Study onSome Parameters for Removal of Color from Cottage Textile Industrial Effluent by Using Various Adsorbents

Cho Mar Kyi*, Aye Mar Htun, Mu Mu Naing***,Wai Phyo Mon****, Yon Hline Barani*****, Khin Thet Htar Nwe******

Abstract

Textile effluent causes many environmental problems and heavy metals are persistent pollutants, non-biodegradable and can easily be accumulated in organism even at low concentrations, causing serious illness. In this research, experiments were carried out to remove the colour and heavy metal in cottage textile industrial effluents by adsorption technique by using groundnut shell based adsorbents (activated groundnut shell carbon (AGC) and alkali-modified groundnut shell ash (MGA)). Activated groundnut shell carbon (AGC) was prepared by carbonization at 600˚C for 30 minutes and activation with 2N H_2SO_4. Alkali-modified groundnut shell ash (MGA) was prepared by washing, drying, modification with 2N NaOH solution. Physico-chemical properties of groundnut shell powder, activated groundnut shell carbon and alkali-modified groundnut shell ash were measured by XRF, SEM and XRD respectively. Selected different process parameters like adsorbent dosage, contact time and initial effluent concentration were conducted for adsorption study to reduce colour and heavy metal in cottage textile industrial effluent. Colour removal efficiencies of adsorbents were determined by using UV spectrophotometer. The results obtained from this study were described by Freundlich and Langmuir adsorption isotherm. Treated Textile industrial effluents were characterized by biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total dissolved solid (TDS). Heavy metal contents were analyzed by atomic absorption spectroscopy (AAS). The results indicate that Freundlich adsorption isotherm fitted the data better than the Langmuir adsorption isotherm. Maximum colour removal efficiencies 99.8% were obtained by treating with 1 g of MGA or AGC per 25 mL of cottage textile industrial effluent for 2 hr contact time of each treatment. Results suggested that AGC could be reduced (30.77) % of BOD and COD while MGA could be reduced (10.77%) of BOD and COD of cottage texitile industrial effluent. In this research, highly cadminum (Cd) removal efficiency (76%) of cottage texitile industrial effluent was obtained by alkali-modified groundnut shell ash(MGA).
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Keywords: Activated Groundnut Shell Carbon,Alkali-modified Groundnut Shell Ash, Colour Removal Efficiencies, Heavy metals, Adsorption

Introduction

This study area selected cottage industries at Kyae Toe Village and Taunggyi Village near Taungthaman lake, Amarapura township, Mandalay. Weaving industry is one of the main professions of the Amarapura people. Dyes are widely used in these cottage industries. In the process of washing and finishing coloured products, wastewater contaminated with dyes is generated (Visa, M., *et al*., 2007). Most of these dyes are toxic and potentially carcinogenic in nature. Discharge of hazardous wastewater without treatment can seriously damage the environment. It can cause some aesthetic problems and also reflection of sunlight penetrated into the water body. Beause of their complex structures and high solubility in water, the treatment of these pollutants in wastewater is troublesome (Taha N.A, 2015).

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Adsorption has been proven to be an excellent method for removing dyes from aqueous solutions because of its significant advantages. It is cheap, easily available, most profitable, easy to be used and most efficient in economic and environmental points of view compared to the conventional treatment (Mittal A.2009). The most common adsorbent materials are alumina, silica, metal hydroxide and activated carbon. Unfortunately, this effective adsorbent is expensive and has high regeneration cost. For these reasons, different studies have been carried out in order to find out inexpensive adsorbing materials. Some of the agricultural waste materials can be effectively used as low-cost adsorbents. Modification of agricultural by-product could enhance their natural adsorption capacity or add another additional value to the by-product (Aadil Abbas *et al*., 2012).

In this research,waste groundnut shells were selected for making different adsorbents because abundantly available in Mandalay. Groundnut shell based adsorbents such as activated groundnut shell carbon(AGC) and alkali-modified groundnut shell ash(MGA). were prepared and then studied their colour removal efficiency of cottage textile industrial effluent.

Materials and Methods

Methods

Preparation of Activated Groundnut Shell Carbon(AGC)

Carbonization of Groundnut Shells

The collected groundnut shells were washed with tap water to remove soil and dust and sun-dried for a week. Then dried groundnut shells were crushed manually. Crushed groundnut shells 100 g were placed in a previously weighed crucible and carbonized in a muffle furnace at 600°C for 30 minutes. Carbonized carbon was ground into powder and sieved by 140 mesh (105 µm) screen. Then yield percent of carbon from groundnut shells were determinedand stored in an airtight screw capped bottle.

$$\% \text{ Yield of groundnut shell carbon} = \frac{\text{Weight of carbon residues}}{\text{Weight of groundnut shells}} \times 100$$

Activation of Groundnut Shell Carbon with 2N Sulphuric Acid

Activated groundnut shell carbon was prepared by treating the 100 g of groundnut shell powdered carbon with 200 ml of 2N sulphuric acid in 500 ml beaker and slowly stirred by magnetic stirrer for 30 minutes and then allowed to interact for 24 hr. After 24 hr, the flask contents were filtered through Whatmann filter paper No.41 and treated carbon residue was washed repeatedly till no more acid was left and then air dried for 2 days. The activated groundnut shell carbon (AGC) was weighed and stored in an airtight screw capped bottle.

