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Equilibrium and kinetic studies of adsorption/biosorption of Cu^{+2} and Co^{+2} ions from aqueous solution by different adsorbents

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ABSTRACT

The adsorption/biosorption onto granular activated carbon, waste of fungi (white Agaricusbisporus)and sunflower shells for Cu (II) and Co (II) removal from aqueous solutions was evaluated. The effects of experimental parameters pH, contact time, adsorbent dose and initial concentration on heavy metal sorption were investigated. Maximum sorption capacity was reached at optimum pH 5.0. The results showed that waste of fungi performed better efficiency removed heavy metal compared with granular activated carbon and sunflower shells. Several isotherm models were used to fit the experimental data. Freundlich isotherm model matched very well the adsorption equilibrium data in the studied conditions. Several kinetic models were applied to fit the adsorption results. The experimental data processes were well described by the second-order reaction kinetic. Adsorption of Cu (II) and Co (II) onto different adsorbents was influenced by chemisorption and intraparticle diffusion.

Key words: GAC, *Agaricusbisporus* Adsorption, Biosorption, Isotherm, Kinetics, Heavy metals.

INTRODUCTION

Heavy metals cannot be discharged directly to the environment due to its harmful effects to human. These metals can cause accumulative poising, cancer, nervous excessive ingestion system damage and ultimately death(Corapeioglu andHuang , 1987;Bailey et al. 1999; Issabayeva G. Aroua and Sulaiman,2007).The major source of heavy metal pollution are mining operations, alloy manufacturing, tanneries, electronics, fuel, welding and petrochemical industries(Gupta and Ali, 2000;Basci et al., 2004).The most traditional methods used for removing heavy metals from wastewaters are chemical precipitation, ion exchange, reverse osmosis, coagulation, evaporation, electrochemical treatment, electro dialysis, membrane filtration and adsorption(Brtosh et al.,2000; Georg Steinhauser, 2008).But these traditional physical and chemical methods have significant disadvantages, because of incomplete metal removal, expensive equipment and potential risk of the generation of hazards by-products (Volesky, 1990; Tsezos, 2001).Also, most of these processes suffer from one drawback especially when the metals in solution are in the range of 1-100 mg/L.The high cost of adsorbents such as activated carbon used for the treatment of water and wastewater has conducted to new more effective and cheaperadsorbents (Bailey et al. 1999). The biosorption of heavy metal ions by non-living microbial biomass offers an alternative to the existing physic-chemical technologies for detoxification and recovery of toxic and valuable metals from wastewater.Biosorption is the process in which phscio-chemical interaction between the charged surface groups of micro-organisms and ions in solution takes place by the process of complexation, ion exchange, microprecipitation, physical adsorption etc.(Mise and Rajamanya, 2003).Many biomaterials such as seaweed, micro-algae, plant materials, yeast , bacteria and fungi have been studied for their ion binding abilities. Fungi hashigh metals tolerance, wall binding capacity and intracellular metal uptake capabilities may be better compared with other microbial groups, as well as fungal biomass is cheap and easily produced in rather substantial quantities as by product from established industrial fermentation processes. Fungi can accumulate metal by physico-chemical and biological mechanisms.Many fungal species such as *Aspergillusniger, Peniciliumspinulum and Rhizopusarrzhius*have been extensively studied for removing heavy metals The aim of this study is to evaluate the ability of waste of fungitype (*whiteAgaricusbispo*rus) and sunflower shell for removal of copper and cobalt from simulated wastewaterin batch system and compare with commercial activated carbon by studying the effect of pH, contact time, heavy metal concentration.The equilibrium and kinetic studies are carried out for removal of Cu^{+2} and Co^{+2} ions onto different adsorbents.

EXPERIMENTAL SECTION

2.1 Chemicals:

All chemicals used in this study were of analytical grade supplied by LobalChemie Company, India. These used for the preparing of synthetic wastewater of concentration 1000 mg/L. Stock solutions of $Cu^{2+}$and Co^{2+} were prepared by weighted accurately amount of cupper nitrate ($Cu(NO_3)_2.3H_2O$), cobalt nitrate($Co(NO_3)_2.6H_2O$) and dissolved in distilled water to make up 1L solution. Experimental solutions of the desired concentration were prepared by diluting the stock solution with distilled water.

2.2 Adsorbents:

Commercial granular activated carbon (GAC) was obtained from LobalChemie Company, India. Each of activated carbon,waste of fungi and sunflower shells were ground and screened to give a desired particle size (150-300µm) , activated carbon washed with distilled water and dried over night at 105 °C

Sunflower shells (S.F.) were obtained from raw sunflower, the shells were sequester, washed with distilled water, and dried at 70 °C for 72 h.

Waste of fungi (*white Agaricusbisporus*) was obtained at the end of harvested of mushroom in the north west of Iraq. The waste of fungi (W.F.) was ground, screened, washed several times with distilledwater, dried for 72 h in oven at 70 °C then kept in desiccator.

2.3 Batch experiments

The experiments were conducted at 25±1°C. For each experimental run, 100 ml of Cu^{2+} (II) and Co^{2+} (II) solutions of known initial concentration and pH were placed in 250 ml Erlenmeyer conical flasks. A suitable adsorbent/biosorebentdose (0.2 g) was added to the solution and the mixture was shaken at a constant agitation speed (200 rpm) for 3 h for all sets of experiments of adsorption equilibrium isotherms, while for kinetic conditions, samples were withdrawn at appropriate time intervals (5-180 min).Samples (10 ml) were centrifuged at (3000 rpm) for 10 min and the supernatant liquid was analyzed for the remaining $Cu^{2+}$and Co^{2+} concentrations.

The adsorption/biosorption of heavy metal ions onto GAC, waste of fungi and sunflower shells were investigated as a function of initial pH, dose of adsorbent, contact time and initial concentrations. Optimum conditions needed to attained equilibrium were established for low cost biosorbents (waste of fungi and sunflower shells) and compared with the GAC. All experiments were carried out triplicate.

In order to find the optimum conditions, we used the following variables were used: pH (2-8),dose of adsorbent/biosorbent (0.5-30 g/L), contact time (0-180 min),initial concentration (0-100 mg/L), particle size of adsorbent/biosorbent (150-300 µm) at room temperature (25±1 °C).

The percentage removal of heavy metal ions from wastewater by adsorbent /biosorbent was calculated by using the following equation:

$$\%\text{Removal}=\frac{Co-Ce}{Co}\times 100 \qquad (1)$$

The adsorption capacity q_e (mg/g) was obtained by using a mass equilibrium equation as follows:

$$q_{\mathrm{e}}=\frac{(C_{\mathrm{o}}-C_{\mathrm{e}})V}{m} \qquad (2)$$

Where C_o and C_e are the concentrations (mg/L) of heavy metal ions at initial and equilibrium respectively, V is the experimental volume of heavy metal solution in (L),m is the adsorbent mass in (g)

RESULTS AND DISCUSSION

3.1 Effect of pH

The pH is one of the most important parameters of adsorption/biosorption of heavy metals. It plays an important role in adsorption/biosorptionprocess (Gueu et al., 2007; Mohamad et al., 2008; Vijayakumaran et al., 2009) The adsorption of copper (II) and cobalt (II) onto different adsorbent/biosorbent(granular activated carbon, waste of fungi and sunflower shells) at different pH ranged 2 - 8 was studied to establish the optimum pH for adsorption of each metallic ion. The effect of pH on the percentage Cu(II) and Co(II) were removal are shown in Fig. 1(a and b).In the present investigation, the rate of removal Cu(II) and Co(II) ions in synthetic wastewater is mainly controlled by pH of the solution. From Fig. 1(a and b) and Table (1), it can be confirmed that the optimum pH for removal of copper from wastewater using granular activated carbon, waste of fungi and sunflower shells were 5.5 , 4.0 and 5.5 respectively, while for removal of cobalt were 5.5, 4.0 and 5.5 respectively. At pH higher than 6 both metals were precipitated due to formation of hydroxides. At pH less than 4, little sorption was occurred especially at pH 2. This was due to the concentration of protons was high and metal binding sites became positively charged repelling the Cu (II) and Co (II) cations. With an increase in pH, the negative charge density on the biocarbon increases due to deprotonation of the metal binding sites, thus increasing metal sorption. Generally, the optimum range of pH solution for removing heavy metals was found 4-6. Thus different metals have different pH optima, due to the different solution chemistry of the metals. (Macaskieand Dean, 1989). The low sorption capacity at pH values below 4.0 was attributed to hydrogen ions that compete with metal ions on the sorption sites (Tsezos and Volesky, 1981; Hunag et al., 1991). In other words, at lower pH, due to protonation of the binding sites resulting from a high concentration of protons, negative charge intensity on the sites was reduced, resulting in the reduction or inhibition of the binding of metal ions (Kapoor et al., 1999).Examining the results obtained from the adsorption/biosorption experiments, it can be seen that the highest rate of adsorption by GAC, W.F. and S.F. were 74.34% , 97.62% and 76.84% respectively for removal of Cu(II) ions while 33.66%, 73.46% and 57.7% respectively for removal of Co(II) ions from the synthetic wastewater at optimum pH.

