`Removal of Some Heavy Metals from Electrical Power Plant Effluents Discharged into Aquatic Ecosystem Using Low Cost Adsorbents

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Abstract

The preparation of nano-pore size activated carbon from different biomass (rice husk: RH and sawdust: SD) was investigated as a suitable adsorbent for the removal of some heavy metal ions such as Pb (II), Zn (II), Fe (II), Cd (II) and Cu (II) from Surface water stream through batch adsorption process. The prepared activated carbon (AC) was characterized by Fourier transform infrared spectroscopy (FTIR) and surface area analyzer. The effects of initial metal concentration, contact time, pH and adsorbent dose on the sorption of metal ions were studied. It was found that the sorption capacities of the AC decreased in the order: Pb (II), Zn (II), Fe (II), Cd (II) and Cu (II).

KeyWords: Aquatic ecosystem; Removal; Heavy metal ions; Wastewater; Low Cost Adsorbents.

1. Introduction

Water pollution due to organic contaminants is a serious issue because of acute toxicities and carcinogenic nature of the pollutants. Among various water treatment methods, adsorption is supposed as the best one due to its inexpensiveness, universal nature and ease of operation. Many waste materials used include fruit wastes, coconut shell, scrap tiers, bark and other tannin-rich materials, sawdust and other wood type materials, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and sea food processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals etc. The sediment adsorbents have been found to remove various organic pollutants ranging from 80 to 99.9%[1]. Thermal pollution is the degradation of water quality by any process that changes ambient water temperature. A common cause of thermal pollution is the use o water as a coolant by power plant and industrial manufactures. When water used as a coolant is returned to natural environment at a higher temp. Decreases. Oxygen supply and affects ecosystem composition [2].

Different contaminants are released to water with the rapid industrialization of human society, including heavy metal ions, organics, bacteria, viruses, and so on, which are serious harmful to human health. Among all water contaminations, heavy metal ions have high toxic and non-biodegradable properties; can cause severe health problems in animals and human beings [1, 2].The disposal of heavy metals is a consequence of several activities like chemical manufacturing, painting and coating, mining, extractive metallurgy, nuclear and other industries [1, 2].

Therefore, the treatment and removal of heavy metal ions received considerable attention [3, 4]. A number of techniques have been developed for treating water and wastewaters embedded with heavy metals. It includes chemical precipitation, reverse osmosis, membrane filtration, solvent extraction, ion exchange and adsorption [4, 8]. Adsorption is found to be more appropriate and user friendly technique as it has a lower cost of design and operation and it is simple to apply. The use of nano-adsorbent materials offers significant improvement with their extremely high specific surface area, fast dissolution, high reactivity and associated sorption sites, short intra-particle diffusion distance and tunable pore size and surface chemistry [5].

2. Experimental

2.1 Preparation and characterization of activated carbon

Nano-pore size activated carbon from different biomass (rice husk: RH and sawdust: SD), were supplied from El-Dakahlyia Governorate in Egypt [9]. They were collected, washed with distilled water, dried at 110 ^{o}C for 48 hrs, to facilitate subsequent crushing. The dried RH and SD were crushed and used for preparation of activated carbon by impregnation in phosphoric acid. The concentration of 70 % (w/v) H_3PO_4 (BDH) was obtained by dilution of 85 wt. %. Two equal weights of the crushed agro-residues were prepared; The two samples were impregnated in sufficient H_3PO_4 solution, mixed and heated to 80 ∘C for 1.5 hour and then left overnight. The treated masses were dried at 80∘C overnight, admitted into the carbonization tube, then well-placed in electric furnace. The temperature was increased with the rate of 5

∘C/1min to attain 350 °C which allowed free evolution of volatiles and draining of tarry matter. After that, pure steam is introduced from the top of the tube using a steam generator to hold the internal temperature at 500 °C for 1.5 hours. The obtained materials (activated carbon and b from RH and SD respectively) were washed with hot distilled water. The final products were desiccated at 110 °C for 48 hours, and finally kept in tightly closed bottles.

2.2 Sampling stations

Seven stations were selected at the area affected by thermal pollution produced from electric power plants at Embaba and Shoubra El-Keima electric power stations.