Preparation of Alkali-modified Groundnut Shell Ash (MGA)

The collected groundnut shell ash 100 g was washed in pure water by stirring (50 rpm) at room temperature for 48 hour, to remove the soluble compound and dried in oven at 120ºC for 2 hour. After washing and drying, samples ash were stirred for 48 hour in 400 ml of 2N NaOH alkaline solution. Then, the modified ash was washed with pure water, until constant pH (pH-8) was obtained and dried again at 120ºC for 2 hour. The prepared alkali-modified groundnut shell ash (MGA) was weighed and stored in an airtight screw capped bottle.

Effect of Amount of Various Adsorbents on Removal of Colour in Cottage Textile Industrial Effluent

200 ml dilutedcottage textile industrial effluent were taken in 500 ml beaker. Six 100 ml Erlenmeyer flasks were taken and then 25 ml of diluted cottage textile industrial effluent (at 6.8) was added into each flask. Thenvarious amounts of activated groundnut shell carbon(0.2g, 0.4g, 0.6g, 0.8g, 1.0g, 1.2g) were added to each flask and stirred slowly by magnetic stirrer for 30 minutes and allowed to interact for 6 hr. Then, each of the flask contents were filtered through Whatmann filter paper No.41 and filtrates were analyzed for residual concentrations of colour in treated effluent. The absorbance of cottage textile industrial effluent before and after treatment were detected by using Spectrophotometer. The same procedure was employed for the determination of colour removal efficiency of alkali-modified groundnut shellash.

$$\text{Colour removal efficiency} = \frac{C_1 - C_2}{C_1} \times 100$$

Effect of Contact Time on Removal of Colour in Cottage Textile Industrial Effluent by Treatment with Various Adsorbents

25 ml of diluted cottage textile industrial effluent (at pH 6.5)was added into each flask. (1) g ofThe activated groundnut shell carbon was added to each flask and stirred slowly by magnetic stirrer for 30 minutes and allowed to interact for (1 hr, 2 hr, 3 hr, 4 hr, 5 hr, 6 hr) respectively. After which, each of the flask contents were filtered throughWhatmann filter paper No.41 and filtrates were analyzed for residual concentrations of colour in treated effluent. The absorbance of cottage textile industrial effluent before and after treatment were detected by using Spectrophotometer. The same procedure was employed for the determination of colour removal efficiency of alkali-modified groundnut shellash**.**

Effect of Effluent Concentration on Removal of Colour in Cottage Textile Industrial Effluent by Treatment with Various Adsorbents

25 ml of diluted cottage textile industrial effluent were added into 100 ml Erlenmeyer flask. Then (1) g ofactivated groundnut shell carbon was added to each flask and stirred slowly by magnetic stirrer for 30 minutes and allowed to interact for 2 hr contact time (optimum contact time). After which, each of the flask contents were filtered through Whatmann filter paper No.41 and filtrates were analyzed for residual concentrations of colour in treated effluent. The absorbance of cottage textile industrial effluent before and after treatment were detected by using Spectrophotometer. The above procedure was repeated by using 50 ml, 75 ml, 100 ml and 125 ml of diluted cottage textile industrial effluent. The same procedure was employed for the determination of the colour removal efficiency of alkali-modified groundnut shellash.

Adsorption Isotherms

To investigate an interaction of adsorbate molecules and adsorbent surface, two well-known models, the Freundlish and Lanuir isotherms, were selected to explicate dye- adsorbents (AGC andMGA) interaction in this study. The amount of adsorbed colour was calculated based on the following equation

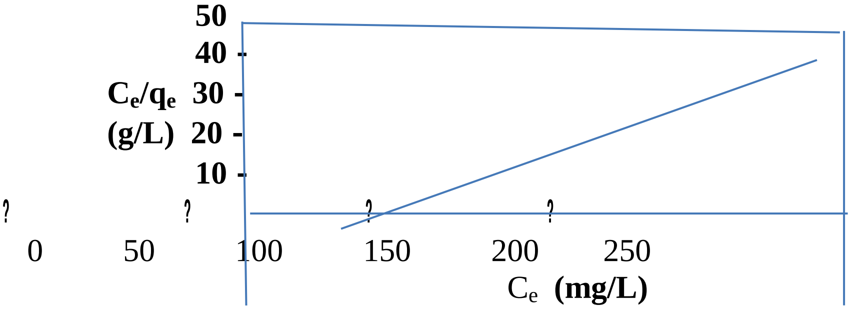
$$qe = \frac{(Co - Ce)\,V}{W}$$

where qe is the equilibrium adsorption capacity per gram dry weight of the adsorbent; Co is the initial concentration of textile wastewater; Ce is the final or equilibrium concentration of dye in textile wastewater; V is the volume of the cottage textile industrial wastewater; and W is the dry weight of adsorbent.

LangmuirAdsorption Isotherms Model

The basic assumption of Langmuir model is that the formation of monolayer takes place on the surface of the adsorbent, indicating that only one dye molecule could be adsorbed on one adsorption site and the intermolecular forces decrease with the distance. It is also assumed that the adsorbent surfacce is homogeneous in character and possesses identical and energetically equivalent adsorption sites. It was presented as following equation.

$$q_e = q_m K_L C_e / 1 + K_L C_e$$



A linear Langmuir adsorption isotherm is presented in figure. The values of q_m and K_L of linear expression of Langmuir adsorption were calculated from slopes and intercept of linear plot of **C_e/q_e**versus C_e.

