Research and Reviews: Journal of Engineering and Technology

Utilization of Fly Ash as Low-Cost Adsorbent for the Treatment of Industrial Dyes Effluents- A Comparative Study.

Abdul Karim Shah[1]*, Zeenat Muhammad Ali[2], Abdul Jabbar Laghari[3], and Syed Farman Ali Shah[2]

[1]Chemical Engineering Department, Dawood University of Engineering and Technology, Karachi, Pakistan.
[2]Chemical Engineering Department, Mehran University of Engineering and Technology, Jamshoro, Pakistan.
[3]Dr. M. A. Kazi Institute of Chemistry. University of Sindh, Jamshoro. Pakistan

Article

ABSTRACT

Coal and sugar manufacturing power generation plants are engender million tons of fly ash as waste per annum. It creates serious disposal and environmental problems. There is no alternative usage for its utilization in industries. In this regard, efforts were taken to utilize fly ash waste in the treatment of highly toxic and polluted dyes effluents. In this advanced research, characterization of fly ash properties, preparation of adsorbent, utilization for the optimum reduction of dyes effluent pollutants, determination of adsorptive capacity and study of isotherm adsorption models were accomplished. Treatment efficiency was optimized using these ashes as adsorbent at optimum dose. Sugarcane bagasse fly ash (SBFA) could reduce the higher concentration of COD (51%), color (70%), turbidity (71%) and TSS (96%) from dyes effluent. All used fly ashes could reduce higher concentration of effluent pollutants at 4 g dosing. SBFA has high porosity, which resulted in high adsorption of effluent pollutants as compared to other fly ashes. The adsorptive capacity of all used fly ash was declined on increasing adsorbent dosing. Langmuir and freundlich isotherm models were evaluated for the determination of chemical adsorption behavior of fly ashes.

INTRODUCTION

Dyes manufacturing and textiles industries are one of the problematic groups due to disposing of highly toxic industrial effluents due to presence of toxic dyes and chemicals, which creates the harmful effects on marine and environment. It was reported that these industries are disposing approximately 100 tons of toxic dyes into effluents streams annually [1]. Recently, the annum worldwide production and consumption of over 10,000 different dyes have been exceeded $7*10^5$ tons [2]. The major consumption of water in industries is due to processing and cleaning operations of chemical process equipments. These industries dispose the highly complex and toxic wastewater into rivers and sea without treatment [3]. In Jamshoro region, dyes manufacturing plants are producing $1200m^3$ per day highly complex and toxic effluents and disposing into rivers without any effective treatment. Dyes effluents contains high range of color, biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity, pH, temperature, alkaline substances, acids, heavy metals and toxic substances [4]. The characteristics of dyes effluents vary according to each dye product manufacturing [5]. Discharge of such dyes effluents in rivers causes environmental pollution and produces allergic diseases [6,7]. It was declared from dyes manufacturing plant effluents analysis that industrial effluents contain high concentration of organic pollutants such as dyes, phenolic compounds, BOD, COD, color, TDS, turbidity, suspended solids and heavy metals. Common treatment technique (flocculation) was unsuitable for the treatment of such effluents due to their complexity.

Adsorption is an effective method for the separation of effluent pollutants and effluents treatment. It is used for the diminution of effluent pollutants, organic and toxic compounds effectively [8]. Adsorption method for color elimination is based on the affinity of

various dyes for adsorbents. Adsorption capacity of adsorbent principally depends on the characteristics of material as specific surface area, pore size, and its distribution [9]. The powdered activated carbon (PAC) is the appropriate adsorbent for effective treatment of dyes effluent, but desorption and regeneration are difficult, uneconomical and expensive [10].

Coal fly ash, a waste generated from coal power plants during burning of powdered lignite coal into fluidized bed combustion technology system for the power generation. This powdered form waste creates serious environmental, disposal and health problems [11]. This waste worldwide production is about 600 millions tones per annum and Pakistan generates 55680 m^3/hr [12].

Coal fly ash is grey in color, abrasive, refractory and acidic in nature. It has specific surface area in the range of 2500 and 7000 cm^2/g, porosity (0.38%), pore volume (0.023 cm^3/g), particle size of 120-960μm to less than 5 μm, specific gravity of 2.3-2.5 and bulk density of 600-900 kg/m^3 [13].

The worldwide researchers have taken effective efforts for the utilization of fly ash into effective industrial applications for the resolution of wastewater treatment problems [14].

The annually production of sugarcane fly ash at world level is 47,800 millions tones and Pakistan baggase ash generation share is about 0.5 millions tones [15]. This ash has porosity (0.36%), pore volume (0.1067 cm^3/g), surface area (168.39 m^2/g) [16]. It has good porous structure and adsorption capacity. Many researchers have developed low cost fly ash adsorbent for the removal of phenolic compound, heavy toxic metals [17], dyes [18], organic pollutants and organic acids [19] from industrial flue gases and effluents.

Purpose of this advanced research was to optimize and compare the treatment efficiency of fly ash adsorbents for reduction of dyes pollutants from industrial dyes effluents via adsorption technique using coal power plant's waste.

