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Taha Utilization of Low Cost Waste Material Bagasse Fly Ash in Removing
**UTILIZATION OF LOW COST WASTE MATERIAL
BAGASSE FLY ASH IN REMOVING OF
CU²⁺, NI²⁺, ZN²⁺ AND CR³⁺
FROM THE INDUSTRIAL WASTE WATER**

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ABSTRACT

Bagasse fly ash, a waste material generated in sugar industry, collected from a local sugar Firm at Kom-Ombo district (42Km – distance, on the northern direction, from the mid city of Aswan), Aswan Governorate, Egypt was utilized as a low cost and effective adsorbing surface for the removal of Cu²⁺, Ni²⁺, Zn²⁺ and Cr³⁺ from the industrial wastewater. The adsorption capacity was followed as a function of pH, adsorbent dose, metal ion concentration, shaking time and divers ions. Under the optimum conditions used, more than 95% of some of the ions under study were successfully removed. The data were fitted utilizing both Freundlich and Langmuir isotherms.

INTRODUCTION

One of the low-cost adsorbents, bagasse fly ash is a waste material obtained from the particular collection devices attached to the flue-gas line of the sugar cane bagasse – fired boilers. Bagasse fly ash has good adsorption properties for organics and heavy metals removal and is, therefore, used as an adsorbent in the treatment of industrial wastewaters (Kumar et al. 2000, quoted in Srivastava et al. 2005).

Fly ash is an efficient adsorbent for water treatment concerning removal of dissolved organic carbon (Banejee et al. 1995) and a useful additive in cement industry due to the pozzolanic and cementation properties (Roy et al. 1991). As a matter of fact, although fly ash is considered as a waste, several studies have pointed out their efficiency in the removal of heavy metallic ions in aqueous phase (Gamgli et al. 1975; Panday et al. 1985; Dasmahapatra et al. 1996). Heavy metals are supposed to be very toxic and carcinogenic in nature. The presence of heavy metals in the aquatic environment has been great concern because of their toxicity at lower concentrations as well. Copper, zinc and chromium are highly toxic as they are mutagens in nature (Moore and Ramamoorthy 1984).

Industrial agricultural and domestic wastes pollute water bodies with heavy metals, which reach tissues through the food chain. The toxicity of heavy metals to aquatic organisms has been a subject of interest to biologists for many years (Ajmal et al. 2000). Among different types of pollution, the industrial waste constitutes the major source of various kinds of metal pollution in natural water.

The removal of toxic metal ions is a very difficult task due to the high cost of treatment methods. In recent years, research interest has increased in terms of the production of low-cost alternatives to activated carbon, which remains an expensive material in spite of its pro-life use (Gupta et al. 1997a, 1997b, 1998a and 1998b, quoted in Ali 2000).

The objective of this work was to use the bagasse fly ash (very low-cost waste material) in removing of Cu^{2+} , Ni^{2+} , Zn^{2+} and Cr^{3+} from industrial waste water.

MATERIALS AND METHODS

ADSORBENT:

Bagasse fly ash was collected from a local sugar Firm at Kom-Ombo district (42 Km– distance, on the northern direction, from the midcity of Aswan, Aswan Governorate, Egypt. A known weight of the collected material was treated with hydrogen peroxide (100-volume) at 60°C for 24h to oxidize the adhering organic matter (Gupta and Ali 2000).

The resulting mass was washed with double distilled water several time and finally washed with deionized water. The mass was then dried at 110°C, powdered, ground and sieved to the desired particle size (100µm that is fine enough and represents ~43% of the mass). The working material was stored in vacuum desiccators for further uses.

METAL IONS (ADSORBATE) SOLUTION:

Stock solutions of Cu^{2+} , Ni^{2+} , Zn^{2+} and Cr^{3+} ions were prepared by weighing the appropriate amounts of their chloride (analytical reagent [AR] grade) so to obtain 1000 ppm metal ion concentration in double distilled water.

