Competitive Removal of Cu^{2+}, $Cd^{2+}$and $Ni^{2+}$by Iron Oxide Nanoparticle (Fe_3O_4)

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ABSTRACT

A competitive adsorption of Cu^{2+}, Ni^{2+}, and Cd^{2+} ions from a synthetic wastewater onto nanomaterial was studied.(Fe_3O_4) nanoparticles obtained from US Research Nanomaterials, Inc., Houston, TX 77084, (USA), was used as nanosorbent. Experimental parameters included pH, initial metal concentrations, and temperature were studied for nanosorbent. The uptake capacity 11.5, 6.07 and 11.1 mg/g for Cu^{2+}, $Ni^{2+}$and Cd^{2+}, respectively, onto nanosorbent . The optimum pH values was 6 and the contact time was 50 min. for Cu^{2+}, $Ni^{2+}$and Cd^{2+}, respectively. The equilibrium isotherm for nanosorbent single system component is of a favorable type and Freundlich isotherm model gives the best fit model for representing the experimental data for this system. Binary and ternary component systems were conducted in order to find the adsorption isotherm constants for each component system using nanosorbent. A set of adsorption models were tested to choose the best fit model for the experimental data, Combination of Langmuir- Freundlich model seems to give the best fitting. In single, binary and ternary component systems, Cu^{2+} always adsorbed more favorable onto nanosorbent than $Cd^{2+}$and Ni^{2+}. The adsorption capacity parameters were: $Cu^{2+} > Cd^{2+} > Ni^{2+}$. Thermodynamic study was carried out for these three pollutants onto nanosorbent. The results of adsorption show that the adsorption nature for heavy metals is an endothermic and physical nature process.

Key Words: adsorption, heavy metals, ions, competitive, nanosorbent

الازالة التنافسية لايونات النحاس والكادميوم والنيكل بواسطة مادة النانو المازة(اوكسيد الحديد)

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الخلاصة

الدراسة الحالية تهدف الى تقييم عملية الامتزاز للمعادن الثقيلة(النحاس،النيكل و الكادميوم) من المياه الصناعية بواسطة مادة النانو. وتم شراء مادة النانوالمازة وهي اوكسيد الحديد (Fe_3O_4) من الولايات المتحدة الامريكية. كذلك تم دراسة تغيير بعض العوامل المختبرية على عملية الامتزاز مثل الدالة الحامضية، التركيز الاولي، والحرارة لمادة النانو. ان سعة الازالة هي 11.1,6.07,11.5 mg/g لايونات النحاس والنيكل والكادميوم على التوالي باستخدام مادة النانو. وجد ان افضل نسب الازالة لمادة النانو تحصل عند قيمة الحامضية 6 لجميع الايونات وان وقت الازالة الامثل هو 50 دقيقة . تم القيام بسلسلة من تجارب الدفعات (batch experiment) للملوثات بصورة منفردة وثنائية وثلاثية لغرض الحصول على مخططات الامتزاز الحيوي لكل ملوث. وقد تم استخدام عدد من الموديلات الرياضية التي تصف عملية الامتزاز. وجد أن موديل (Freundlich) ، أفضل موديل رياضي يمثل النتائج العملية بالنسبه للمنفرده.اما بالنسبة الى التجارب الثنائية والثلاثية ، وجد ان موديل (Combination of

Langmuir- Freundlich) افضل موديل رياضي يمثل النتائج العملية. وجد أن ايونات النحاس اعلى قدرة وملائمة على الامتزاز بواسطة مادة النانو بينما ايونات النيكل اقل قدرة من بقية الايونات . كما وجد ان طبيعية الامتزاز للمعادن الثقيلة هو ماص للحرارة من خلال التجارب الحرارية (thermodynamic study) وذو طبيعة فيزياوية.

