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Assessment and chemical treatment of heavy metals-bearing industrial waste water discharged into the River Nile: case study.

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ABSTRACT

In the present study 12 water samples were collected along the River Nile at the area opposite to the Egyptian Iron and Steel Company (EISC), to evaluate the heavy metals concentrations of Fe, Mn, Zn, Cu, Pb, Cd, Al, Mo, Ba, B, Sn, Ni, Cr, Se, Sn and As. The results revealed that the high concentration levels of studied heavy metals were recorded at the area opposite to (EISC), then the next station (II) after the discharging point and the lower values at station (I) before discharged point. So, two activated carbon treatments were prepared and applied; C-1 (from dates pits) and C-2 (from rice straw). The obtained results showed that C-2 carbon has higher efficiency in the removal of selected heavy metals-bearing waste water of EISC.

1. INTRODUCTION

Heavy metals are elements having atomic weight between 63.5 and 200.6 and specific gravity greater than 5.0 (Srivastava and Majumder, 2008). With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries tanneries, batteries, paper industries and pesticides….etc, heavy metals have become one of the most serious environmental problems. So, these toxic heavy metals should be removed from the waste water to protect people and the environment (Ku and Jung, 2001). Many methods are used to remove heavy metal ions including chemical precipitation and ion- exchange processes that have many advantages such as high treatment capacity, high removal efficiency and fast kinetics (Alyuz and Veli, 2009). Also, heavy metals enter the river and lakes from variety of sources. The rocks and soils directly exposed to surface water are the largest natural source. Dead and decomposed vegetation and animal matter, contribute small amount of metals to adjacent waters. Wet and dry fallout of atmospheric particulate matter arrived from natural sources as well as man's activities can introduce large quantities of metal to rivers and lakes. In addition to discharge of various treated and untreated liquid wastes to the water body (Ku and Jung, 2001).

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Various types of adsorbent were used in heavy metals removal such as, activated carbon (Pollard *et al.*, 1992) and zeolites (Wang and Wu, 2006) and some industrial solid wastes. In rice manufacturing, rice husk is the by- product from paddy grinding. So far, rice husk has been successfully used as fuel in many industrial factories and used as biomass fuel in electricity generation (Jintanawasan *et al*., 2011) because of its low humidity and simple operation. Both rice husk and rice husk charcoal have major components namely, carbon and silica. They have been found to be suitable materials owing to their high carbon and silica and low ash content. Consequently, they are used for the production of activated carbon that commonly used as adsorbents (Cheenmatchaya and kungwankun, 2014).

From previous studies many agricultural wastes such as *Jatropha*, *Curcas* fruit shell (Temyaraslip, 2011), *coconut* hell (Hu and Srinivasan, 1999) *corncob* (Tasi *etal.*, 1998), *Dendrocalanus* aspre Baker and *Dendrocalanus Latiflocus* (Temyarasilp, 2008) have been studied for preparation of activated carbon because of their properties .Thus, a possible solving of rice husk is converting it into value- added activated carbon used as adsorbent and at the same time decreasing exporting of the expensive commercial activated carbon. Normally, the manufacturing of activated carbon involves two major processes, carbonization of raw carbonaceous materials in an inert atmosphere and activation of the carbonized product.

So, the aim of this study were testing the use of rice husk (RH), agricultural waste and date pits (DP) for the preparation of activated carbon by either carbonization by steam or chemical treatment using 5% HCl for (DP) and steam pyrolysis for rice straw (RS). Then using two prepared activated carbons (C-1 & C-2) in the removal of selected heavy metals Fe^{3+}, Mn^{3+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} from waste water of EISC discharged into the River Nile .

2. MATERIALS AND METHODS

2.1 Historical background of the area under investigation:

The studied area was selected because it is affected by the industrial wastes of the Egyptian Iron and Steel Company (EISC). ESIC is one of the major industrial projects, located at Helwan city, 35 km south Cairo. It was established in 1954 year and now it is one of the Investment Ministry companies. It produces about 1.2 million ton/year of crude steel for national market and exportation under the Egyptian Steel Standards. It occupies 1700 feddans at Helwan city with about 14,000 workers. It’s industrial by-products were directly discharged into the River Nile, or recently to the nearby sewage systems to comply with the environmental regulation, the nearby sewage systems. Highly polluted waste water produced having a hydraulic load reached to 600,000 m^3/day (El-sharkawy 2010).

2.2 Sampling program:

Sub surface water samples were collected during four sampling campaigns at three sites of EISC along the River Nile. The three sites (I, II & III) description as follow:

I: The water sample collected from the River Nile before 2km of EISC

II: Point discharged of ESIC waste water into the River Nile water.

III: The next site point discharged of the ESIC with River Nile water (along 500 meter).