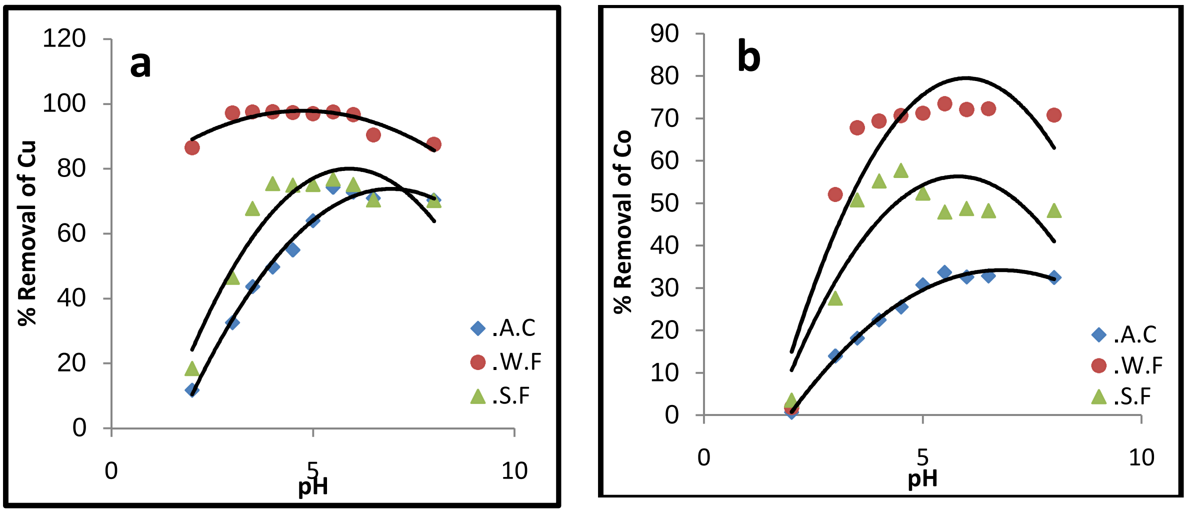


Fig. 1: Effect of pH on the percentage removal, (a) copper and (b) cobalt

3.2 Effect of Adsorbent Dose

The effect of different doses of GAC, W.F and S.F. was investigated using 50 mg/L of initial concentration for each of copper and cobalt at optimum pH. Fig. 2 (a and b) shows an increase in percentage removal of copper and cobalt respectively with the increase in dose adsorbent up to a certain limit and then it remains almost constant. The increase in the adsorption with increasing the dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites. Table (1) shows the optimum values of mass adsorbents 1.7, 0.7 and 1.0 g of GAC, W.F. and S.F. respectively to remove Cu(II) ions from synthetic wastewater , while it was found that1.7, 1.0 and 1.7g to remove Co(II) ions. Fig. 2 (a and b) shows that an increasing the dose of GAC 0.1-1.7 g, the percentage removal will increase from 23-76.5%, waste of fungi 0.1-0.7 g, and 25-96.5% for sunflower shells, it was found that for dose 0.1-1 g, 24-80% for removing Cu(II) ions, while for removing Co(II).Increasing the dose of GAC from 0.1-1.4g gave 11-47%, for using W.F 0.1-1.0g gave 25-90% and finally for using S.F. 0.1-1.7 g gave 7-63% respectively. A further increase above optimum dose values will not have any significant effect on the removal of copper and cobalt ions from the solution. This can be due to the fact that by increasing the mass of adsorbent in the solution can lead to adhere of adsorbents together and decrease the contact surfaces which consequently cause a decrease in the percentage removal.

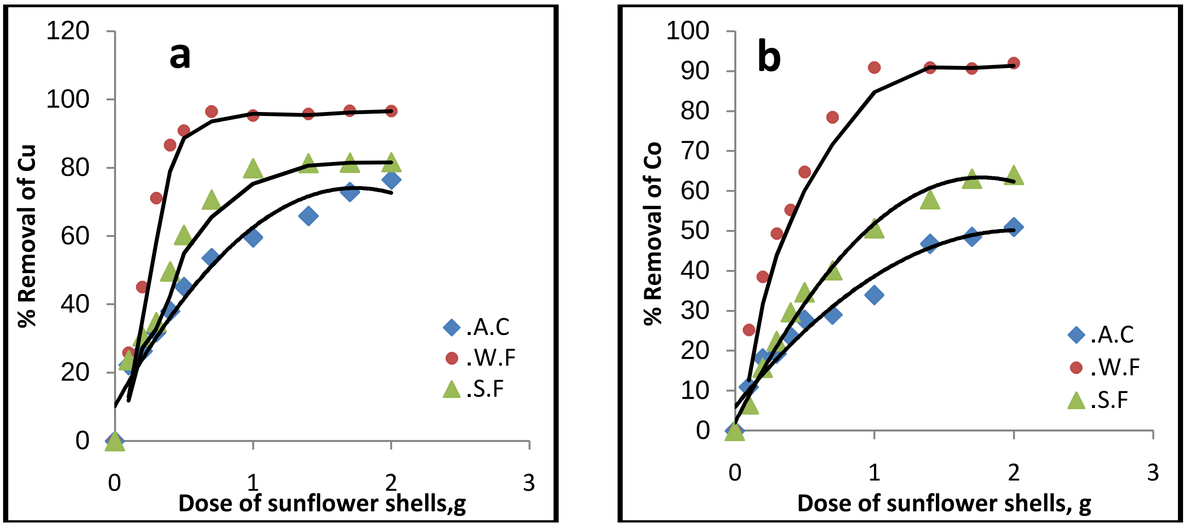


Fig. 2: Effect of adsorbent mass on removal, (a) Copper and (b) Cobalt at initial concentration= 50 mg/L

3.3 Effect of contact time

The effect of contact time on the removal of metal ions was studied, Fig. 3 (a and b).The two metals showed a steady rate increase of sorption during the sorbate-sorbent contact process and the rate of removal became almost insignificant due to a quick exhaustion of the adsorption sites. The rate of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals (Saeed et al., 2005; El-Sayed, 2012).

The effect of contact time on the removal of heavy metals until the equilibrium condition was180 min onto different adsorbents using the optimum values of pH and dose of adsorbent for each of lead and cadmium. Fig. 3(a and b) shows the effect of contact time for the removing of copper and cobalt ions onto different adsorbents These figures and Table (1) showed that the activated carbon needs 30 min to remove maximum amount of copper, 70 min for cobaltand 60 min for copper, 70 min for cobalt when using waste of fungiwhile sunflower shell needs 30 min for copper and 70 min for cobalt. These figures show the maximum removal of heavy metal ions as follows: waste of fungi> sunflower shells > granular activated carbon.

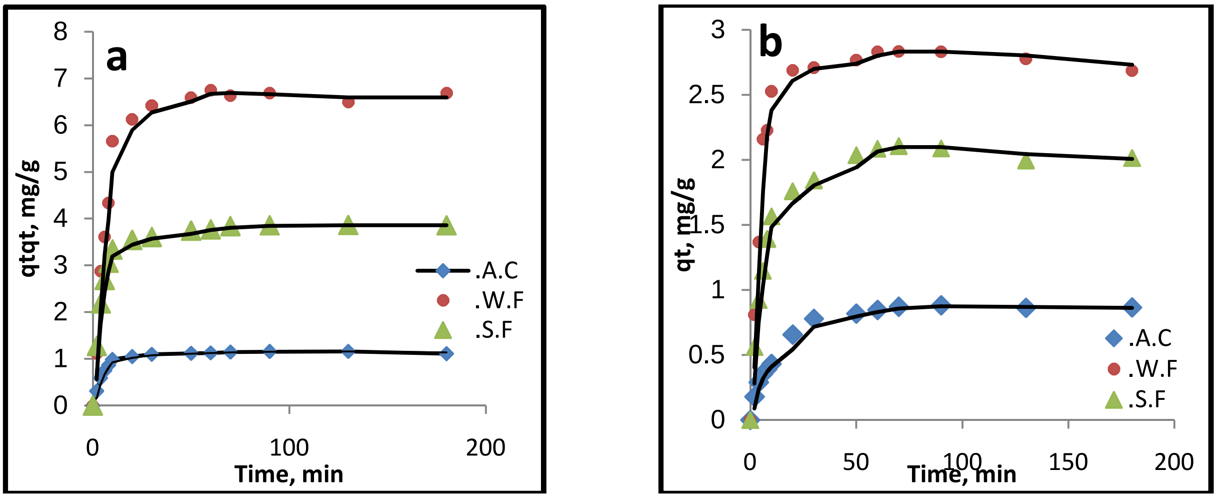


Fig.3: Effect of contact time on the uptake removal of (a) copper and (b) cobalt at initial concentration= 50 mg/L

Fig. 4(a, b and c) shows the comparison uptake removal of copper and cobalt ions at optimum conditions using different adsorbents (GAC, W.F. and S.F.).

