared ash adsorbent. Coagulated samples (100ml) individually were treated with ash adsorbent at dosing of 2g, 4g, 6g, 8g by maintaining process parameters as mixing time (5 minutes), optimum contact time (30 minutes), temperature (30 ºC). After 30 minutes settling time, these samples were filtered through whatmann filter paper (125 µm) through vacuum filtration system and were then analyzed according to standard protocols. The treatment efficiency of single and hybrid process was compared after specific calculation (Shah et al., 2012).

2.9 Determination of Adsorption (%) and Adsorptive Capacity (qe) of Ash Adsorbent

Study of effluents with regard to dosage of adsorption capacity, its contact time and speed of agitation when treated with fly ash was carried out. Calculations regarding adsorption of effluents on fly ash adsorbent were done by following:

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

Where C_i (mg/l) represents initial concentration of effluents before process of adsorption and C_f (mg/l) represents final concentration after adsorption of effluents (Solangi et al., 2010).
Likewise capacity of adsorption (mg/g) was measured as follows:

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

Here Q_e represents capacity of adsorption (mg/g), C_i and C_e represents concentrations at initial and equilibrium states(mg/l) in dyes effluent respectively, V represents volume (mL) and m the mass (g) of fly ash adsorbent (Memon et al., 2011).

3. RESULTS AND DISCUSSION

3.1 Characteristics and Adsorptive Capacity of Fly Ash Adsorbent

From the material composition and structure morphology, it was found that fly ash contains oxides of magnesium, calcium, silica, ferrous and alumina which behave as coagulants in hybrid process. Coal fly ash has low porosity but high surface area which is capable to adsorb higher concentration of pollutants from highly polluted wastewater (**Fig.1**). Particle size affects the adsorption process due to fly ash being less porous type material. The specific surface area is inversely proportional to particle size (Ugurlu et al., 2011). With particle size of fly ash 120-960µm the surface area should be 2500 to 7000 cm^2/g, specific gravity 2.3- 2.5, pore volume 0.023 cm^3/g and density 600-900 kg/m^3(Ramakrishna and Viraraghavan, 1997).

Table 2: Coal fly ash adsorbent dosage effect on the adsorptive capacity for industrial effluent pollutants removal

	Adsorptive Capacity (mg/g)			
Dose	**2g**	**4g**	**6g**	**8g**
COD	16	9	7	5
Color	114	56	40	33
Turbidity	22	11	8	6
TSS	16	8	5	4

After treatment of wastewater through adsorption, the adsorptive capacity of prepared low cost adsorbent was determined for each specific pollutant at dose variations. Fly ash adsorptive capacity is bound to remove color and suspended solids as pollutants from dyes of the wastewater; it shows enhanced settling ability of the fly ash material (Rao et al, 2006). From the observation and calculations, it was found that adsorptive capacity of fly ash for all pollutants was higher at lowest dose (2g/100ml). The adsorptive capacity declined in ever-increasing the adsorbent dosage (**Table 2 and Fig.2**).