2.3 Water analysis:

2.3.1 Field Measurements:

The electrical conductivity (EC) of water samples (µS), temperature (^oC) and pH values were measured in the field using Hydrolab, Model "Multi 340I/SET". Alkalinity CO_3^{2-} and HCO_3^- were measured titrimetrically on spot where samples were titrated against standard H_2SO_4 (0.025 N) using Phenol Phethaline and methyl orange indicators. Also, dissolved oxygen (DO) content was determined by azide modification method as specified in APHA (2008).

2.3.2 Laboratory Measurements:

Water samples were analyzed for all selected variables according to procedures specified in standard method of American Public Health Association, APHA (2008). Total solid (TS) was measured by evaporating a known volume of well mixed samples at 105 ^{O}C. Chemical oxygen demand (COD) was performed by refluxing flask and $K_2Cr_2O_7$ oxidation and biochemical oxygen demand (BOD) by 5 days incubation method . Cl^- was determined by argenometric and SO_4^{2}- by turbidity methods. Na^+& K^+ were measured directly using flame photometer, Model "Jenway PFP, UK". Ca^{2+}& Mg^{2+} were determined by EDTA titrimetric method. NO_2^-,NO_3^-, NH_3 , ortho phosphate and reactive silicate concentrations were determined using colorimetric techniques with formation of reddish purple azo-dye, Cd reduction, Phenate stannous chloride reduction and molybdo silicate methods, respectively. Total phosphorous (TP) was measured as reactive phosphate after ammonium persulphate digestion technique.

2.3.3 Heavy metals measurements:

Preserve samples immediately collected by acidifying with conc. HNO_3 to PH <2 use 5 ml HNO_3 for 1 litre sample. Extract of heavy metals from water sample using HNO_3 digestion method; mix well 500 ml of water sample in a beaker on hot plate, add 10 ml of conc. HNO_3 the slow boil and evaporate till the lowest volume possible 200-100 ml and before precipitation occurs continue heating; then another 10 ml HNO_3 was added until the volume reduced to 80 ml. Transfer to 100 ml volumetric flask and complete to the mark by deionized water. Studied heavy metals were measured using ICP-OES, Model (LEEMAN LABS-profile plus), USA (+ or - 0.1 ppb- up to 10 ppm).

2.4 Preparation of activated carbons:

2.4.1 Steam activated carbons with chemical treatment (C-1):

The raw material, Dates Pits (DP) was chosen for their granular structure, insolubility in water, chemical stability, high mechanical strength and their local availability at almost no cost. Natural DP used in this work was obtained from food industry wastes in Egypt. DP was collected, washed by deionized water, dried at 110 ^{O}C, crushed and immersed in 10% calcium acetate solution, and then the mixture was left over night in drying Oven. The impregnated sample was weighed and placed into the tubular furnace. Pure steam was introduced into the hot mass and heating was continued up to 700 ^{O}C. The products were soaked at this temperature for 1 hr., cooled and weighed then boiled in 5% HCl, washed with deionized water and dried then weight. This gives adsorbent (C-1) (EL- Sharkawy, 2010).

2.4.2 One step steam pyrolysis of rice straw:

Rice straw is one of the main cereal straws and is produced as by- product of rice milling processes in large quantities world wide every year. Straw makes up about 50% of the dry weight of rice plant. The fluidized reactor was heated until the bed temperature reach to 150 ^{O}C. 0.5 Kg of the dried rice straw was injected into the reactor and subjected to heating rate of 50^{O}C/10 min under inert environment of nitrogen. The flow rate of nitrogen used was sufficient to provide good mixing of the rice straw within the reactor (300ml/min). When the temperature of the furnace reach to 350 ^{O}C, steam produced by a steam generator, entered the reactor at a rate of approximately 5 cm^3/min and furnace heating was continue up to final temperature of 750 ^{O}C, holds at this temperature for one hour. After the treatment the sample was left to cool down and the steam flow was interrupted at temperature 250-300 ^{O}C, then the sample was down from the reactor and weighted. This gives adsorbent (C-2) (El-Sharkawy, 2010).

3. RESULTS AND DISCUSSION

3.1 Water quality of the River Nile at EISC studied area:

The three fold increase in global water use during the last 50 years clearly indicates the presence of water management. Tebbut (1999) suggests that by 2015, 1.4 billion people will experience sever water scarcity and further 348 million will face sever economic water scarcity. Constraints on water availability will magnified by the potential deterioration in quality resulting from increased waste water discharges. Thus it is vital that water resource management strategies are integrated with pollution prevention and control measures. Available information's shows that the River Nile, its branches, canals and the other drains are suffering from an alarming increase in discharge of waste water (El-Gohary, 1994). In the greater Cairo area, serious deterioration of water quality has recorded many pollutants in both river water and bottom sediment has been detected (El-Rafei, 1991).