MATERIALS AND METHODS

Collection and materials analysis of fly ash samples

Low cost adsorbents were prepared from collected fly ash samples and were utilized for the treatment of industrial dyes effluent for an effective reduction of organic pollutants in the course of adsorption technique. Various samples of coal ash were together from FBC boiler of LPGCL, Jamshoro. Samples of SBFA were collected from boiler of power generation plant of Habib Sugar Mills (Pvt.) Limited, Nawabshah. The material composition of collected fly ash samples were analyzed at Fuel Research Laboratory PCSIR, Karachi.

Table 1. Material composition of CFA, BBCA, CCA and SBFA

| Ash Type	LIO (%)	SiO_2(%)	Al_2O_3(%)	Fe_2O_3(%)	CaO(%)	MgO(%)	SO_3(%)
Coal Fly Ash	14.48	23.61	14.09	9.15	22.89	2.71	13.13
Bottom Coal Ash	6.65	3.37	16.41	24.95	10.77	0.61	6.25
Cinder Coal Ash	3.10	38.54	29	18.32	6.20	1.91	2.94[12]
Sugarcane Bagasse Fly Ash	13.45	74.69	3.60	4.9	2.56	0.69	0.11[17]

Preparation of activated carbon adsorbent from fly ashes

These ash samples were converted into fine powder product (mesh 200) by sieving operation using RO-Tap Type Sieve shaker (A-871205, Heiko Seisakusho Tokyo, Japan) at 290 rpm speed.

The fine powdered ash was treated by physico-chemically method. In 1st instant, the ash samples were washed with warm distilled water (60 ℃) for 5 minutes. The diluted solution of sulfuric acid (10% concentrated) was prepared for the washing of ash samples. This chemical washing was performed for 5 minutes using vacuum filtration system. Again ash samples were washed with warm distilled water and samples were kept into Oven (Lo-201C, The Grieve Corporation, USA) at 110 ℃ for drying and adsorbent activation purpose [20].
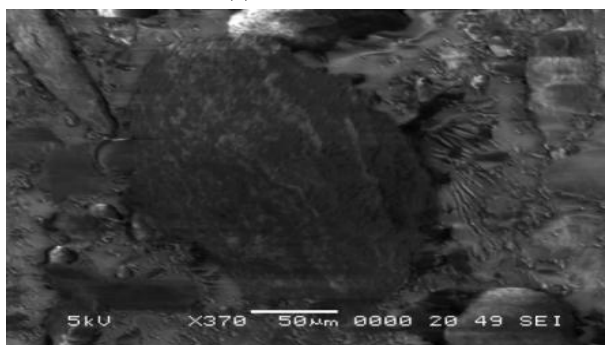
SEM analysis of fly ash adsorbents

SEM analysis of these raw and prepared materials was performed by Scanning Electron Microscope (SEM) (JSM-6380, JEOL Ltd, Tokyo, Japan) by applying 05KV electron acceleration voltage at Advanced Research Laboratory, MUET.
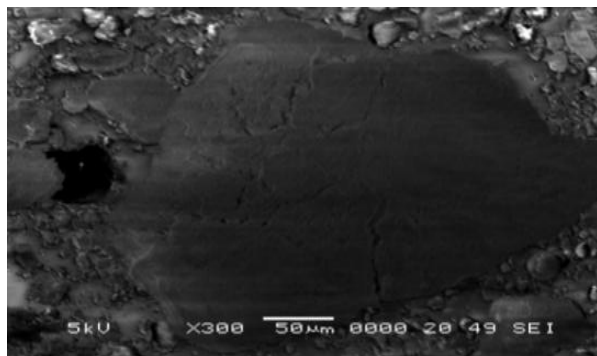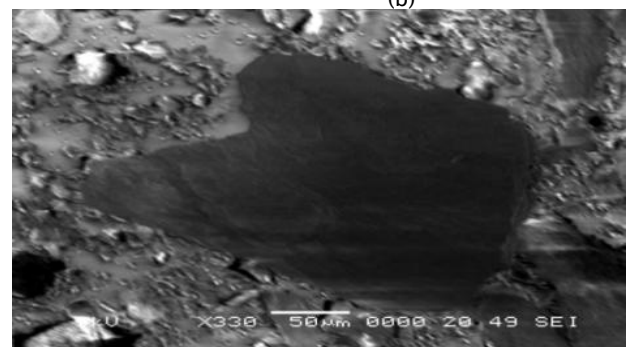

(a)
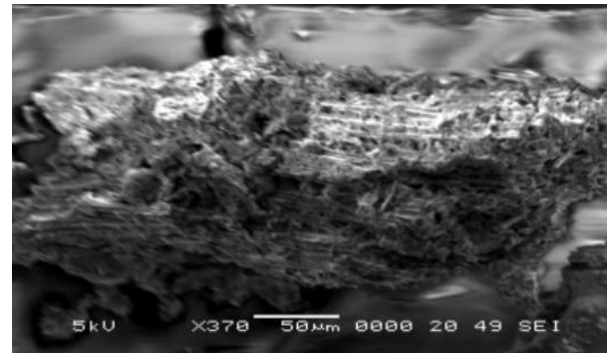
(b)