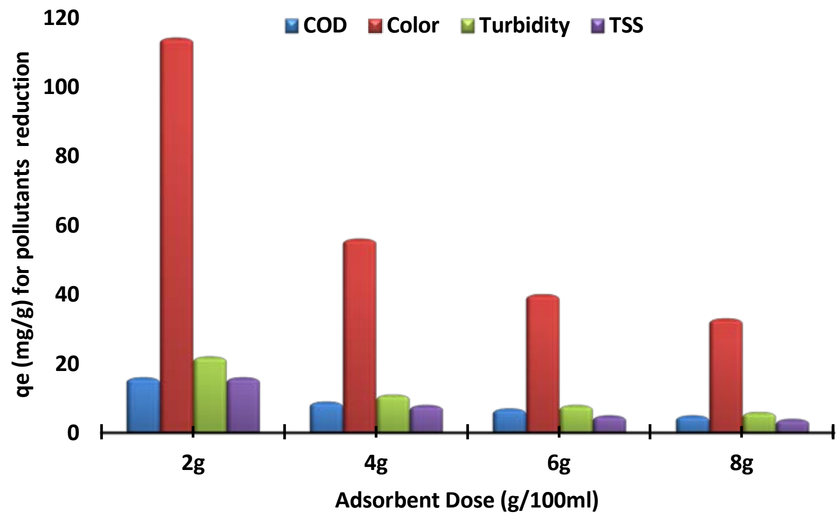

Fig. 2 Adsorptive capacity of fly ash adsorbent for pollutants reduction

3.2 Treatment of Complex Nature Dyes Wastewater

3.2.1 Treatment through Individual Process of Coagulation

When highly polluted dyes wastewater was treated via coagulation technique using ferric chloride, ferrous sulfate and alum along with calcium hydroxide as flocculant. From the experimental work and calculations, it was observed that ferric chloride and alum coagulants are more suitable for the reduction of pollutants from dyes wastewater. Ferrous sulfate coagulant did not show good efficiency for reduction of pollutants because it neither form solid precipitates nor settle downs impurities. Overall efficiency of $FeCl_3$-lime, $FeSO_4$-lime and Alum-lime was determined by 72%, 63%, 42% and 20% for reduction in COD values, color of the solution, tentative turbidity values and TSS respectively. TDS, salinity and conductivity improves by this treatment. $FeCl_3$-lime and Alum-lime condensed the COD (49% & 41%), turbidity (75% & 60%), color (73% & 57%) and TSS (92% & 93%). It was observed that pH of wastewater declined up to 20%. $FeCl_3$ coagulation declined pH swiftly. Alum coagulation declined pH at low rate (<10%). From the coagulation treatment and analysis, it was found that $FeCl_3$ coagulant is most effective in the removing COD, color, total suspended solids and turbidity.

3.2.2 Wastewater Treatment through Adsorption Process

The research study was conducted in order to determine treatment efficiency of adsorption using fly ash adsorbent for the reduction of dyes wastewater pollutants. The effects of adsorbent dosing were determined in reduction of pollutants rates. It was observed that high dosing of adsorbent gave increased removal efficiency for pollutants. Whereas reduced dosage of adsorbent (2g/100ml) reduces COD (37%), color (46%), turbidity (47%) and TSS (89%). The optimum dosage (8g/100ml) produced reduced COD (49%), color (53%), turbidity (55%) and TSS (92%). From the material analysis, it was found that fly ash has low porosity but have high surface area, which make it capable for the adsorption of pollutants on its surface. The chemical components of fly ash also behaved as coagulants and helped in pollutants reduction. At 30miuntes, the equilibrium condition was observed for all specific pollutants at constant temperature 30 ºC (**Fig.3**).