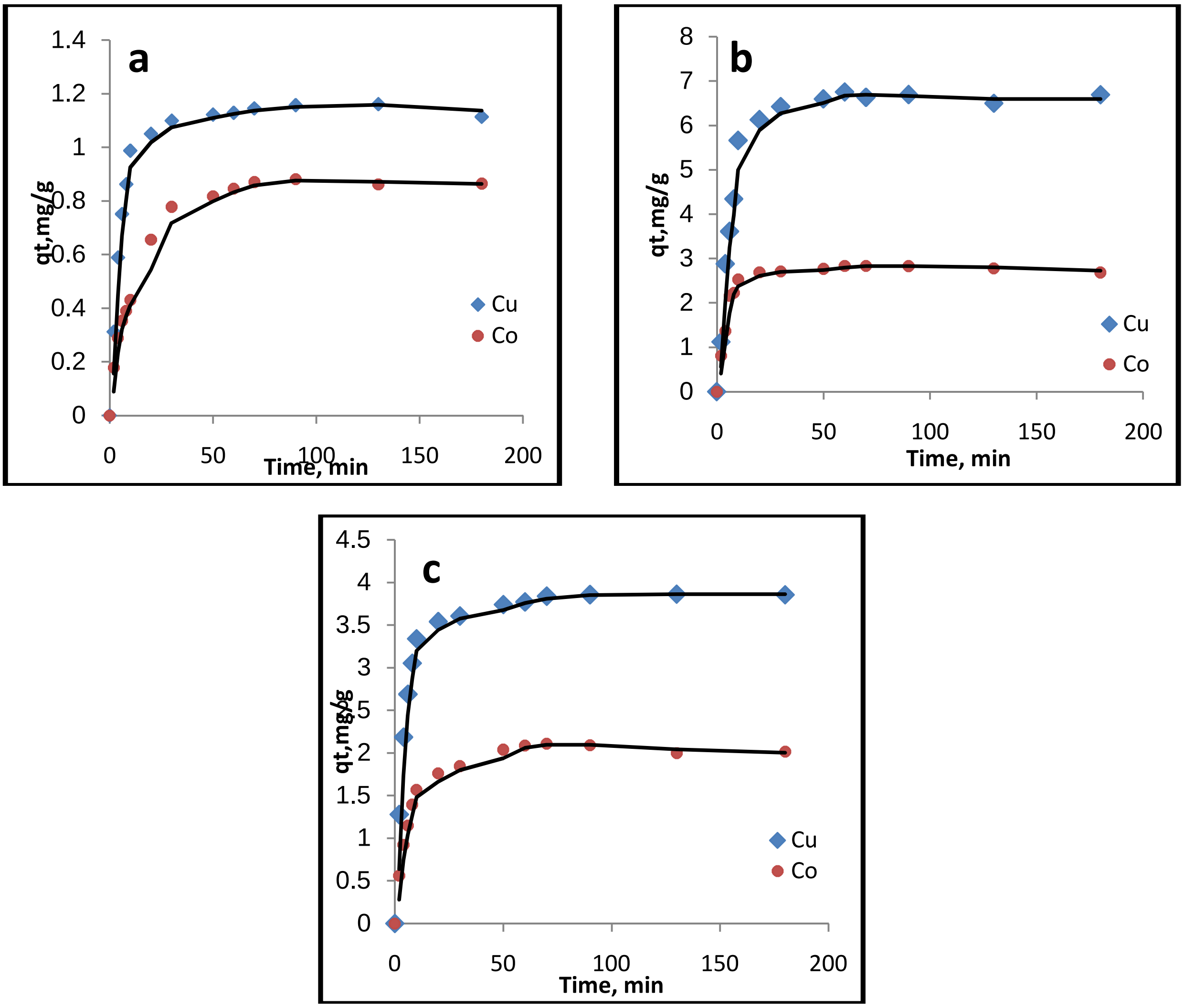


Figure 4:Comparison uptake removal of copper and cobalt for (a) activated carbon (b) waste of fungi (c) sunflower shells

Table 1 summarize the maximum removal of the heavy metals from wastewater using various kinds of adsorbent/biosorbent(GAC, W.F. and W.F.).

Table 1: Optimum conditions for different adsorbents at 50 mg/L solutions

Copper			
Adsorbent type	Activated carbon	Waste of fungi	Sunflower shells
pH	5.5	4	5.5
Contact time ,min	130	60	130
Adsorbent mass ,g	1.7	0.7	1.0
Cobalt			
Adsorbent type	Activated carbon	Waste of fungi	Sunflower shells
pH	5.5	5.5	5.5
Contact time ,min	70	70	70
Adsorbent mass ,g	1.7	1	1.7

3.4 Effect of initial concentration of solutions and mass of different adsorbents

The metal uptake mechanism is particularly dependent on the heavy metal concentration. Initial concentrations of 25, 50, 75 and 100 mg/L of metal ions were selected for the comparative study of Cu (II) and Co (II) ions using different adsorbents (GAC, W.F. and S.F.). Fig. 5 (a, b and c) and Figure 6(a, b and c) showed the effect of metal concentration on the removal of copper and cobalt ions from simulated wastewater. . Basically, it was clear that the percentage removal of eachions increase with decreasing the initial ion concentration, and the percentage removal onto waste of fungi is greater than sunflower shells and GAC. The percentage removal of copper was greater than cobalt .Also, the percentage removal of each ion adsorbed increases sharply with dose of adsorbent (0-0.5)g for copper and (0-1.0)g for cobalt, and then gradually increases to reach equilibrium value approximately (1-2)g, while a further increase in dose had a negligible effect on the percentage removal. The equilibrium dose was found to be independent of the initial concentration. According to these results, the optimum doses found earlier were used for the rest of batch experiments to make sure that the equilibrium was reached. As a result, the removal percent had shown small decreasing changes when used doses between (1-2) g, this can be due to the fact that by increasing the mass of adsorbent in the solution willincrease its concentration which can lead to adhere of absorbents together and decrease the contact surfaces which consequently causes a decrease in the percent of removal, this behavior emphasized the above mentioned analysis. Therefore, it is clearly indicates that the removal of metal ions mainly depends on the amounts of adsorbents and contact time.