APPARATUS:

- pH-meter (Orion Research Model SA211/Digital pH-meter, USA).
- Phillips x-ray diffractometer, USA.
- Surface area analyzer (Quantasorb Surface Area Analyzer, England).
- Solar 969 atomic absorption spectrophotometer, direct readout concentration using hollow cathode lamps of the elements at their characteristic wavelengths, England.
- Wirst-action shaker (Burrell Corporation Scientific Instruments, Germany).
- 100-µm test Sieve (K. Kurt Retsch GmbH & Co. K.G., Germany).

ADSORPTION STUDIES:

Adsorption studies were done at room temperature (25°C) by batch process. A 0.3 g sample of fly ash was placed in a conical flask containing 50 mL metal solution in the desired concentration. The mixture was then shaken for different intervals of time. The solutions were then centrifuged and the concentrations of the ions under study were estimated in the supernatant.

RESULTS AND DISCUSSION

The chemical analysis and the physicochemical characteristics of the used fly ash are recorded in Table 1.

TABLE 1
CHEMICAL AND PHYSICO-CHEMICAL CHARACTERISTICS
OF FLY ASH SAMPLE

Item	Value	Item	Value (%)
Moisture	9.80 %	Al ₂ O ₃	7.0 %
Surface area	480 m ² g ⁻¹	Fe ₂ O ₃	2.20 %
Density	1.50 gcm ⁻³	CaO	2.00 %
SiO ₂	86.0 %	MgO	2.30 %

The resulting data for the different items studied are discussed as follows:

EFFECT OF pH:

The adsorption of Ni²⁺, Cr³⁺, Cu²⁺ and Zn²⁺ was studied covering the pH range of 2.0- 8.0, at constant adsorbent dose of 20 g/L and shaking time for 3h. The temperature was controlled at room temperature, 25°C Figure 1. From the plots, it can be easily seen that the maximum uptake for Ni²⁺, Cr³⁺, Cu²⁺ and Zn²⁺ takes place at a pH 6.0, 4.0, 4.0 and 5.0, respectively. The adsorption capacities for the studied cations were raised from 1.10 to 2.47 mg/g (44.0 to 98.8 %) for Ni²⁺ ion on raising pH from 2.0 to 6.0; from 1.12 to 2.48 mg/g (44.8 to 99.2 %) for Cr³⁺ on raising ion from pH 2.0 to 4.0; from 1.20 to 2.48 mg/g (48.0 to 99.2 %) for Cu²⁺ ion on raising pH from 2.0 to 4.0 and in case of Zn²⁺ ion, it raised from 1.30 to 2.40 mg/g (52.0 to 96.0 %) as a result for raising pH from 2.0 to 5.0. Beyond the respective pH values, the adsorption capacity started to decrease in all cases. This may be due to the hydrolysis of metal ions under study at higher pH (Gupta et al. 2000). The resulting observations are in a good agreement with many works done using fly ash (Gupta et al.1998a quoted in Gupta and Ali 2000; Gupta and Ali 2000).

As shown in Table 1, the main constituents of fly ash are metal oxides. These oxides form metal hydroxide complexes in solution and subsequent acidic or basic dissociation of these complexes at the solid – solution interface leads to development of a positive or negative charge on the surface of the adsorbent. As the pH of the system increases, the number of positively charged sites decreases whereas the number of negatively charged increases and hence favours the adsorption of metal cations due to electrostatic attraction (Vasanth et al. 2005).