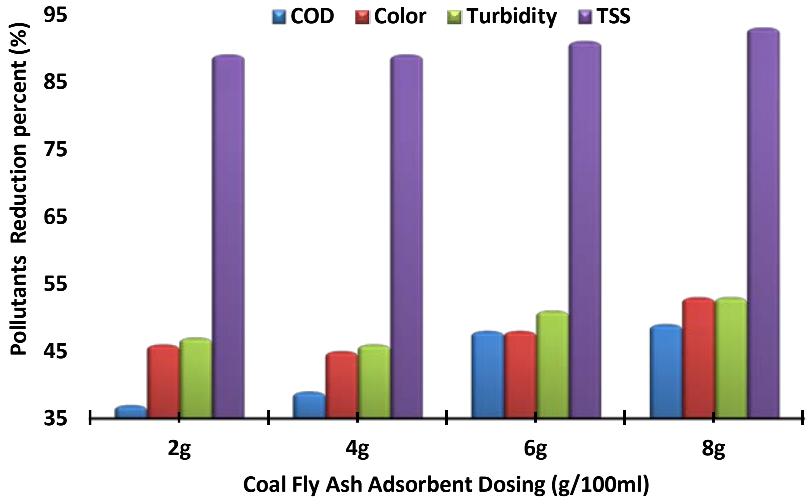

Fig. 3 Pollutant reduction percent of wastewater in adsorption treatment

3.2.3 Treatment through hybrid process of ferric chloride and ash adsorbent

From the above statement observation, it was found that ferric chloride is most effective in complex nature wastewater. The $FeCl_3$ coagulated sample was reacted with variable dosage of coal fly ash as adsorbent at specific parameters. From the observation and laboratory work, it was observed that $FeCl_3$ and coal fly ash as adsorbent combination helped remove COD (63%), turbidity (89%), Color (89%) and total suspended solids (91%) when applied at 8g adsorbent dosage. Whereas electrical conductivity and TDS increased in both cases while decline in pH observed (Fig.4). The reports regarding wastewater of dyes sample when treated with 40mg/L $FeCl_3$ reduced turbidity (66%) and COD (73%), (Joo et al, 2007). It was already discussed that this wastewater has high complexity nature and treatment efficiency varies according to its nature and complexity. The combinations of coagulants and adsorbent behaved chemically and effectively. Many chemical reactions were carried out in contact with dyes and different chemicals which changed the composition and nature of present components of dyes wastewater (**Fig.4**).

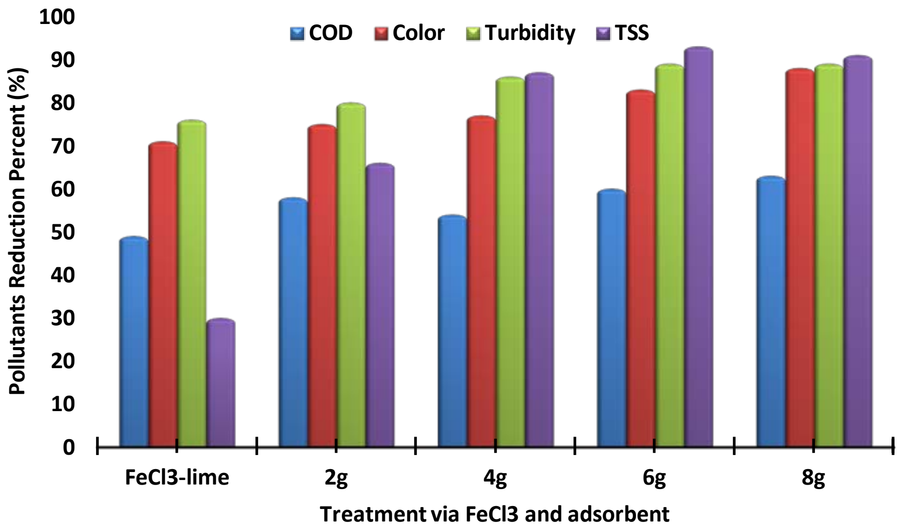

Fig. 4. Treatment of dyes wastewater through $FeCl_3$-lime and ash adsorbent

3.2.4 Treatment through hybrid process of ferrous sulfate and ash adsorbent

When highly polluted wastewater sample was treated via Ferrous sulfate coagulation technique at specific parameters. From experimental work, it was found that ferrous sulfate coagulant could out show good performance in case of pollutants reduction because it did not form any solid precipitates. Its overall performance remained up to 20%. After this treatment, samples were treated with prepared fly ash adsorbent at dose variations. The hybrid process of these combinations improved the treatment efficiency and reduced pollution load of wastewater. The overall performance was improved up to 60%. At lowest dose of ash adsorbent (2g/100ml), it decreased color (68), COD (35%), TSS (83%) and turbidity (69%). It was concluded that in ever increasing adsorbent dose in coagulated sample, reduction rate was improved along with performance efficiency. At optimum dose (8g/100ml) of adsorbent, it reduced the concentration of COD (51%), color (81%), turbidity (82%) and TSS (98%) (**Fig.5**). The weak performance of ferrous sulfate was covered fly ash adsorbent combinations due to their chemical composition and other characteristics. pH rate of wastewater decreased along with increasing adsorbent dose. At 8g adsorbent, 32% pH decline rate was observed. Adsorbent dosage when increased resulted in improved efficiency of salinity, TDS and conductivity.