2.3 Water samples and analysis:

Subsurface water samples (at depth 60 cm) were collected from seven cross sections at the main channel and two banks of the branch by using poly vinyl Van Dorn plastic bottle (2L).Heavy metals water samples were collected at selected stations and preserved by adding 5 ml of conc. HNO3 to one liter of water sample. The digestion of water sample by adding 10 ml of conc. HNO3 and evaporate to reach 50 ml. Iron, copper zinc, cadmium and lead were measured by using ICP-OES, Model (LEEMAN LABS-Profile plus), USA (±0.1 ppb-up to 10ppm).

2.4 Batch adsorption studies

To study the effect of contact time, pH of solution, type of adsorbent and adsorbate; the sorption experiments of heavy metal on synthetic nano adsorbents were carried out at constant temperature (25 ± 1 °C) using 50mL polypropylene tube with screw cap. The solutions pH was adjusted by additions of HNO_3 or NaOH and the pH values at the beginning and the end of experiments were measured using a digital pH meter of Hanna Instruments type at the ambient laboratory temperature degree 25 ± 1 °C with a BNC water proof electrode. All tests were conducted using 0.05gm of adsorbent with 10 ml solutions containing the metal ions of initial concentration 50mg/l for various time ranged from5 to 120 minutes. In all cases, the sorbent were removed from the solutions by centrifugation for 20 minutes 4000 rpm using Hettich Centrifuge, model ROTOFX32A. Atomic Absorption Spectrometer (AAS), Model (S4) thermo Electron Corporation was used for the measurement of the metal ions concentration in the aqueous phase. For batch investigation, a good shaking for the two phases was achieved using a thermostatic mechanical shaker of the type Julabo SW-20C, Germany. The amount of metal adsorbed was calculated by the simple mass balance relationship:

$$q_e = \left(C_O - C_e\right) x \frac{V}{W} \qquad \text{... (1)}$$

Where Co and Ce are initial and final concentration, V is the volume of solution per liter and W is the weight of adsorbent in g and the % removal of each metal was calculated from the following equation:

$$\% \text{ removal} = \frac{\left(C_O - C_e\right)}{C_O} x100 \qquad \text{... (2)}$$

2.4.1 Effect of pH

The pH of metal solutions has been identified as the most "important variable governing sorption. This is partly due to the fact that the distribution of metal chemical species in solution varies with the pH and partly that this parameter influences on the net charge of the sorbent. The effect of pH on the species sorption was studied by adjusting the initial solution pH within the range 1.0-8.0 using 0.1MHCl and 0.1M NaOH. In these experiments, metal initial concentration was around 50 mg/L.

2.4.2 Sorption study

For the adsorption isotherm experiments, the initial metal concentration was varied within the range 0-50mg/L; temperature was 25±1 °C, and pH=8,this pH was selected based on batch tests conducted to determine the effect of pH on the sorbent capacities.

3. Results and discussion
## characterization of prepared activated carbon
a-Surface area

The surface area analysis of the two prepared activated carbon from rice husk and sawdust and the pore size distribution are summarized in the following Table (1) and Figure (1,2).

3.1 Effect of pH

The effect of pH, while keeping all other experimental conditions fixed as mentioned in the experimental section, was investigated in the range (1–8). It was found that the adsorption of Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) increases by increasing pH from 1 to 8 in case of using A.C (A) as adsorbent, whereas in case of using A.C.(B) as adsorbent the adsorption of Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) increases by increasing the pH within the investigated range. Results of the Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) sorption as a function of initial pH are presented in Fig.3. and Fig.4.For Activated carbon (A) and (B), respectively.

Table 1. The surface area analysis of the two prepared activated carbon.