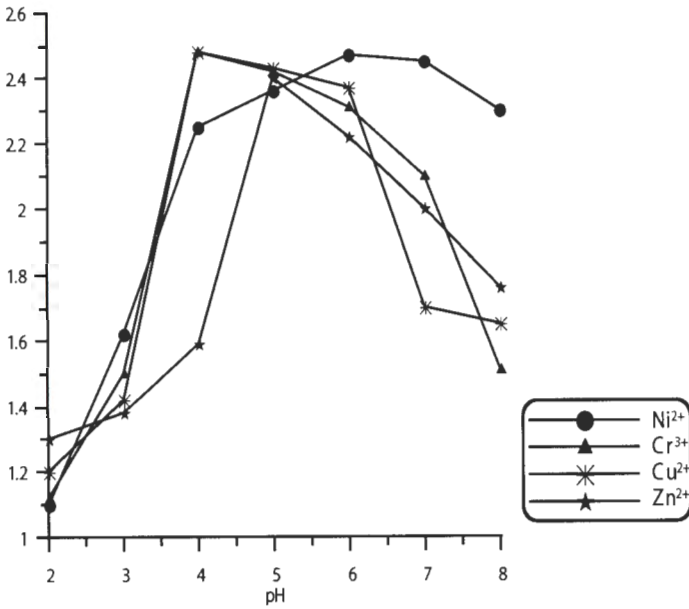


FIGURE 1. EFFECT OF pH ON THE ADSORPTION CAPACITY OF Ni²⁺, Cr³⁺, Cu²⁺ AND Zn²⁺ ON FLY ASH.

EFFECT OF SHAKING (CONTACT) TIME:

Figure 2 shows the adsorption experiments for the metal cations under test at different contact times. The adsorbent dose was fixed at 20 g/L and at the respective pHs (6.0 for Ni²⁺, 4.0 for both Cr³⁺ and Cu²⁺ and 5.0 for Zn²⁺). All experiments were done at room temperature, 25°C. The plots revealed clearly that optimum contact times are 50 min in the case of Ni²⁺, Cu²⁺ and Zn²⁺ where adsorption capacities are 2.35 mg/g (94.0%), 2.41 mg/g (96.41%) and 2.39 mg/g (95.6%), respectively. In case of Cr³⁺, the highest adsorption capacity (2.38 mg/g; 95.2 %) takes place at 70-min contact time.

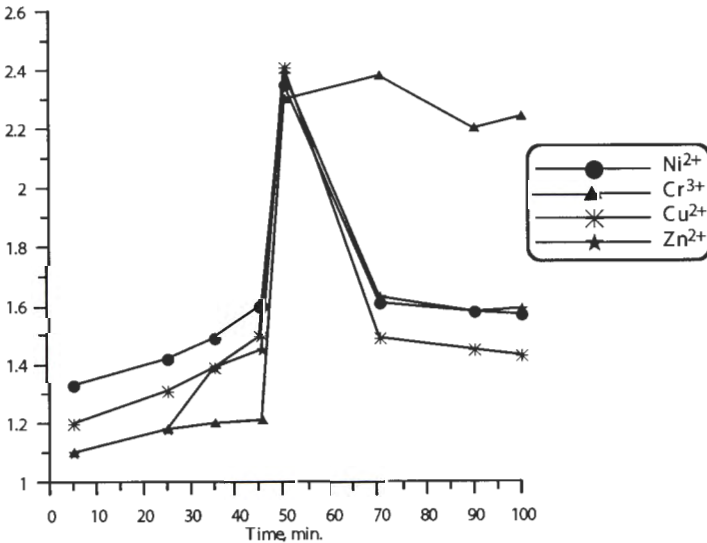


FIGURE 2. EFFECT OF CONTACT TIME ON THE ADSORPTION CAPACITY OF Ni²⁺, Cr³⁺, Cu²⁺ AND Zn²⁺ ON FLY ASH.

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EFFECT OF METAL ION CONCENTRATION:

The adsorption studies for the metal cations under investigation were done in the range of 5.0 up to 100 mg/L. Shaking time and pH of the solutions were adjusted at the optimum value for each metal ion. The results are figured in Figure 3. A metal ion concentration of 30 mg/L is the best for all the metal ions studied. The metal uptake and the adsorption percent for Ni^{2+} , Cr^{3+} , Cu^{2+} and Zn^{2+} are 1.42 mg/g (97.7%), 1.40 mg/g (93.0%), 1.41 mg/g (94.0%) and 1.43 mg/g (95.3%), respectively.