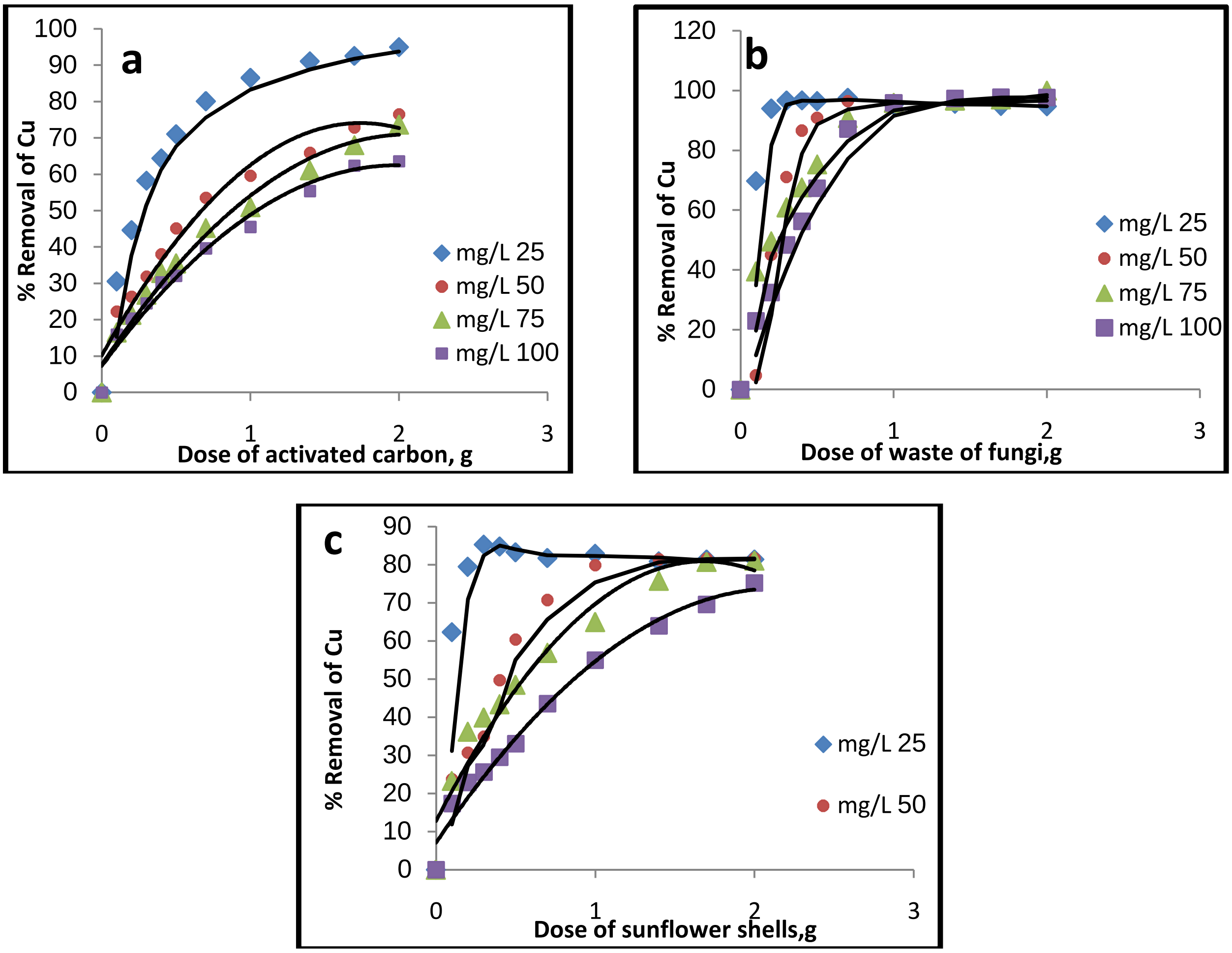
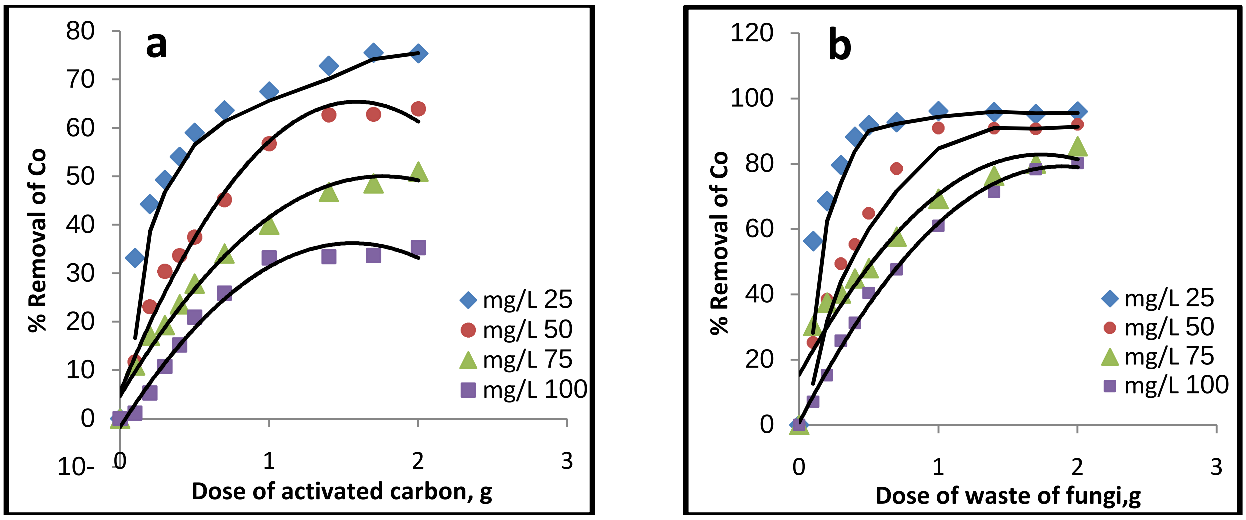


Fig.5: Effect of initial concentrations on uptake removal of copper using (a) activated carbon, (b) waste of fungi and (c) sunflower shells



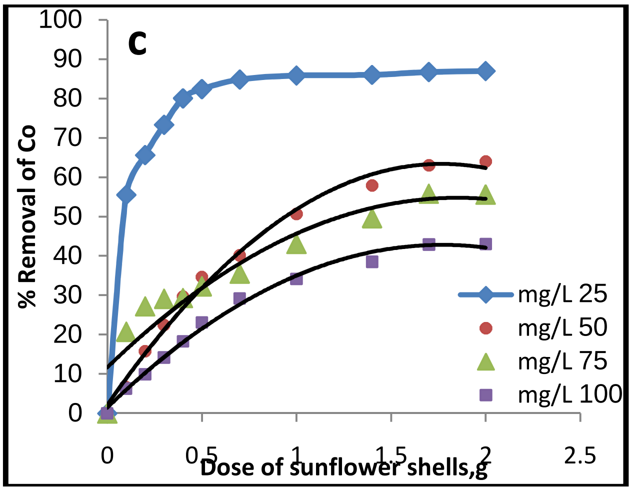
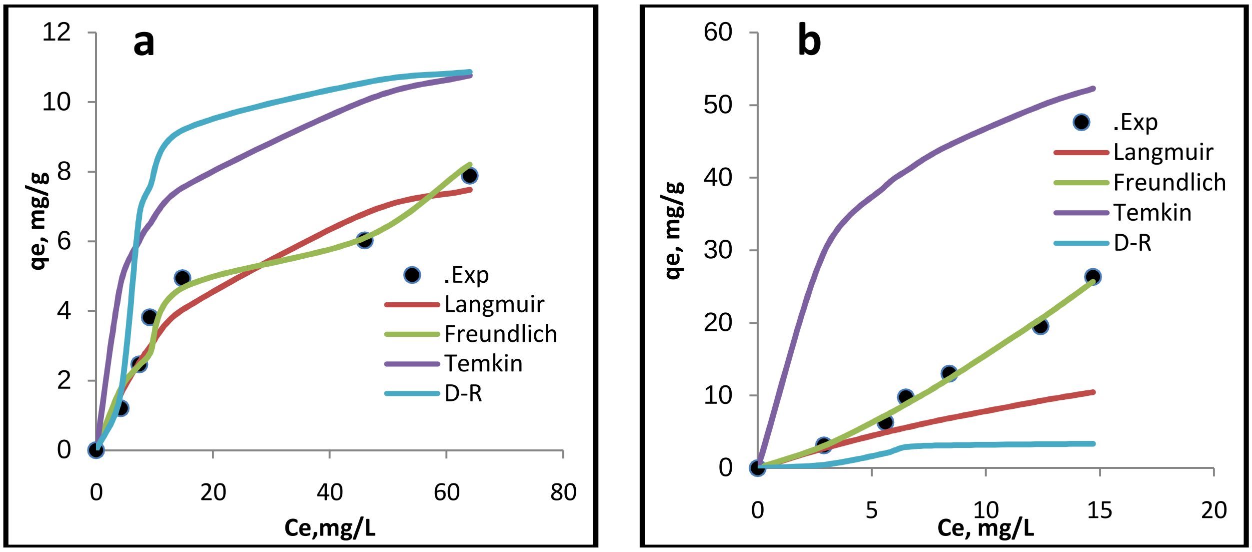


Fig.6: Effect of initial concentrations on uptake removal of cobalt using (a) activated carbon, (b) waste of fungi and (c) sunflower shells

The heavy metals are adsorbed by specific sites provided by the acidic functional groups on the adsorbents, while with increasing metal concentrations ,the specific sites are saturated and the exchange sites due to excessive surface area of the adsorbent are filled(El-Ashioukhy et al., 2008). It is clear that with increasing initial concentrations, the metal removal decreases.