(c)

(d)

Figure1: SEM photos of prepared adsorbents of (a) CFA (b) BBCA (c) CCA and (d) SBFA

Analysis and treatment of dyes effluent via adsorption technique

The wastewater samples were collected from the main disposal point of dyes manufacturing industry and collected samples were kept in laboratory for analysis. The specific wastewater pollutants parameters were measured according to the standard laboratory protocols. COD of effluent samples was measured through dichromate method using COD vial, COD heater (TR-320, Merck, USA) and spectrophotometer (DR-2000, Hach, U.S) using by adjusting stored COD program 435 and wavelength 620 nm. Color, turbidity and TSS of dyes effluents were measured through absorptometric method using Spectrophotometer at wavelengths by 455 nm, 450 nm and 810 nm respectively.

Effluent samples volume was measured through volumetric measuring cylinder and was poured into a number of Erlenmeyer flasks (100ml). Entity quantities of all prepared fly ash adsorbents were measured through analytical balance and were poured directly into each effluent samples in Erlenmeyer flasks. Hot plate magnetic stirrer was used for proper mixing and adsorption rate of fly ash adsorbents in effluent samples. Process parameters such as agitation time 5 minutes, speed 150 rpm, settling time one hour and temperature 30°C were maintained. After treatment, samples of treated effluent were filtered via vacuum filtration system using whatman filter paper (125 µm). Finally quality parameters of treated effluent samples were analyzed according to standard laboratory protocols. The comparative study was conducted for all fly ash samples' adsorption capacity in effluent treatment [20].

Determination of adsorptive capacity and adsorption (%) of prepared adsorbents

The adsorption capacity of all prepared adsorbents was determined regarding to the pollutants adsorption from dyes effluents. In this case, contact time, adsorption equilibrium and constant agitation speed were considered in the adsorption process. The adsorption (%) of effluent pollutants on fly ash adsorbents was calculated as follows:

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

Where C_i (mg/l) is the initial concentration of effluent pollutants before adsorption and C_e (mg/l) is the concentration of pollutants at equilibrium state [21].

In same way, the adsorption capacity (mg/g) was calculated as follows:

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

Where Q_e is the adsorption capacity (mg/g), C_i and C_e is the initial and equilibrium concentration (mg/l) of pollutants in dyes effluent respectively, V is the volume (mL) of effluent and m the mass (g) of fly ash adsorbent [22].

RESULTS AND DISCUSSIONS

Material composition and SEM analysis of fly ash adsorbents

The adsorption is the process of absorbing pollutants into the pores of adsorbent. The rate of adsorption depend upon surface area, pore size, surface area and composition [23]. Material composition showed that these fly ashes have suitable chemical composition. Oxides of alumina, silica and iron in fly ash behaved also as good coagulants for the reduction of effluent pollutant's concentration. Due to high surface area, porosity and adsorption capacity, fly ashes worked as activated carbon adsorbents. The percentage of oxides of iron and aluminum was high in material composition of fly ashes. Fly ashes' chemical behavior proved effective for the treatment of industrial effluent (Table 1). Sugarcane bagasse fly ash has high porosity and surface area than coal ashes. When coal fly ashes have high surface area and less porosity. High porosity and surface area results in high adsorption capacity for pollutants removal [24]. Physico-chemical treatment could enhance adsorption capacity of prepared adsorbent (Fig.1). Adsorption capacity was mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their adsorptive properties [25]. Effective effluent treatment via adsorption depends upon porosity, chemical structure, particle size, surface area and adsorption capacity of fly ashes.

Adsorptive capacity and adsorption (%) for the adsorption of pollutants by use of fly ash adsorbents

Fly ash adsorptive capacity allowed reduction of pollutants from dyes wastewater. The prepared adsorbents have good porosity and adsorption capacity and could reduce the concentration of suspended solids by behaving as a settling aid. Industrial dyes effluent sample (100ml) was treated via adsorption process using prepared adsorbent from fly ashes at dose variations for removal of effluent pollutants. The experimental study declared that SBFA adsorbent could adsorb maximum percentage of effluent pollutants such as COD, color, turbidity and TSS. From coal fly ash type's adsorption study, it was concluded that CFA has high potential for adsorption of effluent pollutants, but less than SBFA as compared. Maximum adsorption rate was found in TSS removal in all used fly ashes (Table 2). In same way, adsorptive capacities (mg/g) of all used fly ashes adsorbents were found. Industrial effluent was treated via adsorption method using ash adsorbents at different dosing for dyes effluent pollutants reduction.