Parameters	RH activated carbon	SD activated carbon
Surface Area	261.593 m²/g	1033.588 m²/g
Total pore volume	0.2372 cc/g	0.6640 cc/g
Average pore Radius	18.1315 Å	12.8492Å
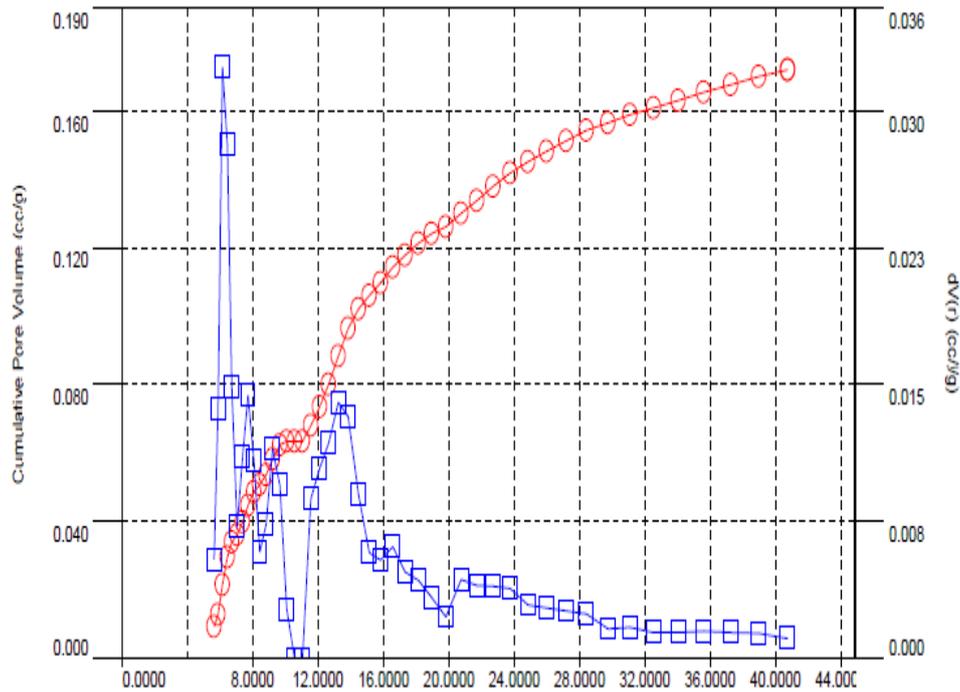
Fig 1. Half pore width (A) of RH activated carbon.
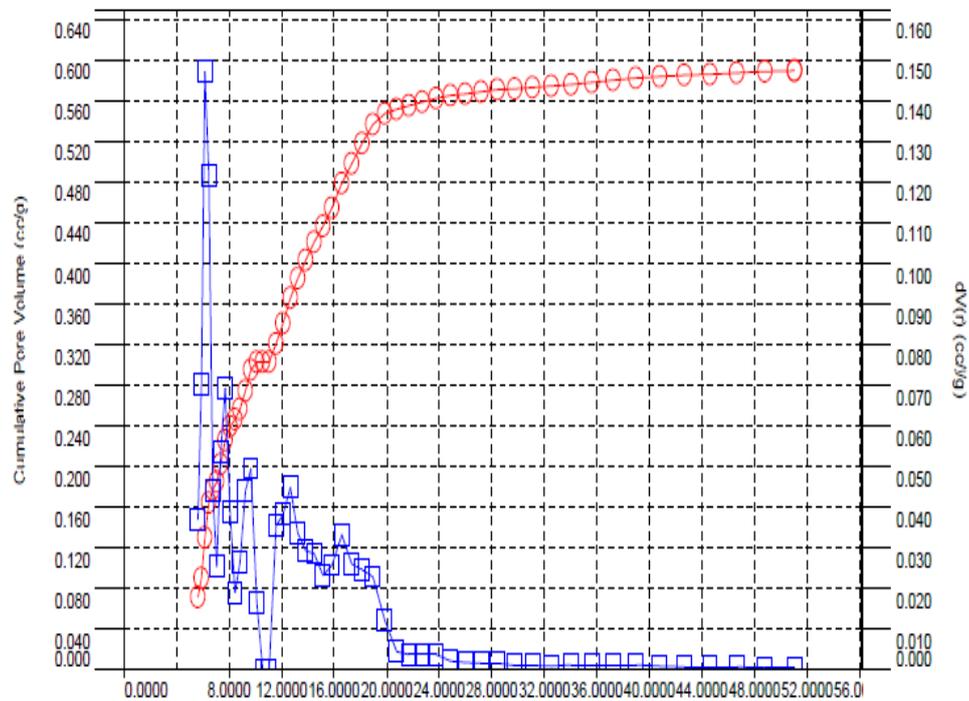
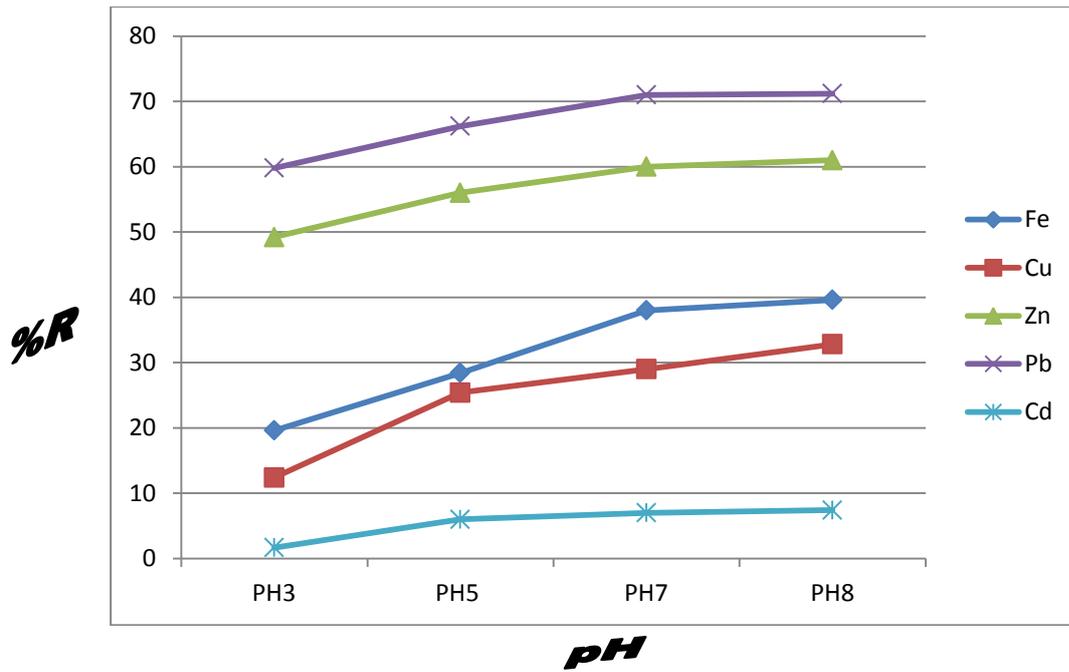**Fig 2.** Half pore width (B) of SD activated carbon.