3.8.2Freundlich Adsorption Isotherms Model

The empirical Freundlich equation, based on sorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is given by following equation:

$$q_e = k_f C_e^{1/n}$$

equation can be rearranged to obtained a linear form by taking logarithms:

$$\ln q_e = \ln k_f + 1/n \ln C_e$$

The slope and the intercept correspond to 1/n and k_f respectively.

Results

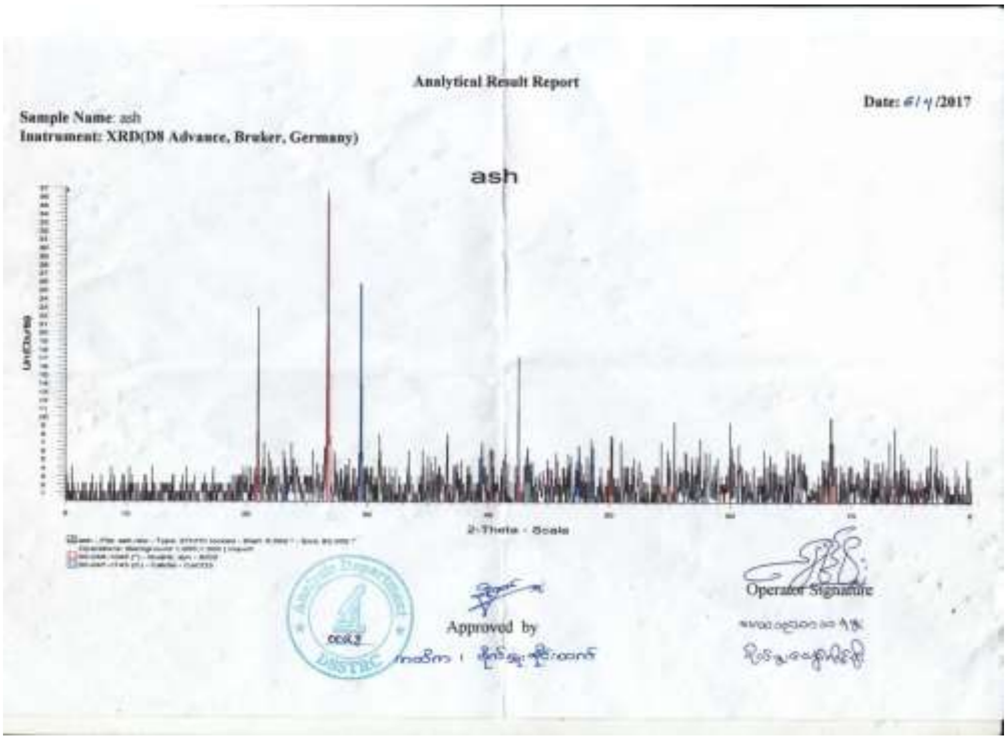


Figure (1) X-ray Diffraction Pattern of Groundnut Shell Ash before Treatment with Alkali

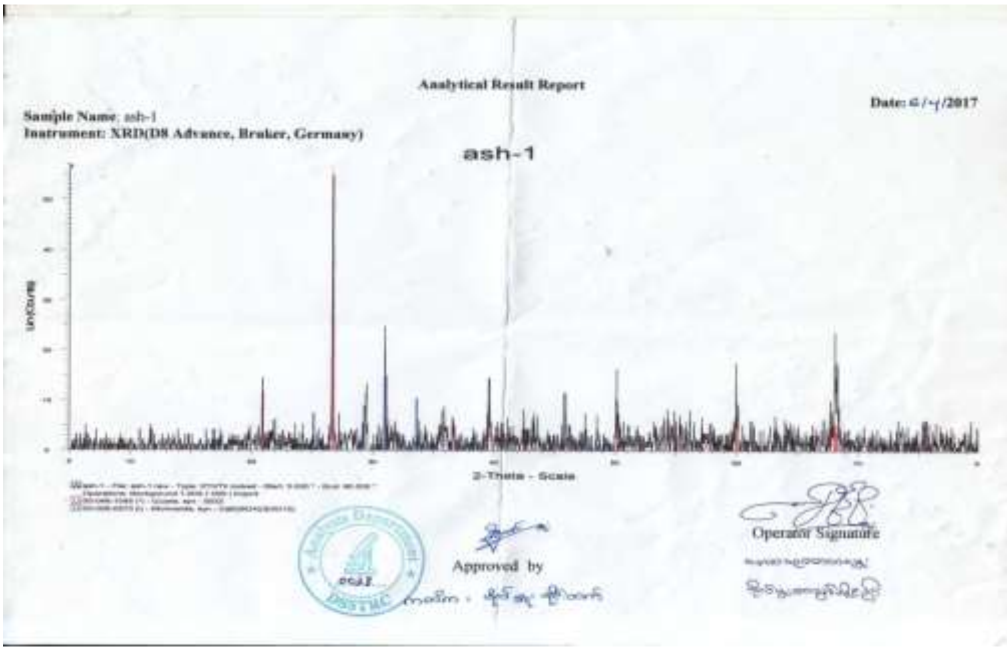


Figure (2) X-ray Diffraction Pattern of Alkali-modified Groundnut Shell Ash

XRD diagram were obtained from Analysis Department, Defence Service Science and Technology Research Center, Pyin Oo Lwin