3.5 Adsorption Isotherms

Adsorption isotherms is also termed as equilibrium data, which describes the information of the nature of solute-surface interaction and specific information about concentration of the adsorbate and the degree of the accumulation onto the surface of the adsorbent at specific temperature(Tashauoei et al., 2010;Thirumal and Kaliappan, 2011). Isotherms are very helpful in designing adsorption system (Zawani et al., 2009). Equilibrium isotherms are usually measured to determine the capacity of the adsorbent for metal ions. An adsorption isotherm describes the relationship between the amount of adsorbate onto the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. In order to optimize the design of a sorption system and explain adsorption equilibrium, various adsorption models have been used. From theses models ,it can be studied the adsorption capacity and equilibrium coefficients for adsorption of copper and cobalt ions from wastewater onto three types of adsorbents (GAC, waste of fungi andsunflower shells).The most commonly used models for solid-liquid adsorption are Langmuir , Freundlich , Temkin and Dubinin-Radushkviech (D – R) isotherms. Figure 7(a, b and c) for copper and Figure 8(a, b and c) for cobalt show the experimental and fitted isotherm data by above models at optimum conditions.



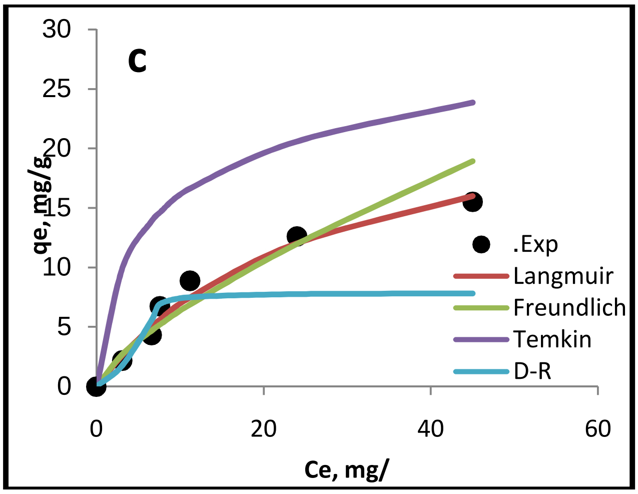


Fig. 7: Adsorption isotherm of copper onto (a) GAC, (b) W.F. and (c) S.F. using different models

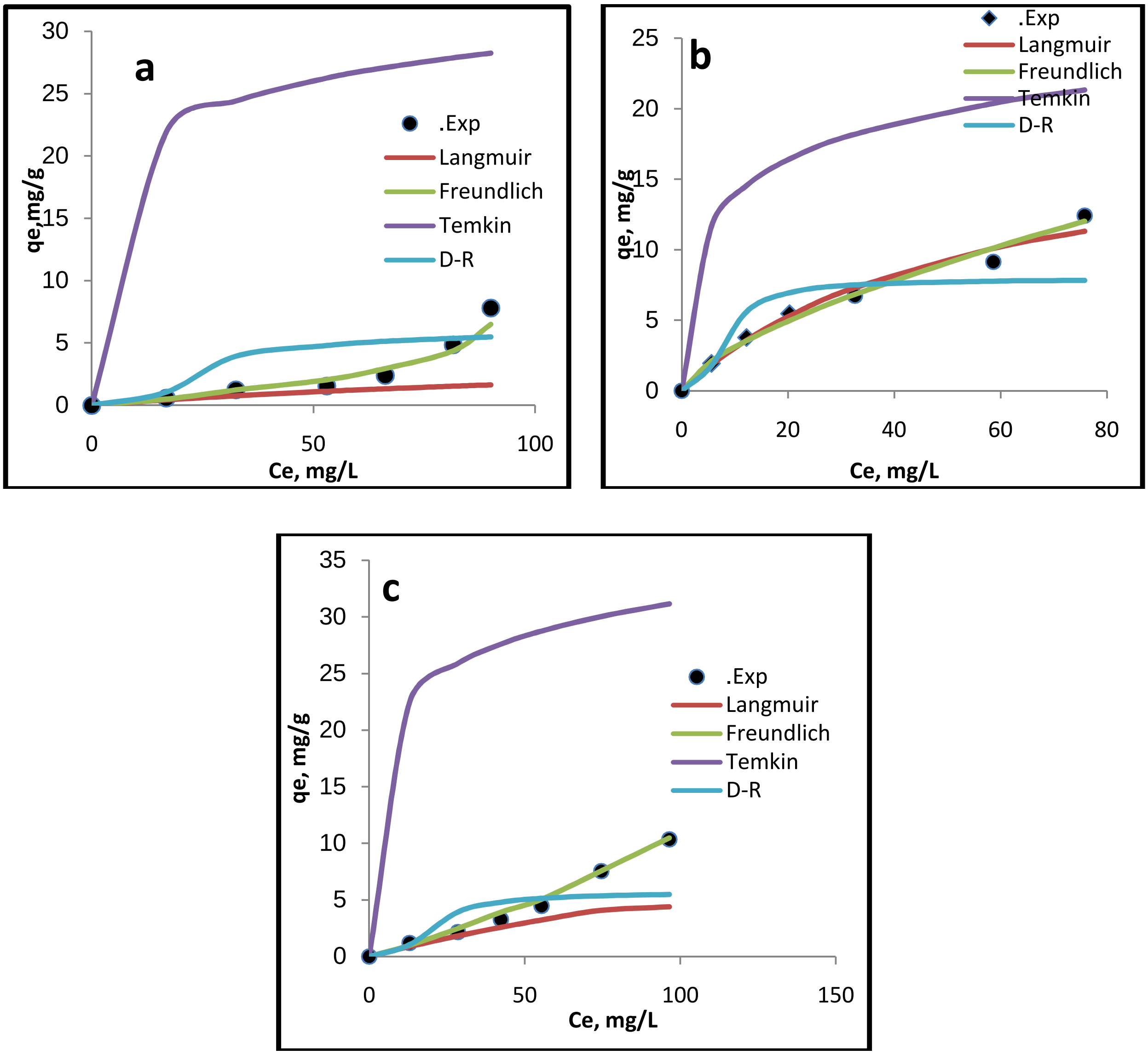


Fig. 8: Adsorption isotherm of copper onto (a) GAC, (b) W.F. and (c) S.F. using different models

3.5.1. Langmuir model

Langmuir adsorption isotherm model is the most important model of monolayer adsorption, base on the assumption that all sites posses an equal affinity for the adsorbate and are energetically identical. Each site can hold only one adsorbate molecule. It describes the adsorption behavior of solutes on the specific adsorbents. Langmuir isotherm can be defined through the following equation

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad (3)$$

This equation can be expresses in the linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} b + \frac{C_e}{q_m} \qquad (4)$$

Where q_e is the amount of metal ion uptake per unit weight of adsorbent (mg/g), q_m is the maximum amount of metal ion (mg/g), C_e is the solution ion concentration at equilibrium (mg/L) and b is the Langmuir adsorption constant related to the free energy of adsorption. The model provides the maximum values where they could not be reached in the experiments (Ali Hosseini et al., 2010; Tashauoei et al., 2010). Langmuir isotherm model will be very helpful in predicting the favorability of adsorption system, which based on the following dimensionless factor(Mohan and Bittman, 2006).

$$R_L = \frac{1}{(1 + bC_o}$$

Where$C_o$is the highest initial metal ion concentration (mg/L). The value of $R_L$indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_{L <} < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). All the R_L values when applied the values of b from Table 3 (C_o equal 50 mg/L) in above expression were found to be less than 1 and greater than 0 indicating the favorable sorption isotherms of eachcopper and cobalt ions..