Fig 3. The effect of pH on the adsorption of heavy metals by activated carbon (A) at (contact time=24 h, agitation speed = 150 rpm, concent. = 50 mg/l, mass of adsorbent=0.05 g, volume of solution = 10 ml and temp. = 25 ^{O}C.
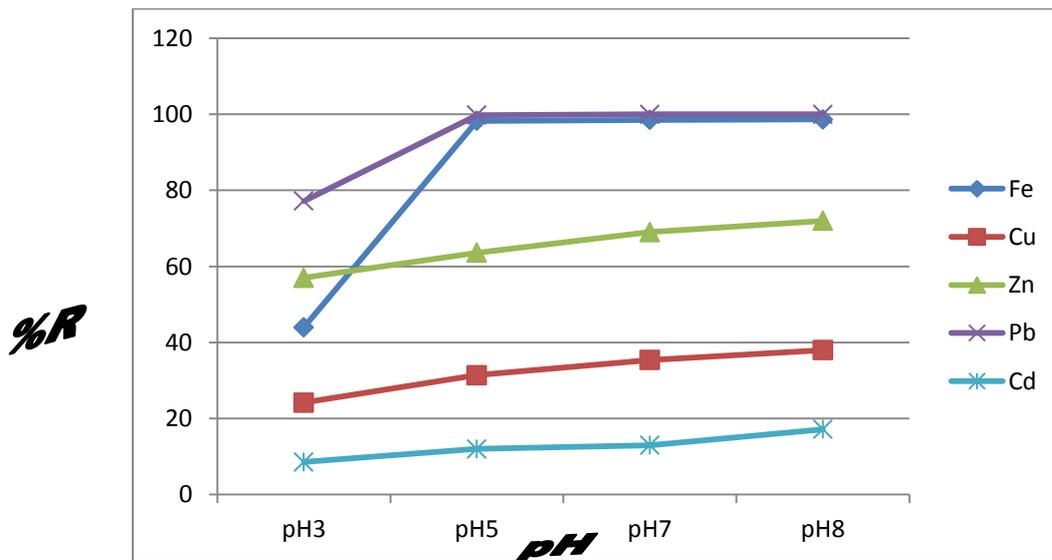