Table 2: Fly ashes adsorbents dosage effects in sorption of industrial effluent pollutants

Dose	COD Adsorption%				Color Adsorption%				Turbidity Adsorption%				TSS Adsorption%			
	SBFA	CFA	BCA	CCA	SBFA	CFA	BCA	CCA	SBFA	CFA	BCA	CCA	SBFA	CFA	BCA	CCA
2 g	44	37	34	39	48	46	44	39	68	88	48	41	24	89	87	65
4g	51	39	43	34	70	45	39	53	71	46	40	54	93	89	88	91
6g	48	48	40	37	59	48	48	46	63	51	48	49	87	81	89	91
8g	49	49	42	35	56	53	51	51	61	55	53	53	96	92	87	90

Table 3: Fly ash adsorbents dosage effect on the adsorptive capacity for industrial effluent pollutants removal

Dose	COD Adsorptive capacity (mg/g)				Color Adsorptive capacity(mg/g)				Turbidity Adsorptive capacity(mg/g)				TSS Adsorptive capacity(mg/g)			
	SBFA	CFA	BCA	CCA	SBFA	CFA	BCA	CCA	SBFA	CFA	BCA	CCA	SBFA	CFA	BCA	CCA
2 g	26	16	17	15	95	114	111	97	27	22	22	20	4	16	16	12
4g	15	9	7	10	69	56	49	66	14	11	10	13	8	8	8	8
6g	9	7	5	6	39	40	40	38	8	8	7	8	5	5	5	5
8g	7	5	4	5	28	33	32	32	6	6	6	6	4	4	4	5

Comparative study for COD removal from effluent via adsorption technique

The initial COD concentration of collected dyes effluent sample was 1164 mg/lit. Industrial dyes effluent samples (100 ml) were treated through prepared ash adsorbents for effluent's COD removal at different doses. SBFA dose (4g) and CFA dose (8g) could reduce COD by 51% and 49% respectively. Equilibrium state condition was observed in increasing adsorbent dose and uniform removal rate was observed. BCA (2g) and CCA (4g) could reduce higher COD rate by 39% and 44% respectively (Fig.2b). From the experimental study, SBFA showed good performance in COD reduction SBFA gave the most effective results than coal fly ashes because SBFA has high porosity and could capture organic compounds effectively. Srivastava et al. (2005) reported removal rate of COD (50%) of pulp mill wastewater using sugarcane bagasse fly ash adsorbent at pH 4 and BFA dosage of 2 g/l [26]. Adsorption capacity depends upon the interface of effluent pollutants with the prepared material from fly ashes. The presence of inorganic salts could enhance the adsorption of organic species to carbon. These salt ions of activated carbon which carried out charges opposite to that of the adsorbed organic ions were attracted to the spaces between adjacently adsorbed organic ions and could reduce the strength of repulsion of the adjacently adsorbed organic ions [27]. Sun et al. (2008), reduced COD (44%) from paper making wastewater using bottom coal ash at 8g/100ml dosage [28]. Coal fly ashes showed less effect on pH reduction. pH range was under NEQS. pH rate declined vs. SBFA adsorbent dosage and result in effluent in acidic nature. Lime as pH maintaining agent should be used for maintenance of pH of effluent.
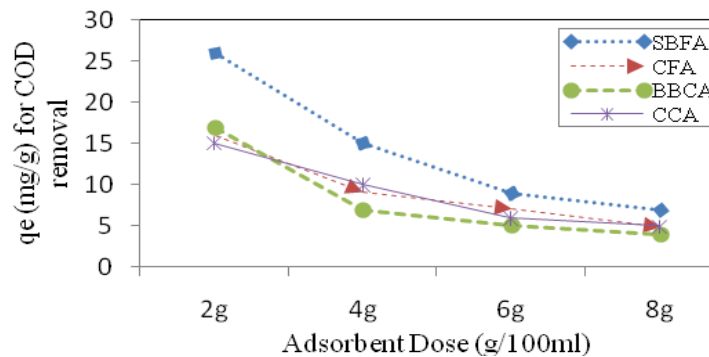

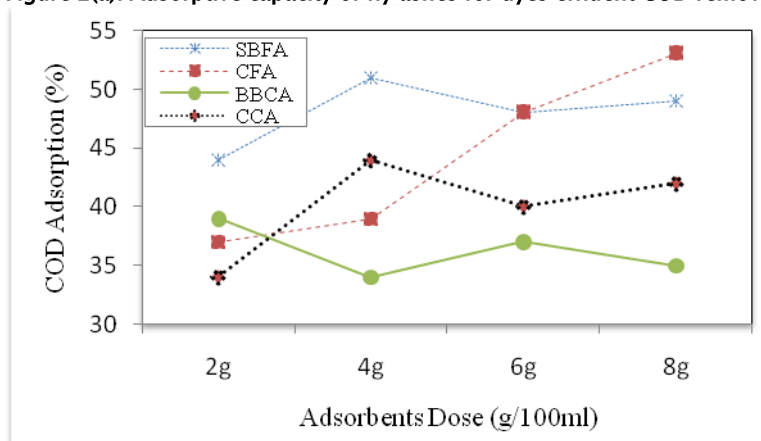**Figure 2(a): Adsorptive capacity of fly ashes for dyes effluent COD removal**

Figure 2(b): Dyes effluent COD adsorption in use of fly ash adsorbents at dose variations