الكلمات الرئيسية: امتزاز,المعادن الثقيلة,ايونات,التنافس,مادة النانو

1. INTRODUCTION

Presence of heavy metals in wastewaters causes significant environmental problems. High concentrations of heavy metals are known to be toxic and carcinogenic to living organisms. When heavy metals are present even in a very low concentration, their concentration may be elevated through bio-magnification to a level that they start to exhibit toxic characteristics. Therefore, heavy metals are major pollutants in many industrial wastewaters and are toxic to human and aquatic life **,Taghi *et al.*, 2005**. Due to their elemental non-degradable nature, heavy metals always and regardless of their chemical form, pose serious ecological risk, when released into the environment. The metals which are of greatest environmental concern are cadmium, mercury, lead, chromium, cobalt, copper, nickel and zinc **,Sahmoune *et al.*, 2009**.The presence of heavy metal ions in the environment has been a matter of major concern due to their toxicity to human life. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions will not degrade into harmless end products. Heavy metal ions such as cobalt (Co), copper (Cu), nickel (Ni),chromium (Cr), mercury (Hg), lead (Pb), cadmium (Cd), zinc (Zn) ions are detected in the waste streams from different industrial activities such as mining operations, tanneries, electronics , electroplating, petroleum refineries, and petrochemical industries **,Cheueh, 2005**.

The toxicity of heavy metals can be listed in order of decreasing toxicity as Hg > Cd > Cu > Zn > Ni > Pb > Cr >Al >Co, although this is only approximate as the vulnerability of species to individual metals varies. Toxicity also varies according to environmental conditions that control the chemical speciation of the metals**, Gray, 2005; Saleem *et al.*, 2011**.

Heavy metals can pose health hazards if their concentration exceeds the allowable limits. Even when the concentration of metals does not exceed these limits, there is still a potential for long-term contamination. As they are non-biodegradable, and persistence their threat is multiplied by their accumulation in the environment elements such as food chain and thus poses a significant danger to human health and life**, Manhan, 2005.**

The removal of heavy metals ions from wastewater involves high cost techniques such as ion-exchange, evaporation, precipitation, membrane separation etc. However, these common techniques are too expensive to treat low levels of heavy metals in wastewater. Adsorption techniques are widely used in the field of removing small quantities of pollutant present in large volume of fluid, which can be carried out in batch wise or continuous manner of operation **Rao, 1994**. Many factors that affect the decision of choosing an adsorbent for removal of pollutants from water such as: economical factor (cost of the adsorbent), abundance, availability and effectiveness of the adsorbent**, Sulaymon and Ahmed, 2008**.

The last decade has seen a continuous improvement in the development of effective\noble adsorbents in the form of activated carbon **,Huang et al., 2007**, zeolites **, Panuccio et al.,2009**, clay minerals **,Hizal and Apak,2006**, chitosan **,Bamgbose et al.,2010,** lignocelluloses **,Shin,2007,** natural inorganic minerals **,Sevgi,2009** functionalized polymers **,Panda *et al.*,2008**, etc. However, most of these adsorbents are either not effective (due to diffusion limitation or the lack of enough active surface sites) or have shown problems like high cost,difficulties of separation from wastewater, or generation of secondary wastes. Nowadays there is a continuously increasing worldwide concern for the development of wastewater treatment technologies. Considering such drawbacks, recently nano-adsorbents viz. nano-alumina **,Srivastava *et al.*2011,** functionalized carbon nanotubes **, Gupta et al.2011,**and hydroxyapatite nanoparticles **, Feng *et al.*2010,** have demonstrated high adsorption efficiency for metal ions removal. The utilization of iron oxide nanomaterials has received much attention due to their unique properties, such as extremely small size, high surface-area-to-volume ratio, surface modifiability, excellent magnetic properties, **Xu *et al.,* 2012**. One such advanced class of adsorbent – magnetic nano-adsorbent with the help of an external magnetic field has been further successful in circumventing the solid–liquid separation problem usually encountered with nanoparticle. Such adsorbent combining nanotechnology and magnetic separation technique has not only demonstrated high adsorption efficiency due to its large surface to volume ratio, but have also shown additional benefits like ease of synthesis, easy recovery and manipulation via subsequent coating and functionalization, absence of secondary pollutants, cost-effectiveness and environmental friendliness **,Gupta and Nayak , 2012** . Till date, several magnetic nanomaterials, including maghaemite nanoparticles **,Hu *et al.,* 2005**, Fe_3O_4 magnetic nanoparticles **,Shen *et al.*,2009,** Fe_3O_4 nanoparticles functionalized and stabilized with compounds like humic acid **,Liu *et al.*,2008** have been explored for the removal of metal ions. In nanotechnology focuses on the fabrication of nano-sized adsorbents with enhanced adsorption capacity and rapid sorption rate for the removal of target contaminants. This is due to the large surface area and highly active surface sites of the nanoadsorbents **,Bhaumik *et al.*,2012.**Iron oxide nanoadsorbents are cost-effective adsorbents that provide high adsorption capacity, rapid adsorption rate and simple separation and regeneration **,Nassar,2010.**In the present study, were used for the competitive removal of heavy metals (Cu^{2+}, Ni^{2+} and Cd^{2+}) in batch reactors at different operating conditions.