Fig 4. The effect of pH on the adsorption of heavy metals by activated carbon (B) at (time=24 h, agitation speed = 150 rpm, concent. = 50 mg/l, mass of adsorbent=0.05 g, volume of solution = 10 ml and temp. = 25 ^{O}C.

3.2 Sorption study

Sorption isotherms could be described by different models such as Langmuir and Freundlich equations, depending on the metal species and the coexistence of other metal ions, at pH 7 potentially190 mg of Fe^{2+}, 145 of Cu^{2+}, 300mg of Zn^{2+} , 355 mg of Pb^{2+}, and 35mg of Cd^{2+} could be adsorbed per Kg of A.C. (A) whereas in case of using A.C. (B) it was found that 492 mg of Fe^{2+}, 175 of Cu^{2+}, 345mg of Zn^{2+} , 499mg of Pb^{2+}, and 65mg of Cd^{2+}. The sorption

equilibrium data were fitted by the non-competitive Langmuir model:

$$\qquad\qquad\qquad\qquad\qquad \text{.... (3)}$$

$$q_e = \frac{q_{max}\, b\, C_e}{1 + b\, C_e}$$

Where q_e is the amount of metal sorbed per unit mass of sorbent, q_{max} is the maximum metal per unit mass of sorbent (mg/g).

C_e is the equilibrium concentration of sorbate in solution (mg/g), and b is the Langmuir constant related to energy of sorption (L/mg) which

reflects quantitively the affinity between the sorbent and the sorbate. From the experimental equilibrium data a nonlinear fit was performed by means of the program MATLAB in order to obtain the Langmuir model parameters this program minimizes the sum square of residuals (SSR)

$$SSR = \sum_{i=1}^{N}(q_{i-}\frac{q_{max} b\, c_i}{1+bC})2 \qquad \dots (4)$$

The experimental data of Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) are plotted in Fig.(3)and Fig.(4) in these figures, it can be observed that experimental data have a good compliance with the calculated Langmuir isotherm curve, this fact indicates monolayer coverage on the A.C (a) and (b) surface by heavy metals investigated. Fitting of Langmuir isotherm equation to the data gathered from the equilibrium sorption experiments (symbols) initial pH:7, temperature 25+1 ^{o}C. The q_{max} obtained in this study for Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) onto A.C. (a) and (b) was compared to the reported in the literature [1-8] for some A.C. and it was found that A.C. (a) and (b) were more effective upon the removal of these toxic heavy metal from water resources.

3.3 Adsorbent dose

The effect of sorbent dose as one of parameters that strongly affects the adsorption capacity is shown in Fig. 5. It can be observed that with the mixed Pb (II), Zn (II), Fe (II), Cd (II) and Cu (II) concentrations, the amount of removed Pb (II), Zn (II), Fe (II), Cd (II) and Cu (II) ions increases with the increase of the adsorbent weight. After a certain adsorbent dosage the removal efficiency is not increased significantly. The maximum removal efficiency was achieved at an adsorbent dosage level 0.1g/l.

3.4 Effect of temperature

To study the effect of temperature on adsorption of Pb (II), Zn (II), Fe (II), Cd (II) and Cu (II),different experiments were carried out in the range 25–60°Cwith a contact time for 24h. It can be observed from Fig. 6.The adsorption percent was increased with increasing the temperature.