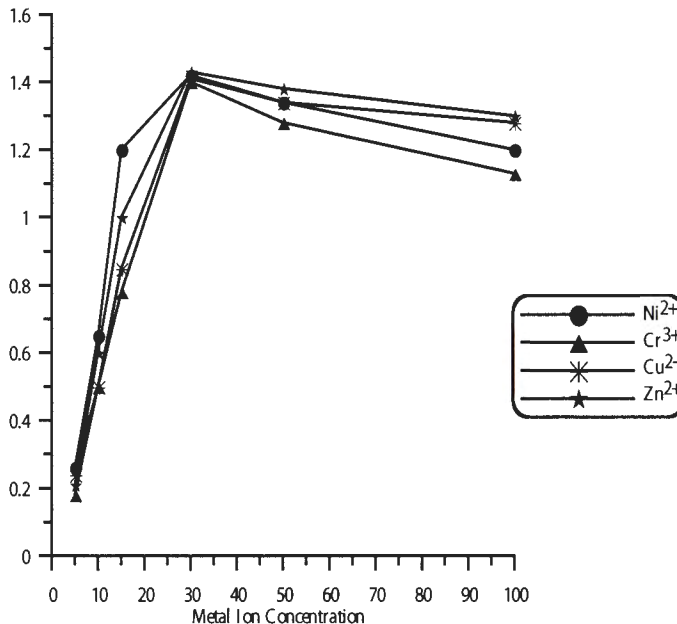


FIGURE 3. EFFECT OF METAL ION CONCENTRATION ON THE ADSORPTION CAPACITY OF FLY ASH.

EFFECT OF ADSORBENT MASS:

The effect of adsorbent mass (dose) on removing of Ni^{2+} , Cr^{3+} , Cu^{2+} and Zn^{2+} cations was studied covering the dose from 2 to 20 g/L. The pH value was adapted at the optimistic value corresponding to each cation and the temperature was 25°C, keeping the adsorbate (metal cations) concentration constant (30 mg/L). Figure 4 shows the resulting data. Twelve grams per liter is the best dose for all the studied cations. The adsorption uptakes at 12 g/L adsorbent dose are 2.40 mg/g (96.0%) for Ni^{2+} , 2.39 mg/g (95.6%) for Cr^{3+} , 2.41 mg/g (96.4%) for Cu^{2+} and 2.35 mg/g (94.0%) for Zn^{2+} . The adsorption capacity and consequently the percentage of removal are then decreased. This may be due to the saturation of the adsorbent surface. These results indicate that the 12 g/L adsorbent dose is sufficient for the removal of the cations under study. The resulting data are compatible with those reported earlier (Gupta and Ali 2000).

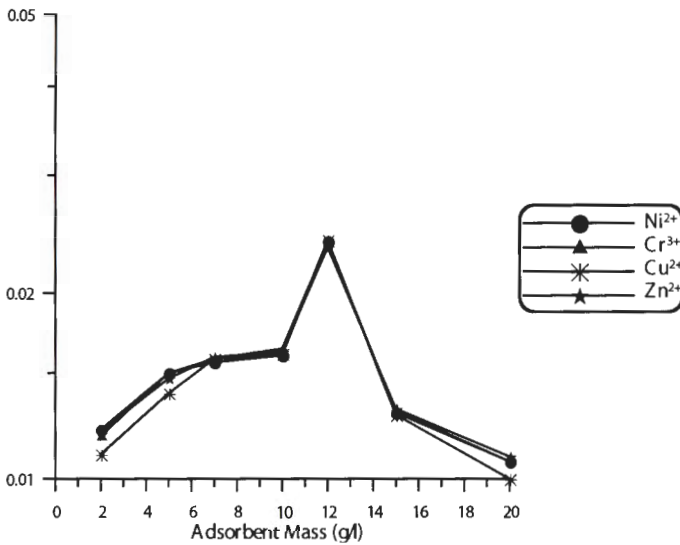


FIGURE 4. EFFECT OF ADSORBENT MASS ON THE ADSORPTION CAPACITY OF FLY ASH.