2. EQUILIBRIUM ISOTHERM BATCH MODELS FOR SORBENT

2.1 Single Component System

Empirical models are simple mathematical relationships, characterized by a limited number of adjustable parameters, which give a good description of the experimental behavior over a large range of operating conditions. The model used to describe the results should be capable of predicting sorbate binding at both low and high concentrations **,Vijayaraghavan and Yun, 2008.**

Although these conventional empirical models do not reflect the mechanisms of sorbate uptake, they are capable of reflecting the experimental curves of adsorption isotherm **,Vijayaraghavan *et al.,* 2008.**

2.1.1 Langmuir Model (1916)

The Langmuir model can be represented as:

$$q_e = \frac{q_{max} b C_e}{(1+bC_e)} \qquad (1)$$

Where q_e is the amount of adsorbate adsorbed per mass of adsorbent (mg/g).C_e is the equilibrium concentration (mg/l).

This classical model incorporates two easily interpretable constants: q_{max} , which corresponds to the maximum achievable uptake by a system; and b, which is related to the affinity between the sorbate and sorbent,(l/mg). The Langmuir constant "q_{max}" is often used to compare the performance of biosorbents; while the other constant "b" characterizes the initial slope of the isotherm. Thus, for a good biosorbent, a high q_{max} and a steep initial isotherm slope (i.e., high b) are generally desirable **,Aksu *et al.*, 2002;Kratochvil and Volesky, 1998.**

The Langmuir model assumes the following: (i) the surface consists of adsorption sites, (ii) all adsorbed species interact only with a site and not with each other, (iii) adsorption is limited to a monolayer, and (iv) adsorption energy of all the sites is identical and independent of the presence of adsorbed species on neighboring sites **, Ridha, 2011.**

Each component is adsorbed onto the surface according to ideal solute behavior; there is no interaction or competition between molecules involved under homogenous conditions, **Mashitah *et al.*, 2008.**

The important characteristic of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter R_L. This is defined by **,Sahmoune *et al.*, 2009**:

$$R_L = \frac{1}{b + C_o} \tag{2}$$

Basha and Murthy, 2007, show, using mathematical calculation, that the parameter R_L indicates the shape of isotherm as follows in **Table 1**

2.1.2 Freundlich Model (1918)

The Freundlich isotherm can be represented as:

$$q = KC_e^{1/n} \quad n > 1 \tag{3}$$

The Freundlich isotherm was originally empirical in nature, but was later interpreted as the sorption to heterogeneous surfaces or surfaces supporting sites with various affinities. It is assumed that (i) the stronger binding sites are initially occupied, (ii) the binding strength decreasing with increasing degree of site occupation. It incorporates two constants: K, which corresponds to the maximum binding capacity; and n, which characterize the affinity between the sorbent and sorbate (adsorption intensity) **Vijayaraghavan and Yun, 2008.**

2.1.3 Redlich–Peterson Model (1959)

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta_{RP}}} \tag{4}$$

Redlich–Peterson isotherm shows that an “area of stability” is reached after a frequent rise in the curve, i.e., several layers of adsorption occurs first. This isotherm assume (i) equilibrium for heterogeneous surfaces as it contains the heterogeneity factor β. (ii) It also converges to Henry’s law at low surface coverage and is, therefore, (iii) thermodynamically consistent. However, it does not have as wide a practical application as the Langmuir and the Freundlich isotherms due to the inconvenience of evaluating three isotherm constants **,Lawrence *et al.*, 2010.**