3.5 Desorption experiments

Desorption experiments put into evidence that after 24 hours contact HCl solutions were more efficient than NaOH solutions to desorbs Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) for the (a) and (b) presented in Fig.7.and Fig.8. As seen , the maximum Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) desorption percentage(98.6%) was obtained for the highest HCl concentration (1.5 mol/L) used.

Table 2. Amount of element adsorbed on adsorbent of heavy metals ions (F$_e$, Cu, Zn, Pb and Cd) of the concentration with variation of pH at temp. of 25 ^{o}C for activated carbon (a).

pH	Fe mg/l	q_e mg/g	Cu mg/l	q_e mg/g	Zn mg/l	q_e mg/g	Pb mg/l	q_e mg/g	Cd mg/l	qe mg/g
3	40.20	0.98	43.80	0.62	25.40	2.46	20.10	2.99	48.20	0.18
5	35.80	1.42	37.30	1.27	22.00	2.80	16.90	3.31	47.00	0.30
7	31.00	1.90	35.50	1.45	20.00	3.00	14.50	3.55	46.50	0.35
8	30.20	1.98	33.60	1.64	19.50	3.05	14.40	3.66	46.30	0.37

Table 3. Amount of element adsorbed on adsorbent of heavy metal ions (F$_e$, Cu, Zn, Pb and Cd) of the concentration with variation of pH at temp.25°C which corresponding to activated carbon (b).

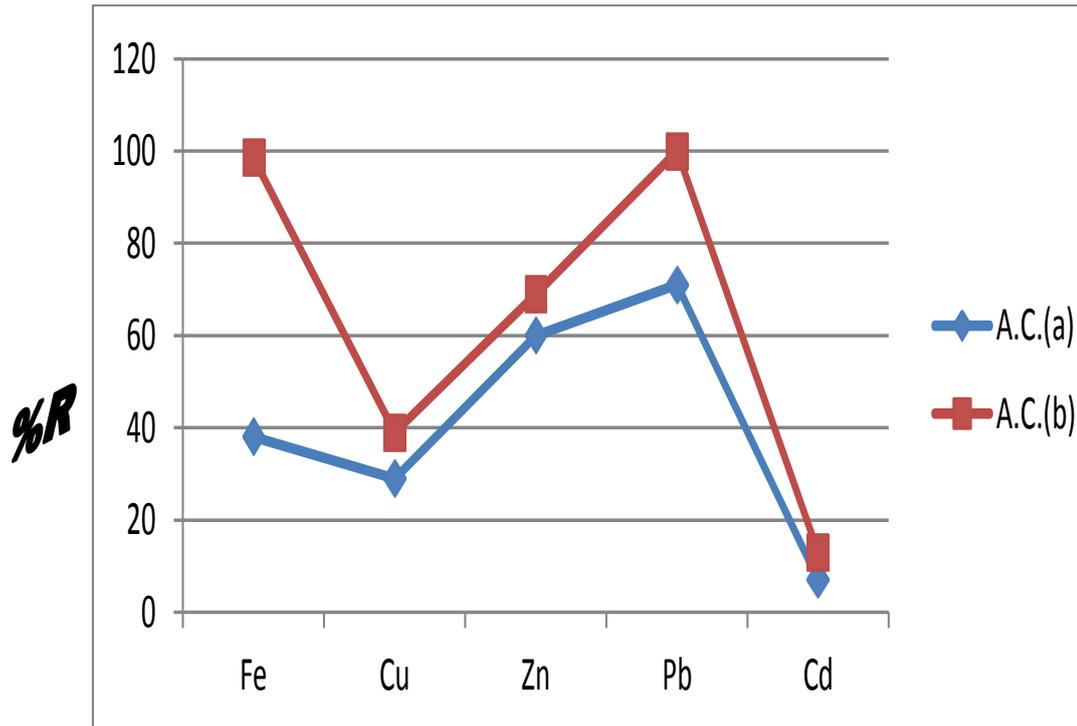| pH	F$_e$ mg/l	q_e mg/g	Cu mg/l	q_e mg/g	Zn mg/l	q_e mg/g	Pb mg/l	q_e mg/g	Cd mg/l	qe mg/g
3	28.00	2.20	37.90	1.2	21.50	2.85	1.40	3.86	45.70	0.43
5	<0.87	4.91	34.30	1.57	18.20	3.18	<0.12	4.98	44.00	0.60
7	0.75	4.92	32.50	1.75	15.50	3.45	0.02	4.99	43.50	0.65
8	0.69	4.93	30.80	1.92	14.00	3.60	0.02	4.99	41.40	0.86