Figure (3) SEM Image of Groundnut Shell Carbon before Activation

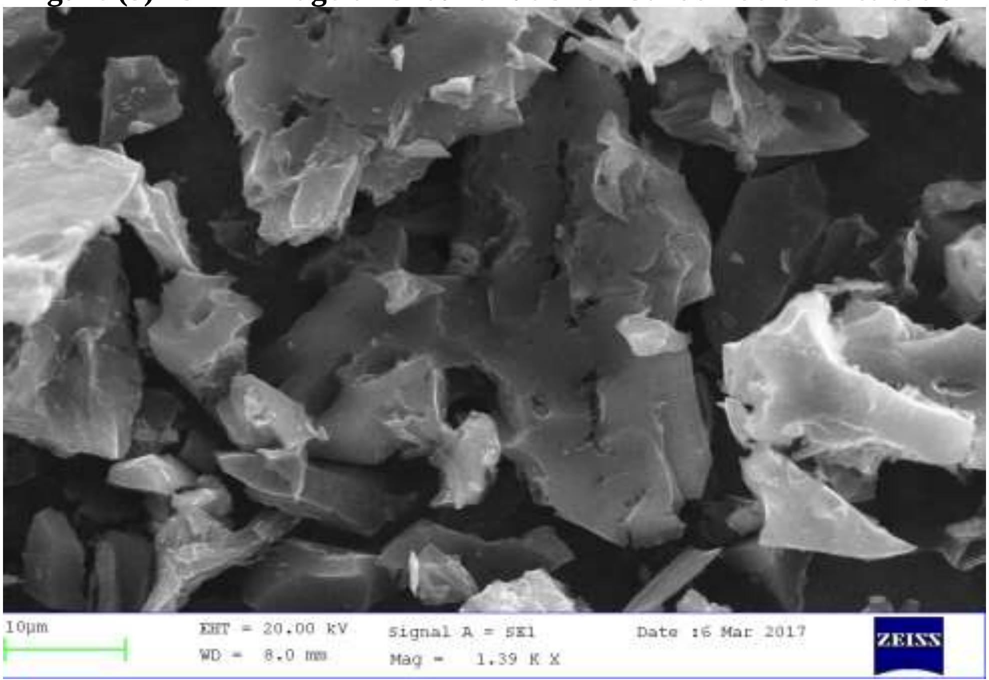


Figure (4) SEM Image of Activated Groundnut Shell Carbon(AGC)

SEM diagram were obtained from Analysis Department, Defence Service Science and Technology Research Center, Pyin Oo Lwin

Table (1) Comparative Study of Effect of Amount of Different Adsorbents on Color Removal Efficiency

Effluent Concentration - (1:99) Stirring Time 30 minute
(Industrial Effluent: Water) Contact Time - 6 hours
Volume of Industrial Effluent - 25 ml (pH - 6.5)

	Before Treatment	After Treatment		ColorRemoval Efficiency (%w/w)	
	Absorbance*	Absorbance*			
		AGC	MGA	AGC	MGA
0.2	1.407	0.173	0.036	87.0	97.6
0.4	1.407	0.150	0.032	89.0	97.9
0.6	1.407	0.063	0.029	95.9	98.1
0.8	1.407	0.040	0.023	97.4	98.5
1.0	1.407	0.022	0.023	98.6	98.5
1.2	1.407	0.008	0.041	99.5	97.3

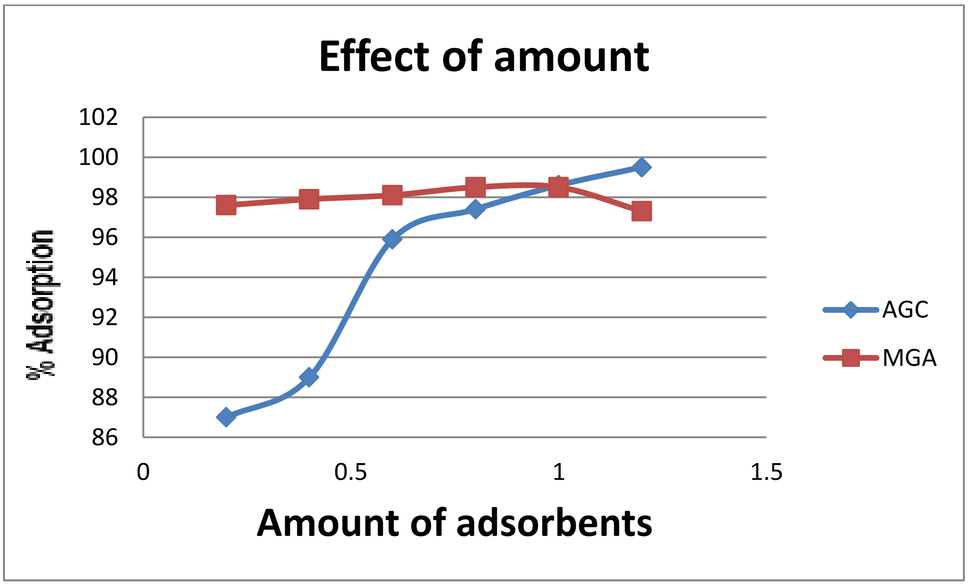


Figure (5) Comparative graph showing effect of amount of adsorbents on colour removal efficiency