Comparative study for color removal from effluent via adsorption technique

The prepared ash adsorbents were utilized at dose variations for the dyes effluent treatment in order to reduce pollutant's concentration. The initial dyes color concentration of collected dyes effluent sample was 6560 ptco. SBFA (4g) and CCA (8g) could reduce effluent color by 70% and 535 respectively. At 8g dose, CFA and BCA could reduce 53% and 51% color of dyes effluent. At optimum dosing of SBFA could reduce higher rate of color of effluent. Due to porosity, chemical composition and specific surface area of fly ashes, high rate of color could be reduced along with adsorbent dose rate. Rao et al (2006) reduced color (96%) from textile effluent at higher dose (12g) of fly ash [29]. High porosity could capture the coloring pollutants of effluent effectively in fly ashes pores. SBFA SEM analysis declared that it has high porosity and can capture organic pollutants due to its high porosity and inorganic salts presence. Dyes coloring compounds were break up and captured by pores of fly ashes as well as elemental chemical behavior of fly ashes. Adsorptive capacity of fly ash for COD adsorption declined on increasing adsorbent dosing. Steady state condition was observed in higher dosing rate.
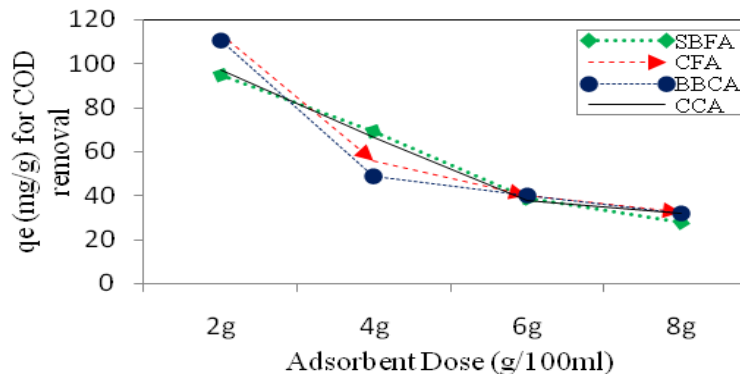
Figure 3(a): Adsorptive capacity (mg/g) of fly ash adsorbents for dyes effluent color reduction
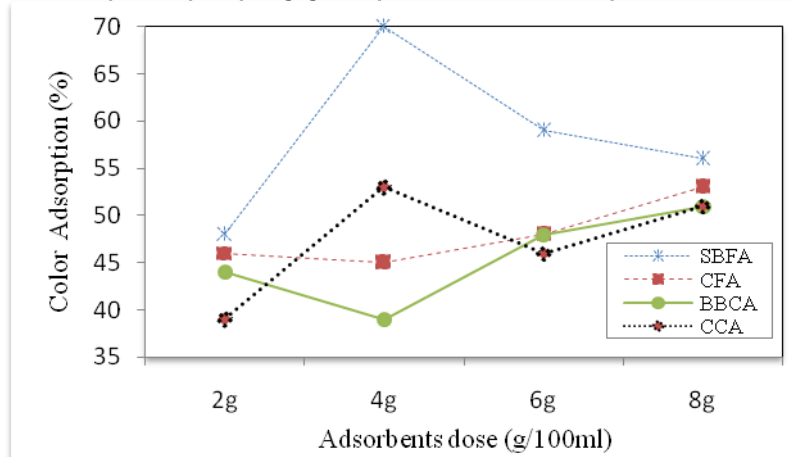

Figure 3 (b): Dyes effluent color adsorption in use of fly ash adsorbents at dose variations

Comparative study for turbidity removal from effluent via adsorption technique

The initial turbidity concentration of collected dyes effluent sample was 1280 FTU. The optimum dose (4g) of SBFA and CCA could reduce turbidity by 71% and 53% respectively. The optimum dosing (8g) of CFA and BCA could reduce color by 55% and 53% respectively (Fig.4(b)). Turbid material of effluent was captured in the pores of fly ash adsorbent. SBFA has high porosity and will result good performance in effluent pollutants reduction. Coal fly ash has high surface area and also reduced the turbid material concentration from effluent. When adsorption equilibrium occurs, maximum contact time did not reduce turbidity rate of effluent. When adsorption equilibrium occurred, it stopped the adsorption of turbid material. Adsorptive capacity of fly ash for color adsorption declined on increasing adsorbent dosing. At lower dose (2g/100ml), higher adsorptive capacity of fly ash for color adsorption was recorded. Steady state condition was observed in higher dosing rate.
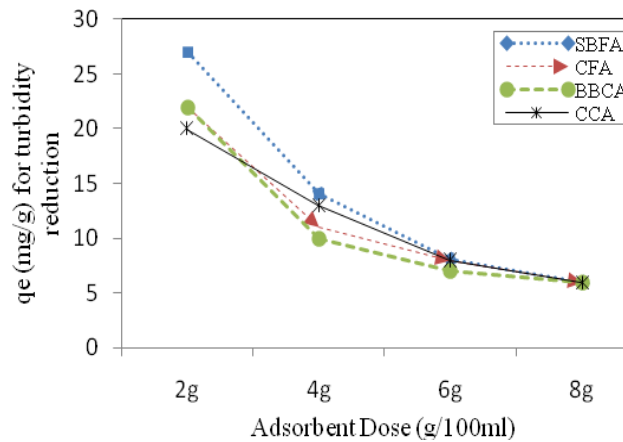