The results were recorded in Table (1) revealed that the increase in the concentrations of physico-chemical parameters e.g. EC, TS, Cl^- , SO_4^{--}, Ca^{2+}, Mg^{2+}, Na^+, K^+, NO_2^-, NO_3^-, NH_3 ,SiO_2^-, PO_4^3- and TP at stations II & III respectively and decreased at station I. This mainly attributes to the effluents discharged of Egyptian of Iron and steel company drains (EISC) at the station II and their effects on the next station III these results are agreement with that reported by (Abdo *et al.*, 2010). On the other side, the lower values concentration at station I was expected due to this area is far from the discharge point of (EISC) with the River Nile and it is considered as a control area.

Table 1: The mean values of water quality parameters of the area under investigation at (EISC)

stations **Physico- Chemical al parameters**	**I**	**II**	**III**
Air Temp. °C	23.5	23.3	23.5
Water Temp °C	20	19.8	19.8
Transp. cm	88	34	58
EC µS/cm	395	1710	510
TS mg/L	257	1109	331
pH	8.3	7.9	8.2
DO mg/L	10	8.3	9.4
BOD mg/L	5	6.5	5
COD mg/L	11	13	12
CO_3^{-2} mg/L	7.3	2.5	2.5
HCO_3^- mg/L	211	459	227
SO_4^{--} mg/L	27	185	44
Cl^- mg/L	26	241	53
Ca^{+2} mg/L	31	127	43
Mg^{+2} mg/L	15	46	18
Na^+ mg/L	34	157	40
K^+ mg/L	5	14	6
NO_2^- µg/L	14	289	53
NO_3^- µg/L	37	1545	69
NH_3 µg/L	570	2360	580
SiO_3^- µg/L	4.18	11	4.41
PO_4^{3-} µg/L	68	145	71
TP	141	261	135

3.2 Heavy metals fluctuations:

In the present study 15 heavy metals were determined and evaluated. The order of these elements according to concentrations recorded in Table (2). Fe > Mn > Al > Ba > B > Zn > Pb > Cd > Mo > Cu > Sn> Ni > Cr> As > Se. The obtained results declare that the high concentration levels of these metals especial, Fe was recorded at station II then III and decrease at I. This could be attributed to the strong effect of industrial wastes that great amount of iron effluents produced from different industries processing in EISC (Abdo *et al*., 2010).

Table 2: The mean concentration values (µg/L) of studied heavy metals of the area under investigation at (EISC)

Stations **Elements (µg/L)**	**I**	**II**	**III**
Fe	560	3561	778
Mn	56	585	81
Zn	9	52	11
Cu	2	3	2.7
Pb	10	26	15
Cd	2	10	5
Al	258	406	288
Mo	1.30	3.30	1.50
Ba	29	146	72
B	47	65	60
Ni	1.55	1.75	1.60
Cr	1.07	1.67	1.20
Se	0.42	0.61	0.50
Sn	1.62	1.81	1.72
As	0.55	0.77	0.16

Most of physico-chemical parameters of the River Nile water quality at the area under investigation were within the permissible limits of USEPA (1999) except for ammonia. On the other hand, the most studied heavy metals concentration levels were found in the permissible limits of USEPA (1999) except for Fe, Pb and Cd.

3.3 Characterization of prepared carbons:

The physical and chemical properties of prepared carbons (C-1 & C-2) were recorded in Table (3).

Table 3: Physico- chemical parameters of prepared activated carbons

Parameters	**units**	**C-1**	**C-2**
Apparent density	g/ml	0.45	0.21
Bulk (packed) density	g/ml	0.64	0.28
Ash content	(%)	7.2	40
BET- Surface area	m^2/g	290	63
Pore volume	CC/g	0.248	1.35
Pore diameter	A°	17	16.5
Methylene blue (MB) index	mg/g	275	41
pH		8.16	9.07

From the above mentioned results in Table (3) it is declare that there are two types of densities associated with activated carbons named apparent and packed (bulk) densities. The apparent density of C-1 is more than C-2. This may be related to the nature of precursor, i.e. the density of date pits is higher than the rice straw. According to Awwa (1991), the lower limit of the bulk density at 0.25 g/ml for GACs to be particle use. The high bulk density can be explained by the high lignin of the precursors. The ash content of the adsorbent depends on the chemical composition of the raw materials (mainly inorganic compounds) and the degree of carbonization (Zanzi, 2001). Among the agro-residues, Rice Straw (RS) has the highest ash content 18% (Marshall, 1999). Therefore, starting with (RS) it was possible to produce adsorbent with high ash content than that obtained by Date Pits (DP). This implies that C-2 is dual carbon (ash content 40%) where, the chemisorptive properties of the high ash content carbon may be advantageous in the treatment of waste waters containing heavy metals.