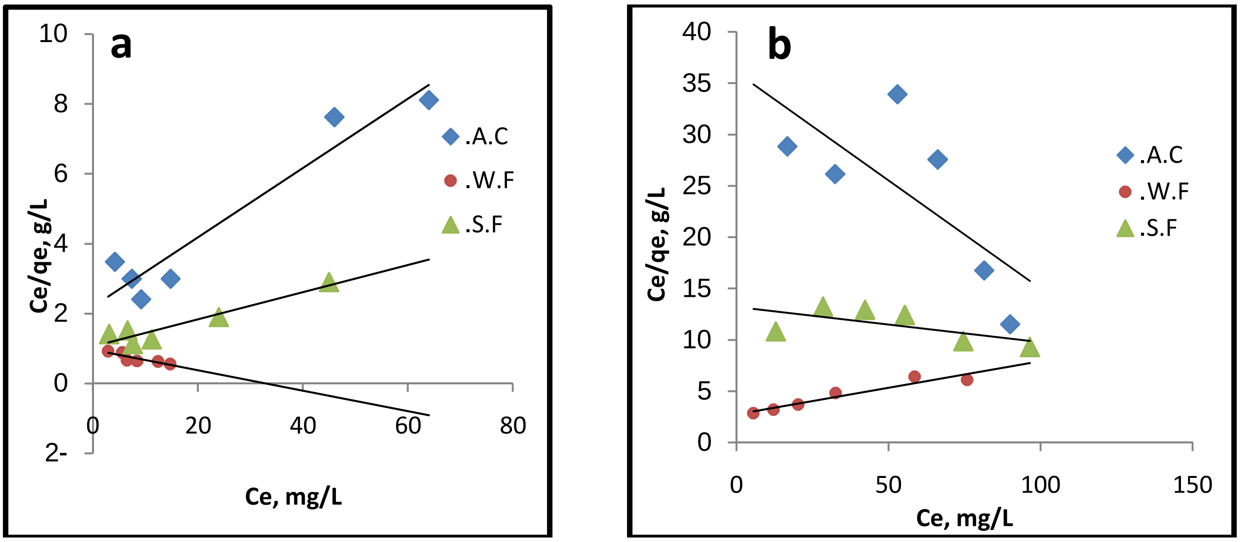


Fig. 9: Langmuir isotherm plots for sorption of (a) copper and (b) cobalt onto different adsorbents

A plot of C_e/q_e versus $C_e$gavestraight lines for both Cu(II) and Co(II) ions adsorbed onto adsorbent/biosorbent (GAC, W.F. and S.F.). Fig. 9(a, b), the slope and intercept of each line are $(1/q_m)$ and $(1/q_m{*}b)$ respectively. The numerical value of constants q_m and $b$were shown inTable 2. Data fitted the Langmuir model well for Cu and Co. The value of saturation capacity q_m corresponds to the monolayer coverage and defines the total capacity of the adsorbent for a specific metal ion. As can be seen, a higher value of q_m can be obtained for removal of Cu (II) and Co (II), when using a waste of fungi (34.12 mg/g) compared with sunflower shells (25.64 mg/g) and granular activated carbon (10.08 mg/g) for removal copper ions and when using a waste of fungi (19.30 mg/g) compared with sunflower shells (17.30 mg/g) and granular activated carbon (4.74 mg/g) for removal cobalt ions respectively. Also, it can be seen, from q_m results, at higher metal concentrations, Cu (II) adsorption was higher than Co (II) for the three adsorbents studied. At lower concentrations, the differences in isotherm slope ($1/q_m{*}b$) showed that, also Cu (II) was higher than Co (II) adsorption therefore the sequence was waste of fungi > sunflower shells > GAC.

3.5.2. Freundlichmodel

Freundlich isotherm model is considered the most important multi-layer adsorption isotherm model for heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The general form of the empirical Freundlich isotherm model is:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{5}$$

Where K_f is Freundlich constant (L/g) as sorption capacity and n is the Freundlich exponent as sorption intensity, the logarithmic linear form of Freundlich isotherm equation may be written as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{6}$$

From Fig. 10 (a and b);A plot of $\log q_e$ versus $\log C_e$gave a straight line of slope 1/n and the intercept $\log K_f$ .The values of n and K_f can be estimated from the reverse of slope and intercept respectively. The estimated values of constant parameters of Freundlich isotherm model for various adsorbents to uptake Cu (II) and Co (II) systems were tabulated in Table (2). The K_f values showed that Cu(II)was the more efficiently removed from wastewater by waste of fungi and less by sunflower shells compared with the lower $K_f$obtained by GAC, each of waste of fungi and sunflower shells showed better performance than GAC. The value of *1/n* ranged 0 - 1 is a measured of adsorption intensity or surface heterogeneity and becomes more heterogeneous as its value gets closer to zero., indicating that Cu (II) and Co (II) were favorably adsorbed by waste of fungi and sunflower shells better than GAC as shown from all parameters were found. Table (2) shows that the Freundlich intensity constant *n* was greater than unity for each studied ions. This has physicochemical significance with reference to the qualitative characteristics of the isotherm, as well as to the interactions between metal ions species and adsorbent. In the present study, *n*> 1 for each ion species, the adsorbents show an increase tendency for sorption with increasing solid phase concentration. This may be attributed to the fact that with progressive surface coverage of adsorbent, the attractive forces between the metal ion species such van der Waals, increases more rapidly than the repulsive forces, exemplified by short-range electronic or long-range Coulombic dipole repulsion, and consequently, the metal ions manifest a stronger tendency to bind to the adsorbent site (Sulaymon et al., 2009; Velit et al., 1980). It is also observed that the Freundlich isotherm model is well fitted for each the metal ions.

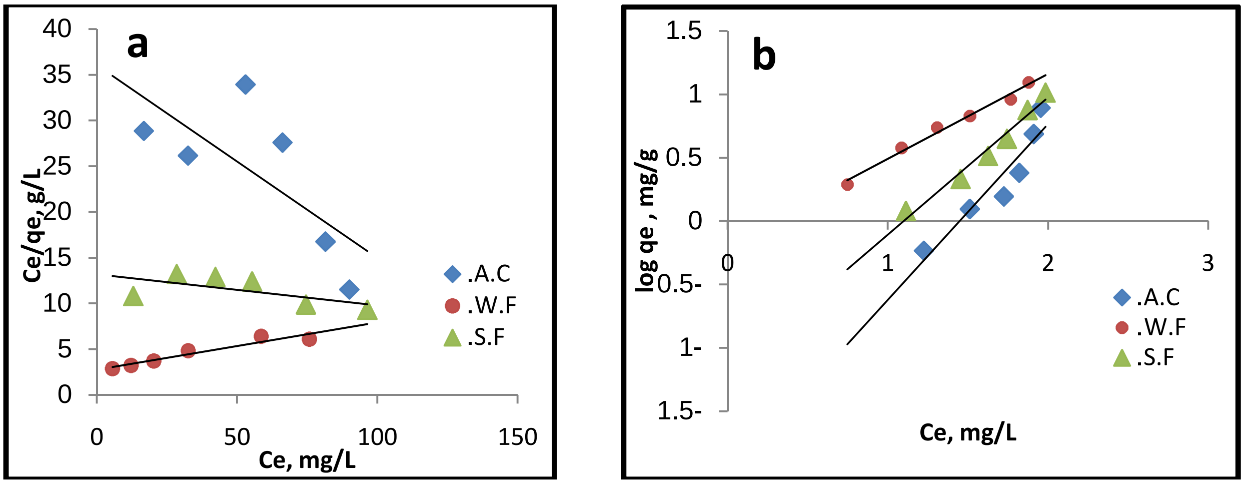


Fig.10:Freundlicg isotherm plots for sorption of (a) copper and (b) cobalt onto different adsorbents

3.5.3. Temkinmodel

Temkin isotherm model is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions. This model contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. Temkin equation is excellent for predicting the gas phase equilibrium (when organization in a tightly packed structure with identical orientation is not necessary), conversely complex adsorption systems including the liquid-phase adsorption isotherms are usually not appropriate to be represented (Kim et al., 2004).

Temkin isotherm considers the effects of the heat of adsorption of all molecules in the layer would decrease linearly with the coverage due to the adsorbent-adsorbate interactions [Kumar and Oommen, 2012; Miretzky et al., 2006]. It was given by:

$$q_e = \frac{RT}{b}\ln(K_T C_e) \qquad (7)$$

Equation (7) can be linearized as:

$$q_e = \frac{R*T}{b} lnk_T + \frac{R*T}{b} lnC_e \qquad (8)$$

$$q_e = B_1 \ln K_T + B_1 \ln C_e \qquad (9)$$

Where k_T (L/g) is Temkin equilibrium isotherm binding constant, *b* (J/mol) is a constant related to heat of sorption, *R* is the universal gas constant (8.314kJ/mol.K) and *T* is the absolute temperature (K).

A plot of q_e versus *ln* $C_e$gives a straight line of slope *B*and intercept*(B ln A)* to give k_T and *b*. The data obtained by usingTemkin isothermmodel are listed in Table 2.