Table (2) Comparative Study of Effect of Contact Time on Color Removal Efficiencyof Different Adsorbents

Effluent Concentration- (1:99) Amount Activated Carbon - 1.0 g
(Industrial Effluent: Water) Stirring Time- 30 minutes
Volume of Industrial Effluent - 25 ml (pH- 6.5)

Contact Time (hr)	Before Treatment Absorbance*	After Treatment Absorbance*		ColorRemoval Efficiency (%w/w)	
		AGC	MGA	AGC	MGA
1	1.407	0.007	0.005	99.6	99.7
2**	1.407	0.003	0.004	99.8	99.8
3	1.407	0.004	0.016	99.7	99
4	1.407	0.005	0.024	99.7	98.6
5	1.407	0.008	0.025	99.5	98.4
6	1.407	0.008	0.026	99.5	98.3

*** Absorbances at the wavelength of 490nm were measured by Spectrophotometer at** the Laboratory of Industrial Chemistry Department, Yadanabon University.

**The suitable condition

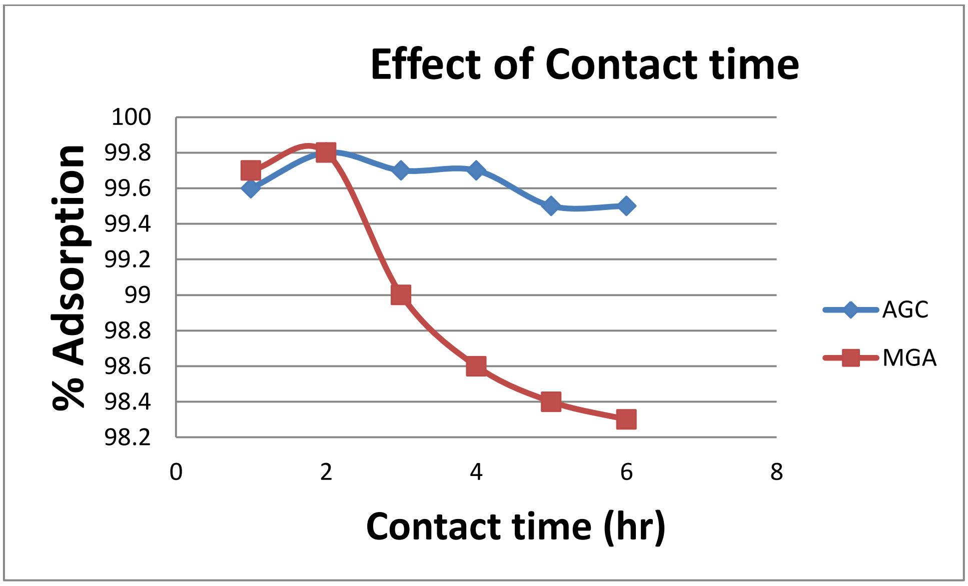


Figure (6) Comparative graph showing effect of contact time on %removal of different adsorbents

Table (3) Comparative Study of Effect of Initial Concentration on Color Removal Efficiencyof Different Adsorbents

Effluent Concentr-ation (ml)	Before Treatment Absorbance*	After Treatment Absorbance*		ColorRemoval Efficiency (%w/w)	
		AGC	MGA	AGC	MGA
25**	1.407	0.004	0.005	99.8	99.7
50	1.407	0.082	0.017	94.7	98.9
75	1.407	0.092	0.018	94.0	98.8
100	1.407	0.149	0.019	90.4	98.7
125	1.407	0.211	0.025	85.0	98.4

*** Absorbances at the wavelength of 490nm were measured by Spectrophotometer at** the Laboratory of Industrial Chemistry Department, Yadanabon University.
**The suitable condition

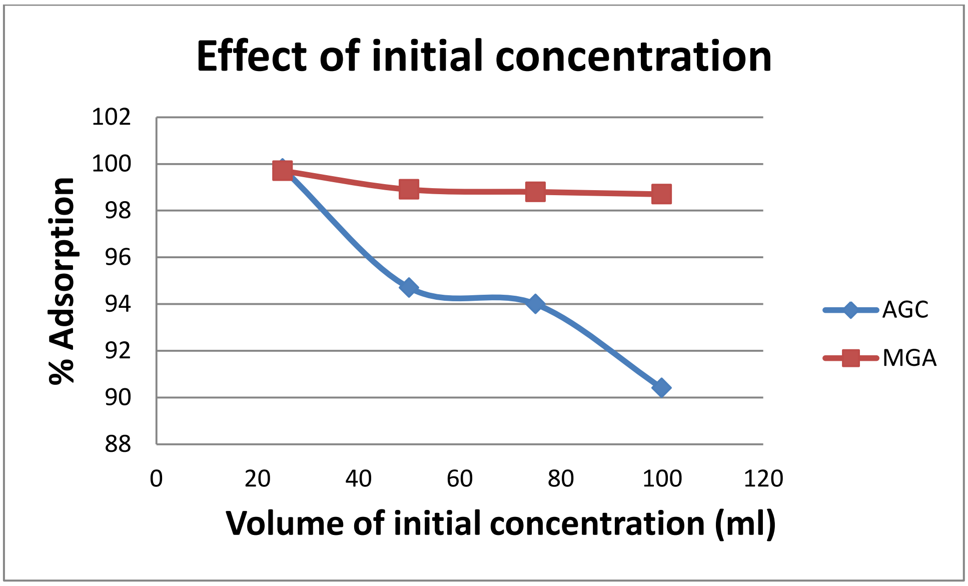


Figure (7) Comparative graph showing effect of initial concentration on %removal of different adsorbents