According to Villar *et al.* (2002) the specific surface area was calculated by applying the BET-equation to get the BET-surface area .S_{BET} is the total pore volume, VP from nitrogen held as liquid at relative pressure $p/p_o = 0.95$ and average pore radius from the empirical relation $r = 2Vp/S_{BET}$. Table (3) shows that the adsorbent C-1 has higher surface area (290 m^2/g) and higher pore volume (0.248 cc/g), than that of (C-2). The pore diameter of C-1 (17 A^O) was very comparable to that of C-2 (16.5 A^O).

The dye adsorption (MB) tests help to determine the capacity of carbon to adsorb molecules of particular size (Pereira *et al.*, 2003). The uptake of MB dye by C-1 follows the N_2 gas adsorption .i.e. the solution uptake is in a good agreement was N_2 gas adsorption.

It is well established that steam activation at high temperature (800-1000 ^OC) is form alkaline oxides, which have chromene and pyrone type structures (Pereira *et al.*, 2003). The most activated carbons are usually basic (pH.≥ 8) and probably the high ash might additionally raise the alkalinity. This is the case of C-2 when compared with C-1.

3.4 Removal of hazardous metals- bearing waste water of EISC by activated carbons

In this concern, the application deals with the removal of (Fe^{3+}, Mn^{2+}, Pb^{2+}, $Cd^{2+}$and Cu^{2+}) ions discharged from spiked industrial effluents of Iron and Steel Company (EISC). The initial concentration (C^O) and final concentrations (Ce-1 and Ce-2) are recorded in Table (4).

Table 4: Initial & final concentrations (µg/L) and removal percent (%R) of selected heavy metals in EISC effluents using C-1 & C-2.

Metal ion	EISC			%R	
	Initial Conc C° (µg/L)	Final Conc. (µg/L) Ce-1	Ce-2	C-1	C-2
Fe	3600	380	180	89.4	95
Mn	660	600	250	9.0	62
Cu	60	28	5.0	53.3	92
Pb	126	18	9.0	86	93
Cd	18	16	4.5	11	75

The obtained results showed that the C-2 has higher efficiency in the removal of the selected heavy metals from EISC effluents. This could be explained related to the lower values of final concentration of Ce-2 compared with Ce-1 as shown in Table (4). Therefore, we can conclude that the removal of hazardous metal-bearing waste water of EISC using C-2 is more efficient than C-1. However, the removal percentage (%R) of (Fe^{3+}, Mn^{2+}, Pb^{2+}, $Cd^{2+}$and Cu^{2+}) from ESIC industrial effluents in case of C-2 ranged between (62-95 %) but in case of C-1 (9.0 - 89.4%).

3.5 Sorption mechanism:

According to Marsh *et al.* (1997) the main constituents of ash content is silica, that represented (95%) of ash content. In the present study C-2 has (40%) and C-1 (7.2%), respectively. The ion-exchange reaction on the silica surface is accomplished through the substitution of protons of the surface silanol group by the metal ions from solution as follows:

$$M^{n+} + x\ (=SiOH) \longleftrightarrow M\ (=SiO)_x^{(n-x)+} + xH^+$$

Where;

M^{n+}= metal ion with n^+ charge.

-SiOH= silanol group on the SiO_2 surface, and xH^+ = number of released protons.

Since electrostatic attraction was not possible between positively charged adsorbent and positively charged metal ion species, it seems that some non- electrostatic force called “specific adsorption” was involved in the process of adsorption (Gharaibeh *et al.*, 1998). The possible adsorption mechanism includes the following:

$$SO^- + M^{2+} \longrightarrow SOM^+$$

$$SO^- + MOH^+ \longrightarrow SOMOH$$
$$SOH + M^{2+} \longrightarrow SOM^+ + H^+$$
$$SOH + MOH^+ \longrightarrow SOMOH + H^+$$

Where SO^- denotes negatively charged surface, SOH denotes neutral surface and M denotes metal ions.

Besides, two major types of chemical bindings can be responsible for the adsorption of various metal ions onto carbon surface: covalent bonding and hydrogen bonding (Gharaibeh *et al*., 1998). The covalent bonding results from the sharing of free electron pairs between the surface oxygen atom and the metal atom or the formation of an O---M bonding. The hydrogen bonding results from the surface oxygen atom and the hydrogen atom of the hydrated metal ions.

3.6 Conclusion and recommendation:

It was clear that adsorbent C-2 is better than C-1 in the removal of Fe^{3+}, Mn^{2+}, Pb^{2+}, $Cd^{2+}$and Cu^{2+} from industrial effluents of EISC. Therefore, we can recommend the application of the chemical treatment using rice straw and dates pits (agro residuals) modified adsorbents C-2 & C-1, respectively in the removal of hazardous heavy metals-bearing waste waters in different industrial installations and facilities.

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