3.2.4. Dubinin-Radushkviechmodel (D – R)

This type of model proposed by Dubinin, it depends upon the assumption that the characteristics of the sorption curves are related to the porosity of the adsorbent. The general equation of this model is:

$$q_e = q_m exp\left[-B_D\left(RT\ ln\left\{1+\frac{1}{C_e}\right\}\right)^2\right] \qquad (10)$$

The linear form of the isotherm model can be expresses as follows:

$$\ln q_e = \ln q_m - B_D\,\varepsilon^2 \qquad (11)$$

Where q_m is the theoretical maximum capacity (mol/g) of ion that can be sorbet onto unit weight of adsorbent, B_D is the D-R model constant (mol^2/kJ^2) related to the sorption energy, ε is the Polanyi potential and is equal to:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \qquad (12)$$

The mean energy sorption, *E* (kJ/mol) is calculated by the following equation:

$$E = (-2B_D)^{-1/2} \qquad (13)$$

The magnitude of *E* can be related to the reaction mechanism. If *E* is in the ranged 8-16 kJ/mol, sorption is governed by ion exchange. In the case of $E < 8$ kJ/mol, physical forces may affect the sorption mechanism. The mean adsorption energy was found to be in the ranged 0.9-4 kJ/mol, which is in the energy range of physical adsorption reactions. The calculated D-R constants and mean free energy for adsorption are shown in Table 2

Langmuir, Freundlich, Temkin and D-R constants are presented in Table 2. It can be seen that the regression correlation coefficient R^2forFreundlich equation for each heavy metal ions withdifferent adsorbents is more linear when compared with that of the other model equations, implying that the adsorption isotherm data are well fitted by the Freundlich isotherm model. The monolayer adsorption capacity, according to the Freundlich isotherm model, was found for Cu(II):0.7596, 1.7909 and0.7599 mg/g when used waste of fungi, sunflower shells and GAC respectively, while for Co (II): 0.6635, 0.0641 and0.0097 mg/g when used waste of fungi, sunflower shells and GAC respectively at 25 °C.

Table 2 Numericalvalues of isotherm models coefficients for Cu(II) and Co(II) using different adsorbents

Isotherm Model	Parameters	Copper			Cobalt		
		GAC	W.F.	S.F.	GAC	W.F.	S.F.
Langmuir	q_m(mg/g)	10.08	34.12	25.64	4.748	19.3	17.3
	b(L/mg)	0.0451	0.03	0.0369	0.0058	0.0187	0.0041
	R^2	0.919	0.749	0.896	0.511	0.916	0.422
Freundlich	K_f(mg/g)	0.7599	0.7596	1.1909	0.0097	0.6635	0.0641
	n	1.7129	0.763	1.3758	0.7204	1.4945	0.9219
	R^2	0.933	0.988	0.925	0.882	0.985	0.971
Temkin	B(L/mg)	1124.65	177.81	477.45	733.63	667.26	573.17
	A(mg/g)	2.071	2.902	2.211	19.746	4.111	14.041
	R^2	0.944	0.898	0.981	0.613	0.931	0.806
D - R	q_D(mg/g)	6.086	18.84	11.001	3.6	7.893	5.674
	B(L/mg)	0.000006	0.000004	0.000004	0.0001	0.000009	0.00005
	R^2	0.924	0.822	0.834	0.633	0.784	0.663

3.6 Kinetic Models

The study of sorption kinetics describes the uptake rate of copper and cobalt ions, and evidently this rate controls the residence time of these ions at the solid liquid interface. Consequently it is important to establish the time dependency of such systems for various pollutant removal processes. Therefore, the required contact time for the sorption to be completed is important to give insight into a sorption process. This also provides information on the minimum time required for considerable adsorption take place and the possible diffusion control mechanism between the adsorbed ion as it moves from the bulk solution towards the adsorbent surface (Al Dwairi and Al Rawaifeh, 2012). At the beginning stage of the adsorption process, the removal rate of the ions is higher; this faster removal is due to the availability of the uncovered surface area. The adsorption kinetics depends on :(1)the surface area of the adsorbent, (2) the nature and concentration of the surface groups (active sites), which are responsible for interaction with targeted ions (Al-Anber, 2010).

In order to design the sorption systems, chemical kinetics is very important as it explains how slow and fast the rate of chemical reaction occurs and the factors which affect the reaction rate. Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process (Sampranpiboon and Charnkeietkong, 2010; Gueu et al., 2007).In order to gain some insight into the sorption process of Cu(II) and Co (II) ions onto the surface of granular activated carbon, waste of fungi and sunflower shells were used. Fig. 11(a, b) shows the effect of contact time onto amount of copper and cobalt onto different adsorbent/biosobentmaterials. In order to evaluate the kinetics of the sorption process, data from the kinetic studies were fitted with the pseudo-first order and pseudo-second order models.

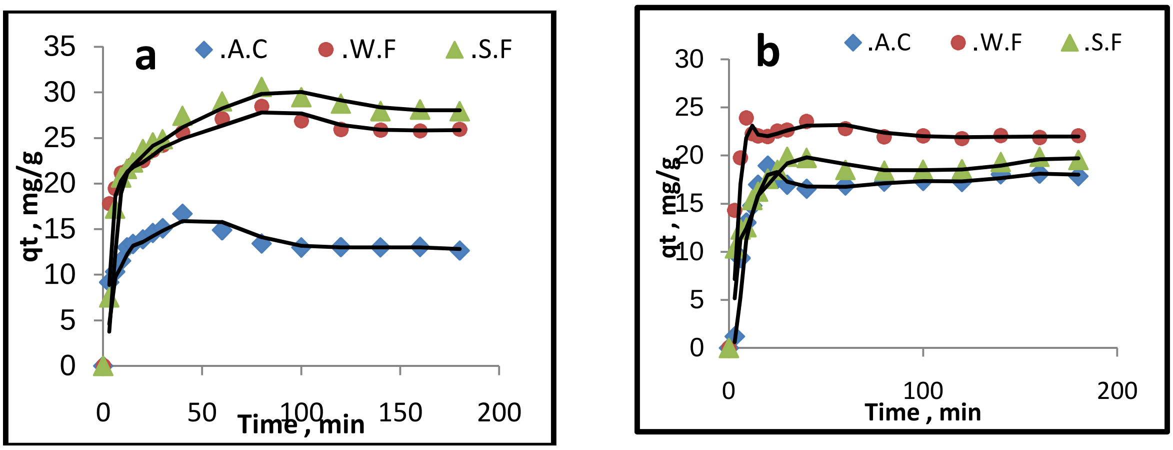


Fig. 11: Effect of contact time into amount of (a) copper and (b) cobalt onto different adsorbents

3.6.1Pseudo First-Order Model

The pseudo first-order equation based on equilibrium adsorption is generally expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{14}$$

Where, q_e is the amount of Cu(II) and Co(II) ions adsorbed at equilibrium (mg/g) , q_t is the amount adsorbed at time t (mg/g), K_1 is the rate constant of first order adsorption(min¬1).

By integration and applying boundary conditions for Eq. (14)

$At\ t=0 q_t=0$;
$At\ t=t$ $q_t=q_e$

Equation (14) can be obtained

$$\log\left(\frac{q_e}{(q_e-q_t)}\right)=k_1t/2.303 \qquad (15)$$

The plot of $log\ (q_e\text{-}q_t)$ versus t gave the slope K_1 and intercept of $log\ (q_e)$ as shown in Fig.12 (a, b). The calculated values of K_1 and q_e with the values of the linear correlation coefficients (R^2) of each plot are presented in Table 3. Straight lines obtained from the pseudo first –order kinetic plots suggest the applicability of the pseudo first –order kinetic model to fit the experimental data over the initial stage of the sorption process. But it is also required that theoretically calculated equilibrium sorption capacities, qe should be in accordance with the experimental sorption capacity values. As can be seen from Table 3, although the linear correlation coefficients of the plots are so good, but from the q_e (calculated) values are not in agreement with q_e (experimental) for all studied sorption process. So, it can be suggested that the sorption of each metal ions onto adsorbents is not first-order reaction