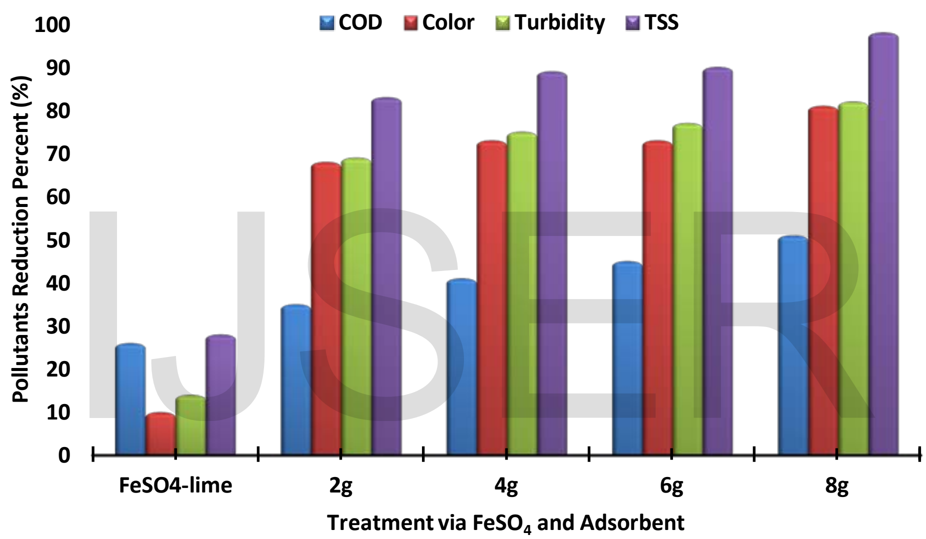

Fig. 5. Treatment of dyes wastewater through $FeSO_4$-lime and ash adsorbent

3.2.5 Treatment through Hybrid Process of Alum and Ash Adsorbent

The wastewater dyes sample; highly polluted was examined via coagulation system combined with variable doses of Alum-lime. The hybrid process resulted in decrease of pollutants; color (59%), COD (41%), TSS (89%) and turbidity (63%). The hybrid process with variable dosages was further reacted with coal fly ash. The effects of adsorbent dosing along with alum coagulants on wastewater pollutants reduction rate were determined. From experimental work, it was found that optimum removal rate of pollutants was observed at 4g adsorbent dose, where reduction was observed up color (69%), COD (46%), TSS (93%), and turbidity (72%). On increasing dosing of adsorbent, higher removal rate could not find. At 2g/100 ml adsorbent dosing, it reduced the COD (47%), color (67%), turbidity (70%) and TSS (90%). In this case, the pH of wastewater was increased slightly up to 15%. Whereas 30% improvement was observed in salinity, TDS and conductivity, but lesser as compared to other combinations. Higher COD removal rate (70%) was observed in dosing of 8g, but other pollutants reduction ratio was lower as compared with above described dosing (**Fig.6).**