Figure 4(a): Adsorptive capacity (mg/g) of fly ash adsorbents for dyes effluent turbidity reduction
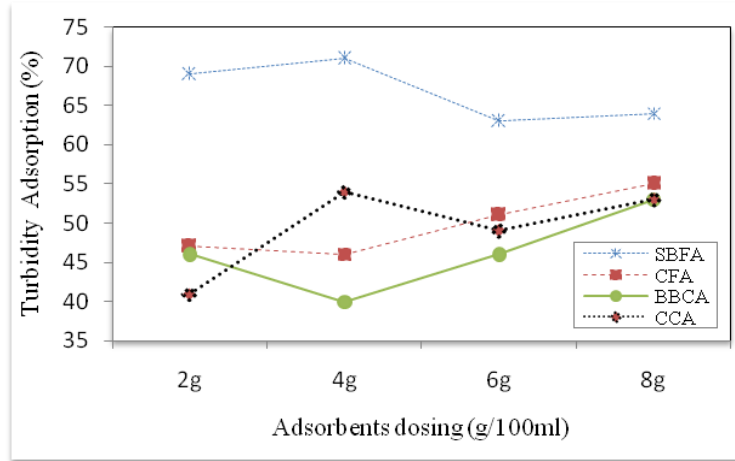
Figure 4(b): Dyes effluent turbidity adsorption in use of fly ash adsorbents at dose variations

Comparative study for TSS removal from effluent via adsorption technique

The initial suspended solids concentration of collected dyes effluent sample was 349 mg/lit. The optimum dosing (8g) of SBFA, CFA, BCA and CCA could reduce TSS by 96%, 92%, 87% and 91% respectively. High porosity of material enables it to adsorb higher rate of suspended solids. According to adsorption capacity of adsorbent, equilibrium state will achieved within specific contact time. SBFA adsorbent reduced maximum concentration of suspended solids from effluent due to its high porosity. Suspended solids were interacted with fly ash pores and surface area and were captured in fly ashes pores, until equilibrium condition was achieved. The adsorptive capacity of fly ashes improved by physico-chemical treatment. In this case, higher turbidity removal rate was observed at lowest dosage (2g). On increasing dosing ratio, steady state condition was observed in higher doses (6-8g).
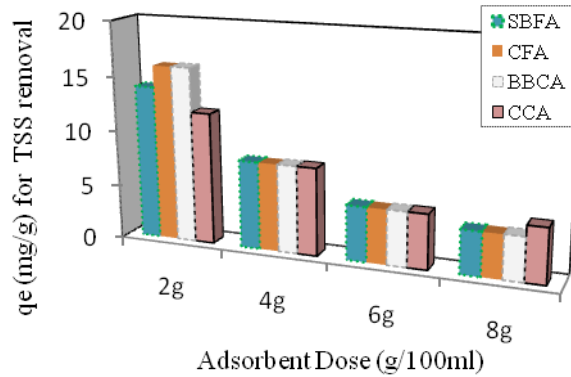

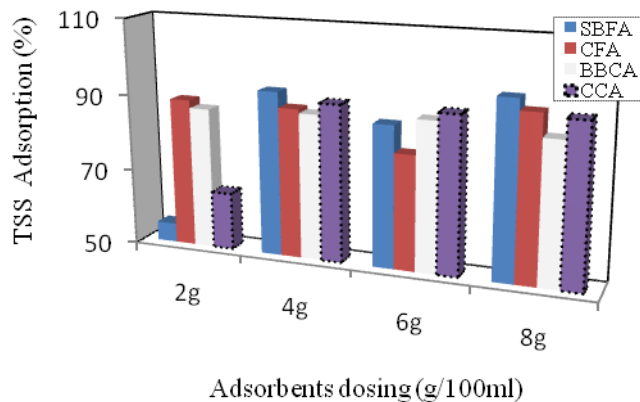**Figure 5(a): Adsorptive capacity (mg/g) of fly ashes for dyes effluent TSS removal**

Figure 5(b): Dyes effluent TSS adsorption in use of fly ash adsorbents at dose variations

Adsorption Isotherm Models Study

The adsorption behavior of adsorbents was determined by statistical analysis using isotherm models of Langmuir and Fruendlich. These models determined liquid/solid phase sorption behavior, sorption capacity, structure of sorbed layer and interaction between sorbet and sorbent. Langmuir isotherm assumes monolayer coverage of the adsorbate on a homogeneous surface of adsorbent, where as Fruendlich isotherm assume the heterogeneity.

The experimental data have been analyzed by using the linear forms of Langmuir and Fruendlich isotherm models in the following way:

$$(C_e/C_{ad}) = (1/Qb) + (C_e/Q) \qquad (3)$$
$$\ln C_{ad} = \ln A + (1/n)\ln C_e \qquad (4)$$

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), and Q is monolayer sorption capacity (mg/g).

R_L value indicate favorability ($0<R_L<1$) of isotherm. $R_L=0$; irreversible isotherm, $0<R_L<1$; favorable isotherm, $R_L=1$: linear isotherm, $R_L>1$: unfavorable isotherm.