β_{RP} has values between 0 and 1. For β_{RP} = 1 the Redlich–Peterson model converts to the Langmuir model. β_{RP}=0 the Henry’s Law form results

2.1.4 Sips Model (1948)

$$q_e = \frac{K_s C_e^{\beta_s}}{1+a_s C_e^{\beta_s}} \qquad (5)$$

K_S is the Sips model isotherm constant; a_S the Sips model constant; β_S the Sips model exponent. This equation is also called Langmuir–Freundlich isotherm and the name derives from the limiting behavior of the equation. At low sorbate concentrations it effectively reduces to a Freundlich isotherm and thus does not obey Henry's law. At high sorbate concentrations, it predicts the monolayer sorption capacity characteristics of the Langmuir isotherm **,Padmesh *et al.*, 2006.**

2.1.5 Khan Model (1997)

$$q_e = \frac{q_{max} b_k C_e}{(1+b_k C_e)^{a_k}} \qquad (6)$$

b_K is the Khan model constant; a_K Khan model exponent ,q_{max} maximum uptake **,Vijayaraghavan and Yun, 2008.**

2.1.6 Toth Model (1971)

$$q_e = \frac{q_{max} b_T C_e}{\left[1+(b_T C_e)^{\frac{1}{n_T}}\right]^{n_T}} \qquad (7)$$

b_T the Toth model constant and n_T the Toth model exponent **,Vijayaraghavan and Yun, 2008.**

It derives from potential theory and is used in heterogeneous systems. Toth model assumes a quasi-Gaussian energy distribution; most sites have adsorption energy lower than the peak of maximum adsorption energy**, Jianlong and Can, 2009.**

2.2 Multi Component Systems

The adsorption of the solute of interest not only depends on the adsorbent surface properties and physical–chemical parameters of a solution such as pH and temperature, but also on the number of solutes and their concentrations. In such cases, the adsorption will become competitive, with one solute competing with another to occupy the binding sites**, Wang and Chen, 2009.**

Multicomponent biosorption has been the subject of limited studies .The uptake of a given metal ion is decreased to a greater extent in ternary combinations and furthermore in quaternary systems compared to the binary combinations. In the presence of co-ions in solution, chemical interactions between the ions themselves as well as with the adsorbent take place resulting in site competition. Therefore metal uptake from multicomponent systems is lower.

For binary solute cases, different isotherm models have been used to correlate single-solute isotherm data and to describe multi-solute sorption isotherms based on the time-consuming iterative algorithm **,César *et al.*, 2010.**

2.2.1 Extended Langmuir Model (ELM)

$$q_i = \frac{b_i q_{m,i} C_{e,i}}{\left(1+\sum_{j=1}^{n} b_j C_{e,j}\right)} \tag{8}$$

Where $C_{e,i}$ is the equilibrium concentration of the component i in the multicomponent solution, q_i is the equilibrium uptake of the component i, b_i and $q_{m,i}$ are the Langmuir isotherm model parameters obtained suitably from Eq. (1) in the single solute system.This model assumes (i) homogeneous surface with respect to the energy of sorption, (ii) no interaction between adsorbed species and (iii) that all sorption sites are equally available to all adsorbed species **,Aksu *et al.*, 2002.**

2.2.2 Redlich-Peterson Model

The three parameter isotherm of Redlich-Peterson that has been empirically developed for multi-component mixtures is given as**, Fahmi and Munther, 2003; Sulaymon *et al.*, 2009:**

$$q_i = \frac{K_{R,i} q_{m,i} C_{e,i}}{\left(1+\sum_{j=1}^{n} a_{R,j} C_{e,j}^{Bj}\right)} \tag{9}$$

Where $K_{R,i}$ and $q_{m,i}$ are the Redlich-Peterson isotherm-model parameter suitably obtained from Eq. (4) in single solute system.