FREUNDLICH ISOTHERM:

The adsorption data for the cations under study were fitted into the Freundlich model, which is given by:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{1}$$

THE LOGARITHMIC FORM IS:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{2}$$

where q_e is the amount of metal ion adsorbed (mg/L), C_e is the metal ion concentration at equilibrium (mg/L) and both the k_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. Both K_f and n which are the Freundlich constants are obtained from the intercept and the slope of the resulting straight line on plotting $\log q_e$ against $\log C_e$.

Figures 5 and 6 represent the Freundlich isotherms for Ni²⁺, Cr³⁺, Cu²⁺ and Zn²⁺ ions. Values of $\log K_f$ and $1/n$ are calculated and tabulated in Table 2.

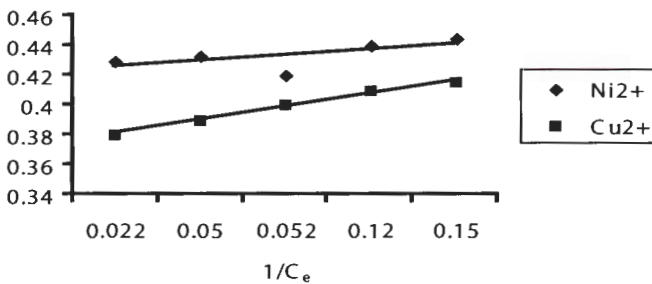


FIGURE 5. FREUNDLICH PLOTS FOR Ni²⁺ AND Cu²⁺ IONS.

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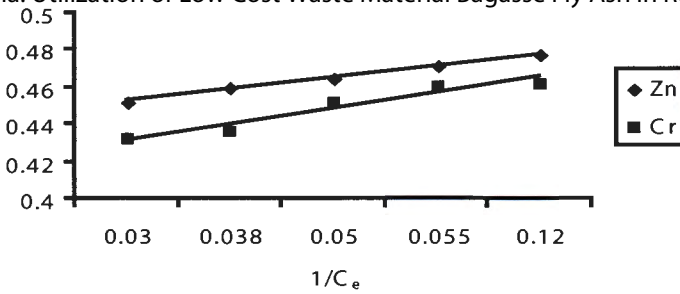


FIGURE 6. FREUNDLICH PLOTS FOR Zn^{2+} AND Cr^{3+} IONS.

LANGMUIR ISOTHERM:

The adsorption results were also fitted into Langmuir isotherm, (Figures 7 and 8) which is given by:

$$q_f = \frac{q_o K_L C_e}{1 + K_L C_e} \quad (3)$$

$$\frac{q_f}{q_e} = \frac{1}{q_o K_L C_e} \quad (4)$$

$$\frac{C_e}{q_e} = \frac{C_e [1 + K_L C_e]}{q_o K_L C_e} \quad (5)$$

$$\frac{C_e}{q_e} = \frac{1}{q_o K_L} + \frac{C_e}{q_o} \quad (6)$$

and thus

$$\frac{1}{q_e} = \frac{1}{q_o K_L C_e} + \frac{1}{q_o} \quad (7)$$

All the items have the usual meaning. Both the Langmuir constants of q_o and K_L are calculated (Table 2) from the slope and the intercept of the straight line of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$.

Based on the magnitude of the correlation coefficient values (Table 2) for both Freundlich and Langmuir isotherms, it can be concluded that Langmuir isotherm is the best model represents all studied systems (Ni^{2+} , Cr^{3+} , Cu^{2+} , Zn^{2+} / fly ash). This observation is compatible with that recorded by Gupta and Ali (2000).