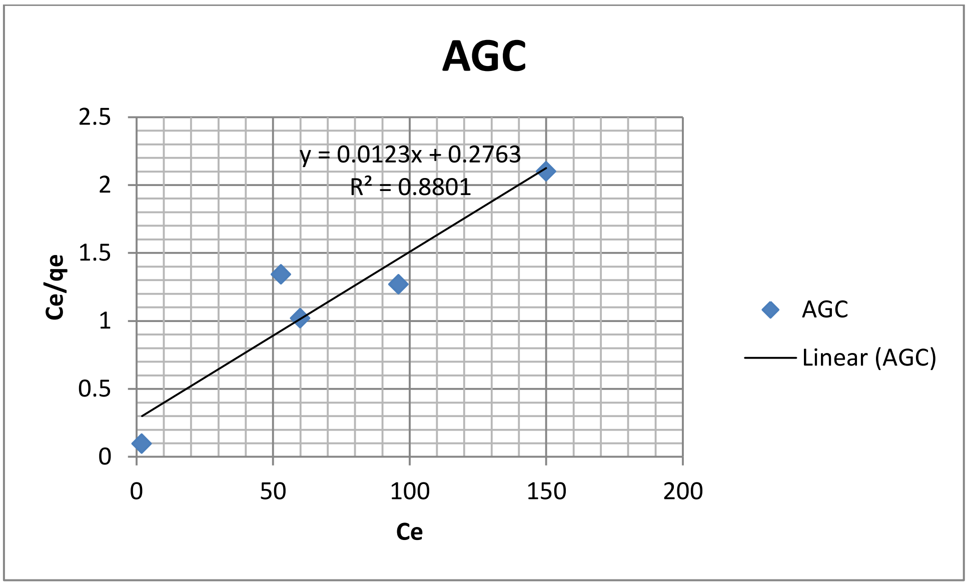


Figure (8) Linear Langmuir adsorption isotherm for AGC

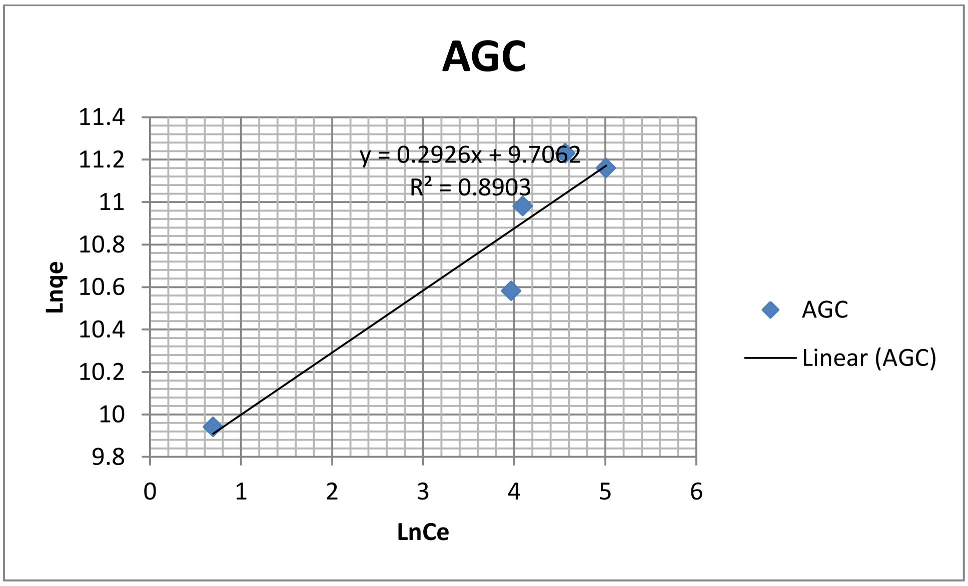


Figure (9) Linear Freundlich adsorption isotherm for AGC

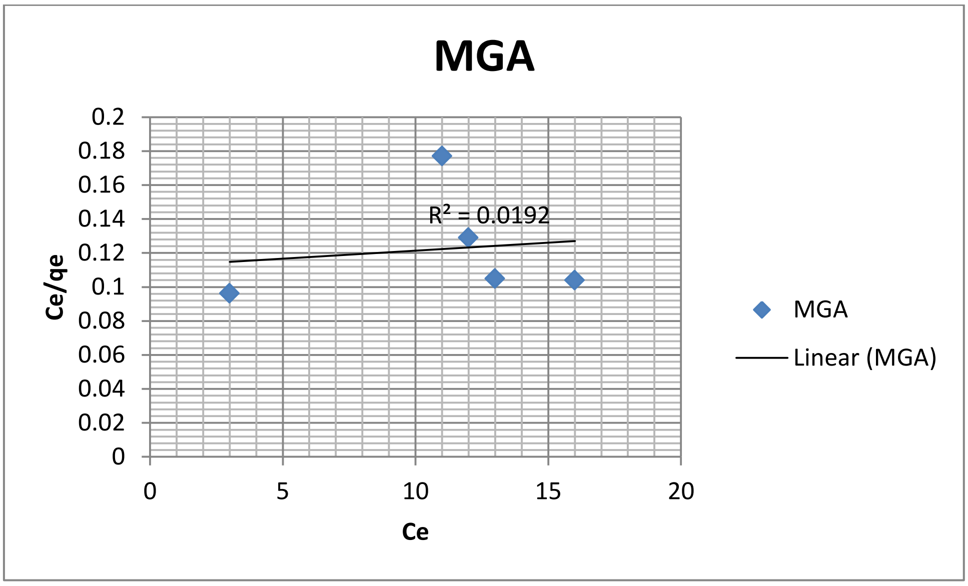


Figure (10) Linear Langmuir adsorption isotherm for MGA

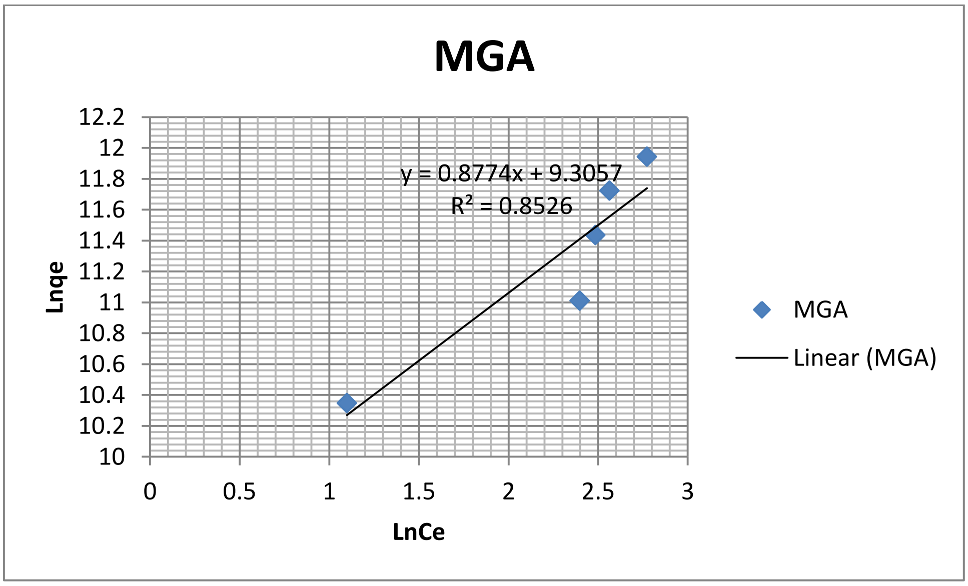


Figure (11) Linear Freundlich adsorption isotherm for MGA

Table (4) Langmuir and Freundlich Adsorption Isotherm Constants

Adsorbents	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	n	k_f	R^2
AGC	0.0123	0.2763	0.8801	3.4176	9.7062	0.8903
MGC	0.0009	0.1119	0.0192	1.1397	9.3057	0.8526

Table (5) pH, BOD, COD and TDS Contents of Cottage Textile Industrial Effluents before and after Treatmentby AGC and MGA

Amount of Adsorbents = 40 g
Contact Time = 1 hr
Amount of Effluent = 1liter

Parameter	Adsorbents				**Effluent Standard (PCC)
	AGC		MGA		
	*Before Treatment	*After treatment	* Before Treatment	*After treatment	
pH	6.5	7.1	6.5	7.5	6.5-9
BOD (mg/l)	650	450	650	580	50