2.2.3 Combination of Langmuir-Freundlich Model

The competitive model related to individual isotherms parameters are expressed in the following equation**, Sips, 1984:**

$$q_i = \frac{q_{m,i} b_i C_{ei}^{\left(\frac{1}{n_i}\right)}}{\left(1+\sum_{j=1}^{n} b_j C_{ej}^{\left(\frac{1}{n_j}\right)}\right)} \tag{10}$$

3. EXPERIMENTAL WORK

The present study is to evaluate the competitive adsorption of heavy metals as inorganic pollutants from wastewater by nanosorbent (Fe_3O_4). In this research nanomaterial will be used for the competitive removal of heavy metals in batch reactors at different operating condition in single, binary and ternary systems.

3.1 Adsorbate (Stock Solutions)

A stock solution of copper, nickel and cadmium ions with a concentration of (1000 mg/l) were prepared by using $Cu(NO_3)_2$, $Ni(NO_3)_2$ and $Cd(NO_3)_2$ (minimum purity 99.5%). A 3.805, 4.945and 2.744g of copper nitrate, nickel nitrate and cadmium nitrate, respectively were dissolved in approximately 200 ml of distilled water.

A 10 ml concentrated HNO_3 was added then it was diluted to 1000 ml with distilled water **,APHA, 1995**. Concentrations of 50 ppm from these salts were used as adsorbate for different weights of nanosorbent.All the glassware used for dilution, storage and experiments were cleaned with extra detergent, thoroughly rinsed with tap water, soaked overnight in a 20% HNO_3 solution and finally rinsed with distilled water before use. Dissolved metal concentrations in solution were determined by a flame atomic absorption spectrophotometer (Buck, Accusys 211, USA).

Table 2 shows the main physicochemical properties of the metals tested.

3.2 Nanosorbent

(Fe_3O_4) nanoparticles obtained from US Research Nanomaterials, Inc., Houston, TX 77084, (USA) were used as nanosorbents. The main physical properties of the Nanopowder / Nanoparticales, Iron Oxide (Fe_3O_4) are listed in **Table 3** . **Table 4** shows Certificate of Analysis -- % of Iron oxide Nanoparticales (Fe_3O_4).

The characteristics of the selected nanosorbents were evaluated ; namely: specific surface area, and external surface area. Results are presented in **Table 5**. External and specific surface areas of the nanosorbent were measured in Ministry of Oil / Petroleum Development and Research Centre. The results show that there is no significant difference between them. This indicates that the nanosorbents have no significant porosity and maintain a high external surface area. **Fig. 1** shows scanning electron micrographs for nanosorbent which carried out in Nano Research Center, University of Technology/Baghdad –Iraq.

3.2.1 Adsorption Experiments for Nanosorbents

A series of experiments were carried out in a batch system to obtain equilibrium data for adsorption of single, binary, ternary and quaternary metals solutions. **Table 6** shows the major varied parameters used in these experiments.

3.2.2 Batch Experiments for Nanosorbent

3.2.2.1 Determination of the optimum pH

The effect of pH on Cu^{2+}, $Ni^{2+}$and Cd^{2+} ions adsorption onto nanosorbent was studied; 0.5 g nanosorbent of Fe_3O_4 was mixed with 100 ml of single metal ion solutions with concentration of 50 mg/l of Cu^{2+}, Ni^{2+} and Cd^{2+} ions respectively. These were maintained at different pH values ranging from 3 to 7 by using 0.1 M NaOH or HNO_3 solution at agitation speed of 200 rpm for a period of 30 min and at room temperature. Separation of nanosorbents from aqueous solution was evaluated by separating them via a small horseshoe magnet and wearing specific suits, thick gloves, special eye glasses, and special mask to prevent the direct contact with nanomaterial. Samples (10 ml) were taken from each volumetric flask and measured by using atomic absorption spectrophotometer AAS.