Fig 5. Effect of adsorbent rice husk and sawdust on the removal of heavy metals with concentration of 50 mg/l, pH=7, temp. 25°C, time=24h and 0.1g of adsorbent with 10ml from solution
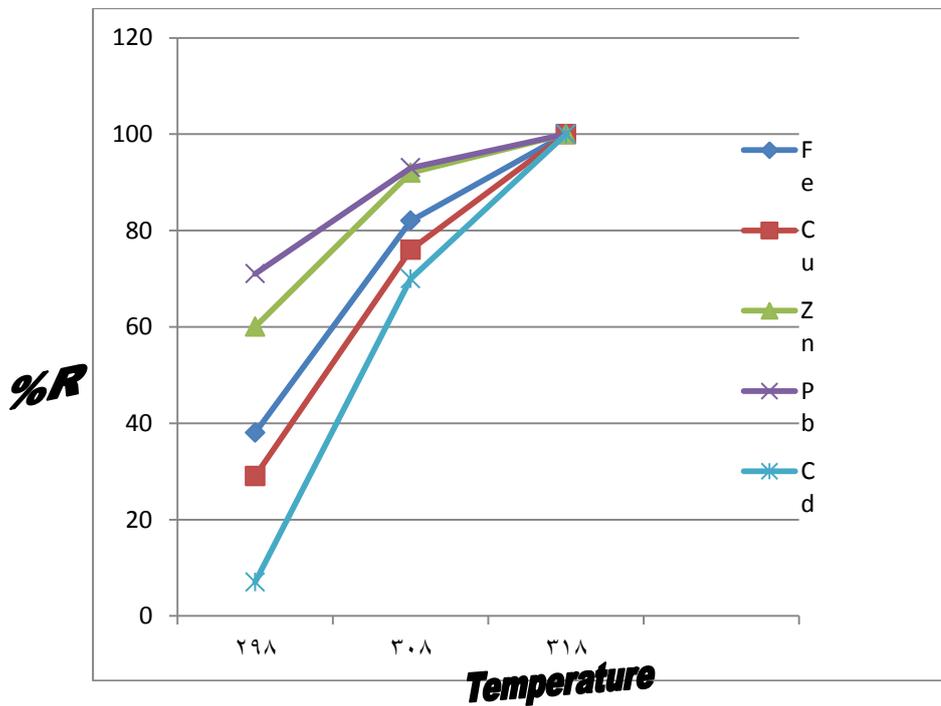