The value of sorption intensity ($1<n<10$) indicates that sorption is favorable. The magnitude of sorption isotherm constants, gives an indication of favorability and unavoidability of sorption process. The values of Q and Langmuir constant b are calculated from the slope and intercept of the plot of Ce/Cads vs. Ce [30]. Adsorption correlation co-efficient (R^2) and other isotherm constants were calculated for all used fly ash for adsorption of dyes effluent pollutants such as COD, color, turbidity and TSS. In this study, two well known models of Langmuir and Freundlich isotherm would be evaluated.

Table 5: Langmuir and Freundlich constants of fly ash for effluent pollutants

CFA	Langmuir Isotherm			Freundlich Isotherm			
	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
BBCA							
COD	−121.3	$7.1*10^{-6}$	0.962	$1.2*10^-$	0.734	1.362	0.970
Color	15.86	$9.6*10^{-6}$	0.918	$5.2*10^{-8}$	0.544	1.838	0.844
Turbidity	11.53	$6.78*10^{-5}$	0.781	$8.7*10^{-8}$	0.5431	1.84	0.934
TSS	1.032	0.00276	0.762	$3.990*10^{-3}$	0.544	1.838	0.939
CCA							
COD	47.95	$1.72*10^{-5}$	0.868	$2.36*10^{-14}$	0.1399	7.14	0.904
Color	−77.83	$2.0*10^{-6}$	0.898	$4.3*10^{-18}$	1.6313	0.613	0.766
Turbidity	16.54	$4.72*10^{-5}$	0.841	$3.8*10^{13}$	0.337	2.967	0.53
TSS	0.537	0.005307	0.880	$6.05*10^{1}$	1.631	0.613	0.965
SBFA							
COD	24.38	$3.5*10^{-5}$	0.906	$2.29*10^{-17}$	0.3037	3.292	0.994
Color	12.28	$1.24*10^{-5}$	0.944	$2.398*10^{-10}$	2.849	0.351	0.776
Turbidity	−12.54	$6.23*10^{-5}$	0.953	$9.33*10^{30}$	0.212	4.716	0.918
TSS	0.242	0.0117	0.988	$6.51*10^{2}$	2.849	0.351	0.972

From the models study, it was concluded that Freundlich isotherm model was found suitable for adsorption of dyes effluent pollutants by use of coal fly ash. Adsorption correlation coefficient (R^2) was higher in Fruendlich isotherm model. In same way, Fruendlich model was also fit for BBCA adsorbent for pollutants reduction. When Langmuir model was fit for SBFA adsorbent in treatment study. In case of CCA adsorbent adsorption study, two parameters such as COD and TSS has higher R^2 (0.904 and 0.965) values in Fruendlich model. Freundlich isotherm model justified that there was multilayer formation on sorbent surfaces of CFA and BBCA and Langmuir isotherm model justified that there was monolayer layer on the sorbent surface of SBFA.

CONCLUSION AND RECOMMENDATIONS

The comparative study of fly ashes adsorption for dyes effluent pollutants was conducted. It was concluded that all used fly ashes have good adsorption capacity for COD, color, turbidity and TSS. CFA, BCA, CCA and SBFA adsorbents declared the effective reduction rates of color (53%, 51%, 53% and 70%), COD (49%, 37%, 44% and 51%), turbidity (55%, 53%, 54% and 71%) and total suspended solids (92%, 87%, 91% and 96%) respectively. It was concluded that SBFA has good porosity and adsorption capacity and was effective for dyes effluent treatment. The adsorptive capacity of all fly ash adsorbent declines vs. adsorbent dose. Adsorption rate improved in ever-increasing adsorbent dose. The pH of effluent declined in ever increasing adsorbent dosing. Freundlich isotherm model was fit for CFA and BBCA and showed multilayer adsorption behavior. Langmuir isotherm model was fit for SBFA adsorbent and declared monolayer adsorption behavior in treatment of dyes effluent.

It was recommended that coal power plant's waste must be utilized as low cost adsorbent for the effective and economical treatment of industrial dyes effluent.

Nomenclature

- ✓ COD: Chemical Oxygen demand
- ✓ TDS: Total Dissolved Solids
- ✓ TSS: Total Suspended Solids
- ✓ CFA: Coal Fly Ash
- ✓ SBFA: Sugarcane Bagasse Fly Ash
- ✓ BBCA: Bottom Based Coal Ash
- ✓ CCA: Cinder Coal Ash