3.2.2.2 Equilibrium isotherm experiments

Different weights nanosorbent of Fe_3O_4 were used, (0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.2, and 1.4 g) , nanosorbents were placed in 9 volumetric flasks of 250 ml. A sample of 100 ml of measured concentration solution of 50 mg/l was added to each flask for single systems of Cu^{2+}, Ni^{2+} and Cd^{2+} respectively. The pH of the metal solutions was adjusted to the optimum pH value for each metal using 0.1M NaOH or 0.1M HNO_3. The flasks were then placed on a shaker (HV-2 ORBTAL, Germany) and agitated continuously for 50 min at 200 rpm and. A few drops of 0.1M HNO_3 were added to samples after separation of nanosorbent from aqueous solution to decrease the pH value below 2 in order to fix the concentration of the heavy metals during storage before analysis **,APHA, 1995**. The final equilibrium concentrations were measured by means of atomic absorption device. The residual concentration of cadmium, copper, and nickel in samples was determined using AAS in laboratory of Environmental Engineering Department/Baghdad University. The adsorbed amount is then calculated by the following equation:

$$q_e = \frac{V_l(C_o - C_e)}{W_{(nanosorbent)}} \qquad (11)$$

The adsorption isotherms were obtained by plotting the weight of solute adsorbed per unit weight of biomass (q_e) against the equilibrium concentration of the solute in the solution (C_e) **,Vijayaraghavan and Yun, 2008**.

3.2.2.3 Thermodynamic parameters of adsorption

The effect of temperature on Cu^{2+}, Cd^{2+} and Ni^{2+} ions adsorption uptake onto nanosorbent was studied, 0.6 g of nanosorbent was mixed with 100 ml of single metal ion solutions with concentration of 50 mg/l of Cu^{2+}, Cd^{2+} and Ni^{2+} respectively. These were maintained at different temperature values ranging from 20 to 50°C for a period of 50 min, agitation speed was 200 rpm. Samples (10 ml) were taken from each volumetric flask and measured by AAS.

4. RESULTS AND DISCUSSION

4.1 Batch Systems for Nanosorbent

4.1.1 Effect of pH

The pH of the metal solution usually plays an important role in the adsorption of metals. As mentioned previously in sec.(3.2.2.1) **Fig. 2** shows the effect of over 6 pH values on the adsorption uptake of Cu^{2+}, Ni^{2+} and Cd^{2+} ions.

Beyond the value of pH 6.0 precipitation will occur to heavy metals, this due to the insoluble metal hydroxides start precipitating from the solutions at higher pH values and make the true sorption studies impossible. This should be avoided during sorption experiments which distinguish between sorption and precipitation metal removal becomes hard **,Quintelas et al., 2008.**At low pH, proton would compete for active binding sites with metal ions. The protonation of active sites thus tends to decrease the metal sorption. At low pH around 2 all the binding sites may be protonated, thereby desorbing all originally bound metals from the sorbent**, Aldre *et al.*, 2007**. Therefore optimum copper, nickel and cadmium ions adsorption process will be at pH 6 as shown in **Fig. 2**. These results agreed with the results obtained by **,Nassar, 2010**,and**,Grossl and Sparks,1994.**

4.1.2Effect of Contact Time

Before the beginning the batch experiments, it was very important to know the required time to reach equilibrium adsorption. In other words, for all batch experiments, the contact time should be fixed at value to ensure reaching equilibrium concentrations. 0.6 g of nanosorbent of Fe_3O_4 was mixed with 100 ml of single metal ion solutions concentration of 50 mg/l of Cu^{2+}, Ni^{2+} and Cd^{2+} ions at pH 6. These were maintained at different time values ranging from 10 to 70 min. **Fig. 3** shows the results of removal efficiency (%) with the contact time of three metal solutions. It can be concluded that 50 min contact time is sufficient to reach equilibrium condition for all heavy metals.

4.1.3 Effect of Initial Heavy Metal Concentration

Different concentrations of 10, 50, 100 and 150 mg/l were selected to study the variation of removal efficiency with different initial concentrations at the same weight of nanosorbent (1 g) and at room temperature. The pH of heavy metal solutions was fixed at the optimum value for each heavy metal obtained from the isotherms experiments, and the agitation speed of the shaker was 200 rpm for contact time of 50min. as shown in **Fig.4.** It can be seen that the percentage removal efficiency was not altered greatly if the concentration increase from 10-50 mg/l, this behavior due to that 1 g of nanosorbent may contain enough sites for this concentration range, but when the concentrations increase to 100 and 150 mg/l the sites in 1 g will not be enough to accumulate these concentrations so that the depletion in percentage removal efficiency was obvious.