TABLE 2

FREUNDLICH, LANGMUIR CONSTNATS, AND VALUES OF CORRELATION COEFFICIENT FOR THE TWO ISOTHERMS

Cation	Freundlich		Langmuir			
	$\log K_F$	$\frac{1}{n}$	r^2	$\frac{1}{q_o K_L}$	$\frac{1}{q_e}$	r^2
Ni ²⁺	1.10	0.025	0.979	0.430	0.078	0.998
Cr ³⁺	1.30	0.030	0.953	0.431	0.093	0.991
Cu ²⁺	1.25	0.024	0.960	0.380	0.324	0.992
Zn ²⁺	1.27	0.032	0.982	0.452	0.617	0.995

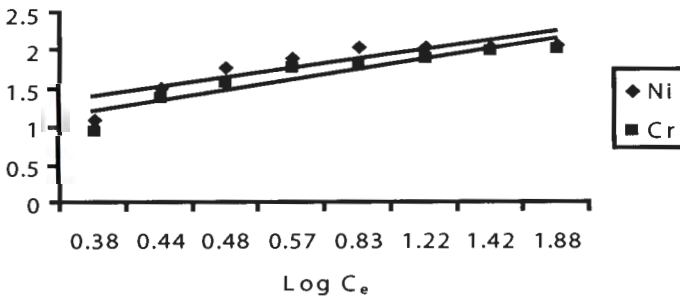


FIGURE 7. LANGMUIR PLOTS FOR Ni²⁺ AND Cr³⁺ IONS.

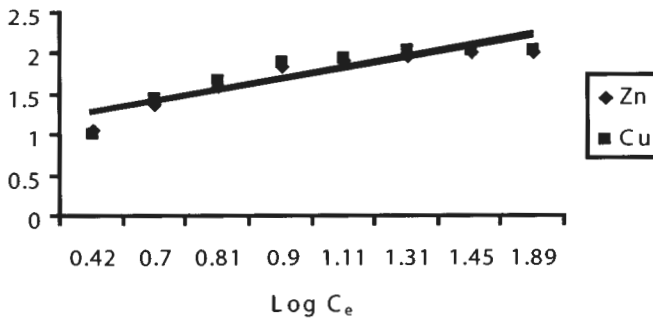


FIGURE 8. LANGMUIR PLOTS FOR Zn²⁺ AND Cu²⁺ IONS.

Taha: Utilization of Low Cost Waste Material Bagasse Fly Ash in Removing EFFECT OF DIVERS IONS:

The effect of the most common ions that expected to be present in water samples on the efficiency of fly ash as an adsorbent was studied. Of these studied divers ions, are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4 , PO_4 and NO_3 . It was observed that a slight decrease in adsorbing of the elements under study (Cu^{2+} , Ni^{2+} , Zn^{2+} and Cr^{3+}). This may be attributed to the competition between the studied elements and the divers to be adsorbed into the fly ash surface. In all cases, decreasing in the fly ash efficiency was not more than 10% from its efficiency without divers ions. This indicates that the developed Cu^{2+} , Ni^{2+} , Zn^{2+} and Cr^{3+} /fly ash systems are still useful for removing the targeted elements from the aqueous samples.

APPLICATION OF THE SUGGESTED SYSTEM:

The suggested system between the bagasse fly ash and the studied heavy metals has been successfully used to remove the studied elements from the industrial waste water of the Egyptian Aluminum Firm, Nagahamadi, Upper Egypt. The efficiency of the system was lower (removal of 60% to 87% of the studied elements was obtained) than that of the stimulated solutions and that is may be due to the matrix effect of the true samples.

Although, regeneration and recovery of the adsorbed elements are very important aspects in waste water treatment processes, they were not performed. This was because the very low cost of bagasse fly ash adsorbent surface.

CONCLUSION:

Bagasse fly ash, a waste material generated in sugar industry, was used, successfully, as a low cost and effective adsorbing surface for the removal of Cu^{2+} , Ni^{2+} , Zn^{2+} and Cr^{3+} from the industrial wastewater. The advantages of bagasse fly ash are:

- 1 Very low cost.
- 2 Highly efficient.
- 3 No needs for regeneration and hence saves time and money.

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