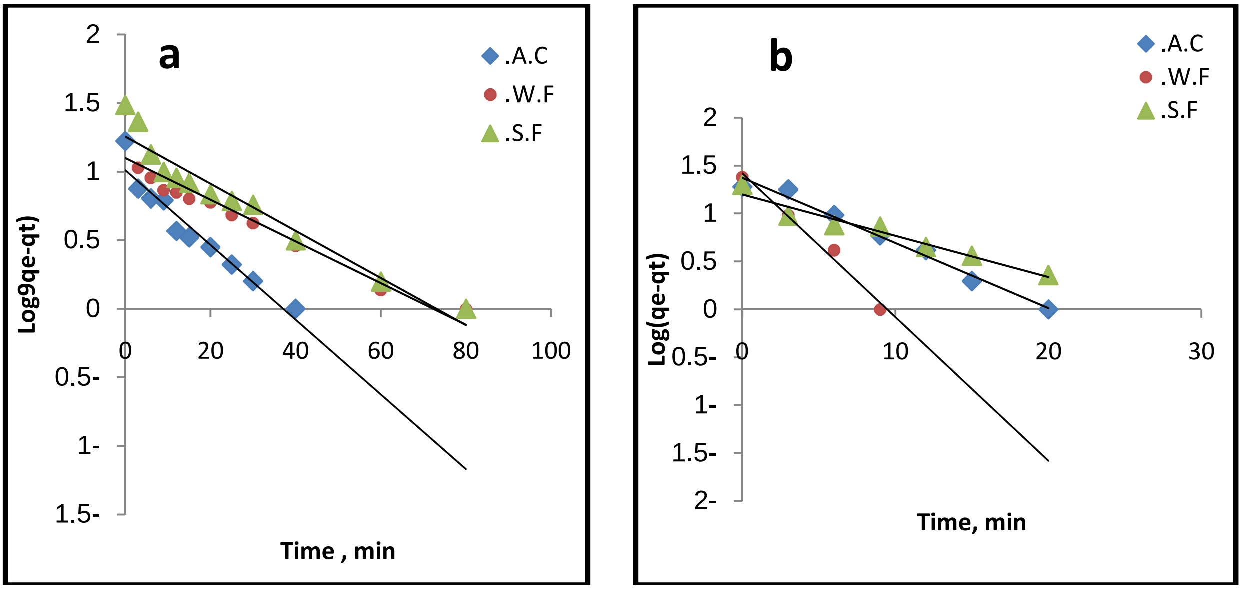


Fig.12: Pseudo first-order kinetic plots for the sorption of (a) Cu (II) and (b) Co (II) ions onto different adsorbents

3.6.2 Pseudo Second-Order Model

The pseudo second-order model is also based on the sorption capacity of the solid phase. It predicts the behavior over the whole range of data. It is in agreement with chemisorption being the rate controlling step .It is expressed as: (Aksu and Isoglu, 2005).

$$\frac{dq}{dt}=k_2(q_e-q_t)^2 \qquad (16)$$

Where K_2 is the rate constant of pseudo second-order equation (g/mg min)

By applying same boundary conditions above and integrating; Equation (16) becomes:

$$\frac{t}{q_t}=\left(\frac{1}{k_2q_e^2}+\frac{t}{q_e}\right) \qquad (17)$$

The kinetic plots of t/q_tversus t for both Cu(II) and Co(II) ions sorption using different adsorbents are presented in Figure 13 (a and b). The relation is linear, and the correlation coefficient (R^2) suggests a strong correlation between the parameters and also explain the sorption process of each ion follows pseudo second-order kinetics.

The initial sorption rate, h (mg/g. min) at $t=0$ is defined as:

$$h = k_2 q_e^2 \tag{18}$$

WhereK_2 and h values were determined from the slope and intercept of the plots of t/q_t against t. From Table 3, it can be seen that the values of the initial sorption rate (h) and rate constant K_2 were varied according to the adsorbent used. High values of h and K_2 were found when used waste of fungi then sunflower shells compared with GAC.As can be seen from Table3, the q_e,(calculated) determined from the plot of the pseudo-first order model for each metal, differs from that obtain experimentally, q_e, (experimental). This implies that the model is not very good in explaining the kinetics of the adsorption of the metals. On the other hand, the pseudo-second order model as shown in Table 3 fits the kinetics better. The correlation coefficient R^2 had very high value (> 0.98), and its calculated equilibrium sorption capacity q_e is consistent with the experimental data. These results explain that the pseudo second-order sorption mechanism is predominant and that the over all rate constant of each sorption process appears to be controlled by the chemisorption process. All these point to the fact that second order kinetic best explain the observed rate, suggesting that the process is the rate limiting step, and that sorption of the metal ions involves two species, in this case, the metal ion and the adsorbent..

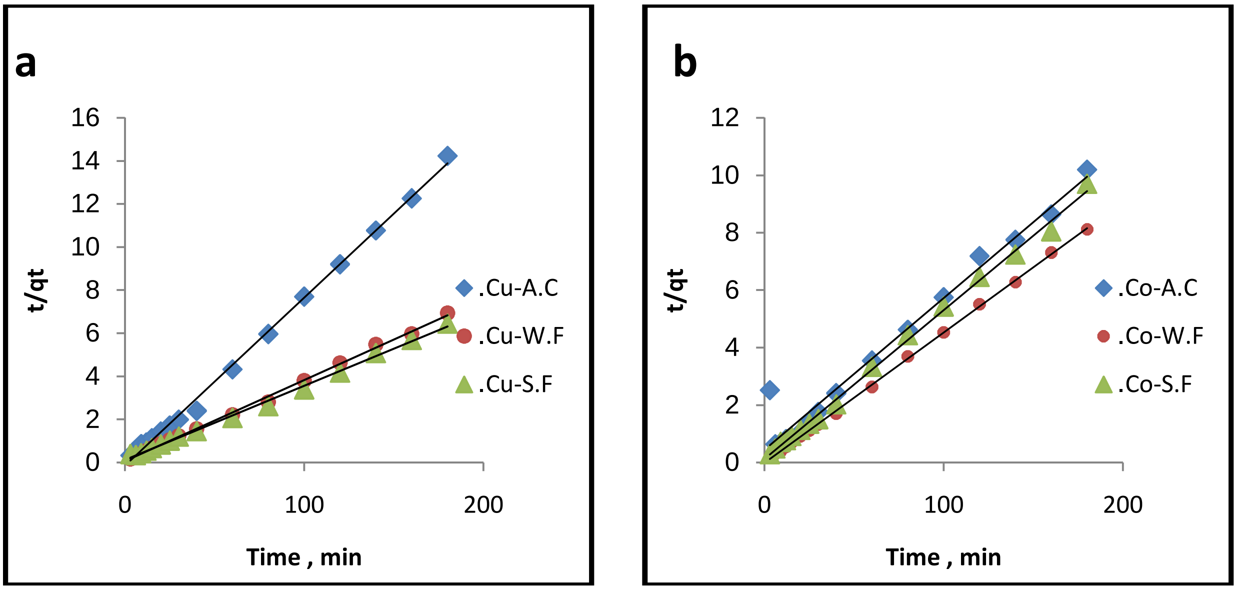


Fig. 13: Pseudo second-order kinetic plots for the sorption of (a) Cu(II) and (b) Co(II) ions onto different adsorbents

Table 3 Calculated parameters of the pseudo first-order and pseudo second-order kinetic models for Pb(II) and Cd(II) ions onto different adsorbent/biosorbent

,	Pseudo-first-order parameters			Pseudo-second-order parameters			
Metal ion	K_1(min¬^{1})	qe,cal. (mg/g)	R^2	K_2(g/mg.min)	qe,cal (mg/g)	h(mg/g.min)	R^2
Cu-A.C.	0.228458	157.072	0.919	2.85924	1.712915	8.389236	0.841
Cu-W.F.	0.067478	9.246	0.749	14.38587	1.129601	18.375209	0.988
Cu-S.F.	0.089817	11.35	0.89	5.983719	1.38677	11.50748	0.914
Co- A.C.	0.485012	1.177	0.511	0.957617	0.720409	0.496993	0.882
Co-W.F.	0.119295	575.439	0.916	2.513727	1.494545	5.614823	0.985
Co-S.F.	0.078532	1.6E+13	0.395	0.986314	0.921914	0.838293	0.971

CONCLUSION

In this study, granular activated carbon, waste of fungi and sunflower shells data were used for the adsorption/biosorptioncopper or cobalt from aqueous solutions. Batch experimental data showed that the solution pH strongly influenced the adsorptive/biosorptive capacity. As the solution pH increased, the removal efficiency of Cu (II) and Co (II) increased. The greatest metal uptake was observed at optimum pH value. The highest cobalt uptake was observed at GAC (18.85 mg/g), W.F. (23.92mg/g) and S.F. (19.87mg/g), while the highest copper uptake were obtained for GAC (16.69 mg/g), W.F. (28.46 mg/g) and S.F. (30.60 mg/g).

Maximum sorption occurred within the first 30 min for the cobalt, 80 min for the copper. Moreover, a pseudo-second order model has been successfully used to fit the copper and cobalt. Initial metal concentration also affected the overall metal uptake capacity of adsorbents. Metal uptake increased as the initial concentration of the metal ions was increased. Adsorption equilibrium data for copper and cobalt were fitting well with Freundlich model.

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