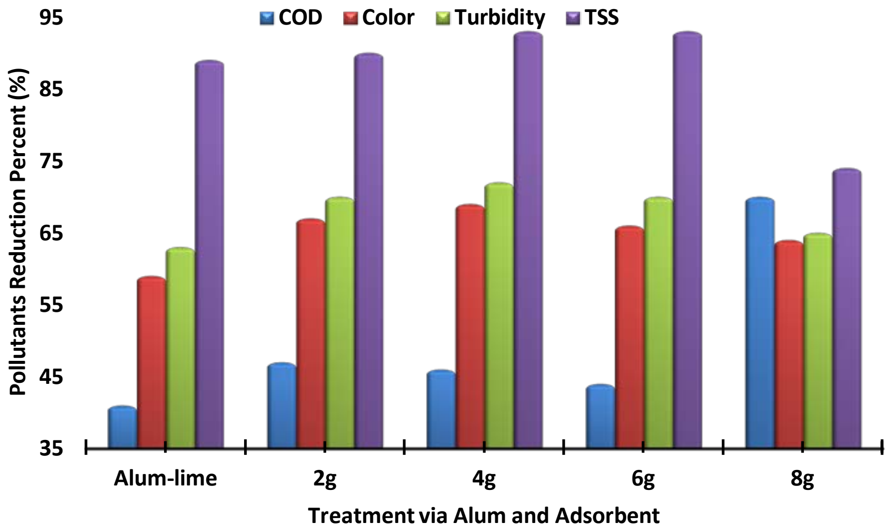

Fig. 6. Treatment of dyes wastewater through Alum-lime and ash adsorbent

3.3 Adsorption Isotherm Models Study

These isotherms models have been reported for solid/liquid sorption behavior, capacity, structure and interaction involving sorbent and sorbate (Kamboh et al., 2011). Freundlich and Langmuir Isotherms explain the nature of sorption process (Memon et al., 2011). Adsorbate according to Langmuir model covers homogenous monolayer on the surface of adsorbent. On the contrary adsorbate maintains heterogeneity according to Freundlich model on the surface of adsorbent (Kamboh et al., 2011). The data obtained have been examined in line with Freundlich & Langmuir models using the linear forms as follows:

$$(Ce/Cad) = (1/Qb) + (Ce/Q) \quad (3)$$

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

The study suggests Freundlich model as the best isotherm models for effluent pollutants. It showed that there is heterogeneity of the adsorbent surface and multilayer formation on the fly ash adsorbent (**Table 3**).

Table 3: Langmuir and Freundlich constants of fly ash adsorbent for effluent pollutants

	Langmuir Isotherm			Freundlich Isotherm			
CFA	**b** L/mg	R_L	R^2	**A** mg/g	**n**	**1/n**	R^2
COD	16.65	$5.16*10^{-5}$	0686	$9.77*10^{-12}$	0.4048	2.4703	0.890
Color	19.25	$7.9*10^{-6}$	0.864	$1.513*10^{-20}$	0.5099	1.961	0.929
Turbidity	21.76	$3.59*10^{-5}$	0.980	$2.88*10^{-24}$	0.218	4.587	0.978
TSS	0.980	0.00291	0.991	$2.63*10^{-3}$	0.5099	1.961	0.999

4. CONCLUSION AND RECOMMENDATIONS

It was concluded that single process of adsorption, $FeCl_3$ coagulation, $FeSO_4$ coagulation and Alum coagulation reduced pollutants concentration by 58%, 72%, 20% and 63% respectively. The hybrid process of $FeCl_3$-CFA, $FeSO_4$-CFA and Alum-CFA reduced the pollutants concentration by 80%, 70% and 78% respectively. These combinations were best for the reduction of dyes wastewater pollutants at higher rates.

Combinations of $FeCl_3$ and coal fly ash were found more effective. Coal fly ash waste can be utilized as adsorbent regarding dyes containing wastewater treatment to remove COD, color, suspended solids and turbidity. When adsorbent dose was increased, it gave best results for treatment of dyes effluent. FA adsorbent dose ratio of 8g was found an effective and $FeCl_3$ was the best coagulant for dyes effluent treatment. It may be recommended to develop a bed of Coal ash at commercial scale by resizing the ash particle through any binding material.

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