Fig 6. Effect of temperature on the adsorption of different metals by activated carbon (a) at concentration of 50 mg/l, adsorbent dose 0.05g and pH=7.
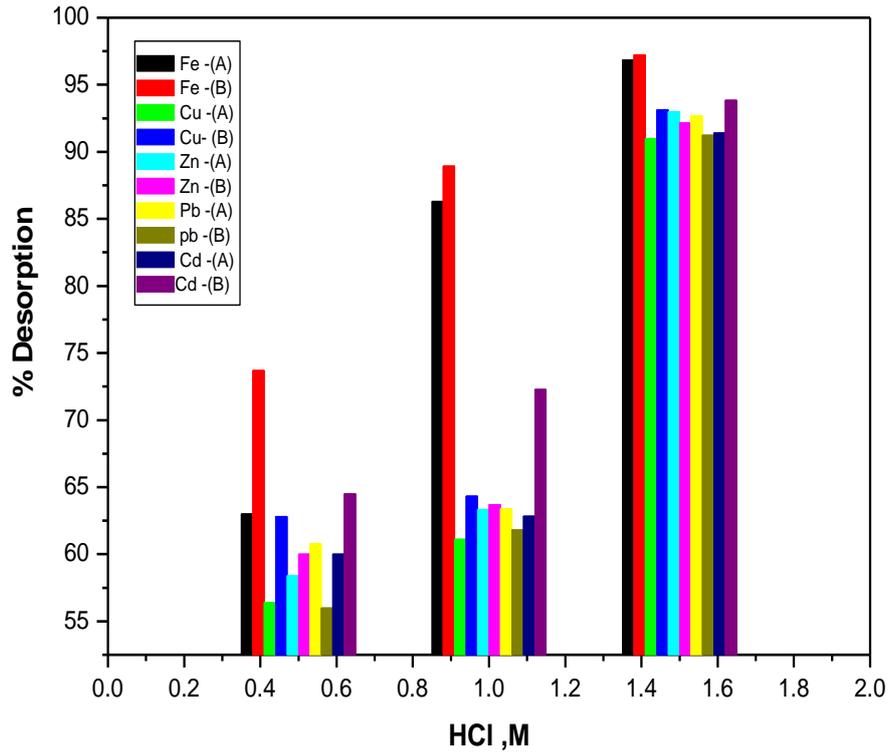
Fig 7. Desorption rate of heavy metals from Activated carbon (a) and (b) by different concentration of HCl
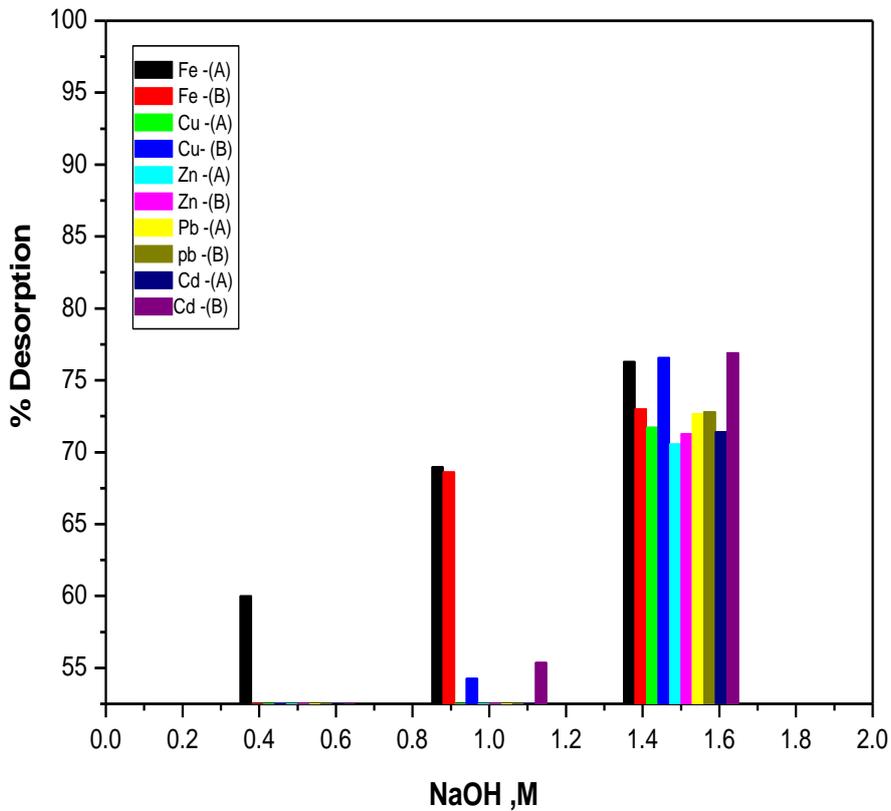

Fig 8. Desorption rate of heavy metals from Activated carbon (a) and (b) by different concentration of NaOH.

4. Conclusion

1- Utilization of material to manufacture activated carbon for treating Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) contaminated River Neil water is value added strategy.

2- Batch adsorption experiments were conducted to investigate capacity of A.C. (a) and (b) possessed significantly higher adsorption capacity for Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II).

3- HCl solutions were more efficient than NaOH solutions to desorbs Fe (II), Cu (II), Zn (II), Pb (II) and Cd (II) from A.C. (a) and (b).

4- The study suggests that ecumenically manufacturing granular activated carbon that is to be used in contaminated River Neil water for removing of heavy metals.

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