COD (mg/l)	1625	1125	1625	1450	250
TDS (mg/l)	596	712	596	1003	500

*Data were obtainedfrom Water and Sanitation Department, Mandalay City Development Committee.
**PCC = Pollution Control Committee, http://pcd.go.th/info-serv/en-reg-std

Table (6) Heavy Metal Contents of Cottage Textile Industrial Effluents before and after Treatmentby AGC and MGA

Dilution ratio (1:99) v/v
Amount of Adsorbents = 40 g
Contact Time = 1 hr
Amount of Effluent = 1 liter

Heavy Metal Contents of Cottage Textile Industrial Effluent	Adsorbents				**Effluent Standard (PPC)
	AGC		MGA		
	*Before Treatment	*After Treatment	*Before Treatment	*After Treatment	
Cd (mg/l)	0.025	0.014	0.025	0.006	0.1
Cr (mg/l)	0.196	0.167	0.196	0.11	0.1
Pb (mg/l)	0.237	0.18	0.237	0.234	0.1

*Data were obtained from Chemical Technology at Defense Services Science and Technology Research Center, Pyin Oo Lwin City
**PCC = Pollution Control Committee, http://pcd.go.th/info-serv/en-reg-std

Table (7) Effectiveness of Activated Groundnut Shell Carbon and Alkali-modified Groundnut Shell Ash