ACKNOWLEDGEMENT

REFERENCES

1. Sun D, Zhang X, Wu Y, Liu X. Adsorption of anionic dyes from aqueous solution on fly ash. J Hazard Mat. 2010; 181: 335–342.
2. Kamboh MA, Solangi IB, Sherazi STH, Memon S. Synthesis and application of p-tert-butylcalix [8] arene immobilized material for the removal of azo dyes. J Hazard Mat. 2010; 186:651–658.
3. Namasivayam C, Sangeetha D, Gunasekaran R. Removal of anions, heavy metals, organics and dyes from water by adsorption onto new activated carbon from jatropha husk, an agro-industrial solid waste. Process Safety Environ Protection. 2007; 85 (2):181–184.
4. Hsu TC, Chiang CS. Activated sludge pretreatment of dispersed dye Factory wastewater. Environ Sci Health. 1997; 32:1921–1932.
5. Rott U, Minke R. Anaerobic treatment of split flow wastewater and concentrates from the textile processing industry. Wat Sci Techn. 1999; 40 (1):169–176.
6. Gupta VK, Ali I. Removal for lead and chromium from wastewater using bagasse fly ash- a sugar industry waste. Colloid Interface Sci. 2004; 271:321–328.
7. Yilmaz E, Memon S, Yilmaz M. Removal of direct azo dyes and aromatic amines from aqueous solutions using two β-cyclodextrin-based polymers. J Hazard Mat. 2010; 174:592–597.
8. Fand S, Chen MC. Coagulation of textile secondary effluents with fenton's reagent. Water Sci Technol. 1997; 36(12):215–222.
9. Jiuhui QU. Research program of novel adsorption processes in water purification: A review. J Environ Sci. 2008; 20:1–13.
10. Gupta GS, Parsad G, Singh VN. Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal. Water Resour.1990;24:45–50.
11. Wang SB, Wu HW. Environmental benign utilization of fly ash as low cost adsorbent. J Hazard Mat. 2006; 136 (3):482–501.
12. Aziz S, Soomro SA, Tunio AH, Nazir I, Qureshi KM, Begum R. Environmental and health hazards of fly ash and Sox from FBC power plant at Khanote. Pak J Anal Env Chem. 2010; 11 (2):56–62.
13. Ramakrishna KR, Viraraghavan T. Use of slag for dye removal. Waste Manag. 2007; 17(8): 483–488.
14. Ahamruzzaman M. A review on the utilization of fly ash. Ener Combus Sci. 2010; 36:327–363.
15. Swamy MM, Mall ID, Prasad B. Resorcinol removal aqueous solution by bagasse fly ash and activated carbon. Int J Environ Eng.1997; 77 (2): 49–54.
16. Gupta VK, Sharma S, Yadav IS, Mohan D. Utilization of bagasse fly ash generated in the sugar industry for the removal and recovery of phenol and p-nitrophenol from wastewater. J Chem Technol Biotech. 1998; 71: 180–186.

17. Ali K, Amin N, Shah MT. Physicochemical study of bagasse and bagasse ash from the sugar industries of NWFP, Pakistan and its recycling in cement manufacturing. J Chem Soc Pak. 2009; 31 (3): 375–378

18. Hsu TC, Yu CC, Meh CM. Adsorption of Cu^{2+} from water using raw and modified coal fly ashes. Fuel. 2008; 87:1335–1359.

19. Rathore HS, Sharma SK, Agarwal M. Adsorption of some organic acids on fly ash impregnated with hydroxides of Al, Cd, Cu, Fe and Ni. Environ. Pollution– SB Chem Phys.1985; 10: 249–260.

20. Shah FA, Shah AK, Mehdi A, Memon AA, Harijan K, Ali ZM. Analysis and Treatment of Industrial Wastewater through Chemical Coagulation–Adsorption Process– A Case Study of Clariant Pakistan Limited. Proceedings of 4th international conference of Porous and Media Material; 2012, June 17–22; Germany, American Iinstitue of

21. Solangi IB, Memon S, Bhanger MI. An excellent fluoride sorption behavior of modified amberlite resin. J Hazard Mat. 2010; 176: 186–192.

22. Memon S, Memon N, Memon S, Latif Y. An efficient calix [4] arene based silica sorbent for the removal of endosulfan from water. J Hazard Mat. 2011; 186: 1696–1703.

23. Kamboh MA, Solangi IB, Sherazi STH, Memon S. Synthesis and application of calix [4] arene based for the removal of azo dyes. J Hazard Mater.2009; 172: 234–239.

24. Ugurlu M, Karaoglu MH. Adsorption of ammonium from an aqueous solution by fly ash and sepiolite: isotherm, kinetic and thermodynamic analysis. Micro porous Mesoporous Mat. 2011; 139 (1–3):173–178.

25. Crini G. Non–conventional low–cost adsorbents for dye removal: A Review. Biores Technol. 2006; 97(9): 1061–1085.

26. Srivastava VC, Mall ID, Mishra IM. Treatment of pulp and paper mill wastewaters with poly aluminum chloride and bagasse fly ash. Colloids Surfaces A: Physico–chem Eng Aspects. 2005;260 (1–3):17–28.

27. Zhang Q, Chunag KI. Adsorption of organic pollutants from effluent of kraft pulp mill on activated carbon and polymer resin. Adv Environ Research. 2001; 3: 251–258.

28. Sun WL, Qu YZ, Yu Q, Ni JR. Adsorption of organic pollutants from coking and papermaking wastewater by bottom ash. J Hazard Mat. 2008; 154: 595–601.

29. Rao VVB, Rao RM. Adsorption studies on treatment of textile dyeing industrial effluent by fly ash. Chemical Eng J 2006; 116 (1):77–84.

30. Li HQ, Huang GH, An CJ, Zhang WX. Kinetic and equilibrium studies on the adsorption of calcium lingo sulfonate from aqueous solution by coal fly ash. Chemical Eng J. 2012; 200–202: 275–28