Adsorbents	Removal % of BOD, COD, TDS and Heavy Metals in Cottage Textile Industrial Effluent				
	BOD	COD	Cd	Cr	Pb
AGC	30.77	30.77	44	14.79	24.05
MGA	10.77	10.77	76	43.88	11.27

Discussion

In this research work, groundnut shell based adsorbents were prepared and used for removal of colour in cottage textile industrial effluent. The emphasis of present research work was to produce cheaper adsorbents and to study the effectiveness of groundnut shell based adsorbents for cottage textile industrial effluent treatment processes. Figures (1) and (2) represent X-Ray diffraction pattern of groundnut shell ash before and after treatment with 2N NaOH solution. The XRD peak in Figures (1) and (2) proved a complex composition, rich in various inorganic components. The datas from these figures also showed crystalline modification of SiO_2 up to 35.08 %. Malaria (2014) reported that alkali-modification enhancing the specific surface, affects SiO_2. During modification, the tetragonal silica (t-SiO2) dissolution followed by the re-precipitation of the orthorhombic (O-SiO_2) forming aggregated particles with more edges, consequently a surface with higher roughness and higher specific surface that can explain the high efficiencies of colour and heavy metals removal even at very short contact times.

Figures (3) and (4) show SEM images of before and after activation of groundnut shell carbon. The results from these Figures showed significant differences in pore volume before and after activation of groundnut shell carbon. Small narrow pores were observed on the surface of the groundnut shell carbon before activation. In contrast, larger pores were observed on the external surface of the activated carbon indicating that it had a large surface area and pore volume, which allowed the removal of liquid phase contaminants, including organic pollutants, heavy metal ions and colours.

Table (1),(2),(3) and Figure (5),(6),(7) showed Comparative study of color removal efficiencies of AGC and MGA at various amount, contact time and initial concentration. The results showed that maximum colour removal efficiencies (99.8 %) for AGC and (99.7%) forMGA were obtainedby treating with 1 g of MGA or AGC per 25 mL of cottage textile industrial effluent for 2 hr contact time of each treatment..The results revealed that both these two cheap agro based adsorbents were effectively could be used in color removal from cottage textile industrial effluent.

Figure (8) and (9) showed Langmuir andFreundlich adsorption isotherm of AGC and Figure (10) and (11) showed Langmuir andFreundlich adsorption isotherm of MGA. The correlation coefficient of examined data(R^2) were found (0.8801) and (0.8903) for AGC and (0.0192) and (0.8526) were found for MGA.The values of correlation coefficient in Langmuir isotherm were lower thanFreundlich adsorption isotherm.The results indicated that Freundlich adsorption isotherm fitted the data better than the Langmuir adsorption isotherm. R^2 values obtained (0.8903) and (0.8526) from these model are fairly good (> 0.83).The slope and the intercept correspond to (1/n) and k_f, respectively. The results are indicated in Table (4) . The favourable adsorption of this model can be characterized such that if a value for n is above unity, adsorption is favourable and a physical process. In the present study, the value of n (n =3.4176 for AGC and 1.1397 for MGA) is greater than 1, indicating that the adsorption process is favourable.

Table (5) showed pH, BOD, COD and TDS contents of before and after treatment of cottage textile industrial effluent. Results suggested that AGC could reduce (30.77%) of BOD and COD while MGA could reduce (10.77%) of BOD and COD incottage textile industrial effluent. However, amount of total dissolved solids in treated cottage textile industrial effluent were increased due to soluble solids in AGC and MGA. Therefore, long term washing of AGC and MGA with water before treatment with cottage textile industrial effluent, that is necessary to reduce soluble solids.

Most of the metal-oxides are negatively charged, thus ash can be a good adsorption substrate for heavy metals removal.The ash modified with 2N NaOH leads to higher specific surface and increased dimension homogeneity that can explain the high efficiencies registered in heavy metals removal even at very short contact times. Table (6) showed heavy metal contents of before and after treatment of cottage textile industrial effluent. Table (7) shows effectiveness of prepared activated groundnut shell carbon (AGC) and alkali-modified groundnut shell ash (MGA). Removal percent of heavy metals (Cd, Cr, Pb) in cottage textile industrial effluent (44, 14.79 and 24.05 %) were obtained for AGC and (76, 43.88, 11.27 %) for MGA. In this research, highly cadmium (Cd) removal % (76%) was obtained by alkali-modified groundnut shell ash (MGA). However, it was found that lower removal efficiencies (24.05 and 11.27%) of lead (Pb) for AGC and MGA were obtained.

Conclusion

In this research work, adsorption of color and heavy metal in cottage textile industrial effluent were carried out by using waste groundnut shell based adsorbents (AGC and MGA).Maximun colour removal efficiencies(99.7 %)and (99.8%) were obtained by treating with 1g of MGA orAGC per 25ml of cottage textile industrial effluent for 2 hours contact time of each treatment . Highly cadminum removal efficiency (76%)from cottage textile industrial effluent were obtained by alkaki modified groundnut shell ash.The results indicated that these two low cost adsorbents, activated groundnut shell carbon(AGC) and alkali modified groundnut shell ash (MGA) from abundantly waste groundnut shells were effectively removed colour from cottage textile industrial effluent.

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