4.1.4 Effect of Temperature and Thermodynamic Parameters

The effect of temperature on the equilibrium sorption capacity for Cu^{+2}, Ni^{+2} and Cd^{+2} ions has been investigated at temperature range between 20-50 °C. **Fig. 5** shows the variation of percentage removal efficiency with temperature.

From **Fig. 5**, it can be concluded that the increase in temperature leads to increase the percentage removal efficiency and the variation of temperature from 20-30 °C has no or little significant effect on the adsorption process, so that the adsorption experiments can be carried out at room temperature without any adjustment.

Thermodynamic parameters were obtained by varying temperature conditions over the range 20-50°C by keeping other variables constant. The values of the thermodynamic parameters such as ΔG°, ΔH° and ΔS°, describing copper, nickel and cadmium ions uptake by nanosorbent, were calculated using the thermodynamic equations: The apparent equilibrium constant for the process has been shown to be:

$$\Delta G = -RT\ ln(K_c) \qquad (12)$$

Where

$$K_c = \frac{C_{ad}}{C_e} \qquad (13)$$

Where K_c is the equilibrium constant, C_{ad} is the amount of metal adsorbed on the adsorbent per liter of the solution at equilibrium (mg/l), C_e is the equilibrium concentration of the metal in the solution (mg/l), T is absolute temperature (K) and R is the universal gas constant (8.314 J/mol K). Also, Gibbs free energy change ΔG^o , enthalpy changes (ΔH) and entropy changes (ΔS) can be estimated by the following equation **,Colak *et al.*, 2009.**

$$\Delta G = \Delta H - \Delta S T \qquad (14)$$

The positive values of ΔH° reveal the adsorption is endothermic and physical in nature. Generally, the change in adsorption enthalpy for physisorption is in the range of −20 to 40 kJ mol^{-1}, but chemisorptions is between −400 and −80 kJ mol^{-1},**Zubeyde *et al.*, 2009. Fig. 6** and **Table 7** show the thermodynamic constants of adsorption obtained for Cu^{2+}, Ni^{2+} and Cd^{2+} ions onto nanosorbents. **Table 7** shows the values of enthalpy ΔH° were 12.8, 7.119 and 10.59 $kJ.mo1^{-1}$ for Cu^{2+},Ni^{2+} and Cd^{2+} ions respectively, reveal the adsorption is endothermic and physical in nature. This is also supported by the increase in the values of uptake capacity of nanosorbents with the rise in temperature.

4.1.5 Estimation of Adsorption Isotherms Constants

The adsorption for a single, binary,and ternary component systems of Cu^{2+}, Ni^{2+} and Cd^{2+} ions onto nanosorbent in batch experiments were conducted with initial concentration of (50 mg/l) and particle size of (20-30 nm) at room temperature in order to determine the isotherm constants for each system using different isotherm models.

4.1.6 Single Component System

The adsorption isotherm for single component systems of of Cu^{2+}, Ni^{2+} and Cd^{2+} ions respectively, onto nanosorbent are shown in Fig. 7 to 9, whereas Fig. 10 shows a comparison between them. The data, for single component systems were correlated with six models illustrated in section (2.1). The parameters for each model obtained from non-linear statistical fit of the equation to the experimental data (STATISTICA software, version 6). **Table 8** shows parameters of single solute isotherm for Cu^{2+}, Ni^{2+} and Cd^{2+} ions uptake onto nanosorbent. **Fig. 11 to 13** show comparison of some selective models applied in single system for copper, nickel and cadmium ions respectively.

Fig. 7 to 13 and **Table 8** show the following:

- The equilibrium isotherm for each single component is of favorable type. n >1.
- The adsorption capacity q_e and heavy metals removal rate were related to the amount of adsorbent added; the greater adsorption capacity was obtained at lower adsorbent dose. The higher removal rate was achieved at higher adsorbent dose.
- The Freundlich model gives the best fit for the experimental data for single component adsorption system for copper, nickel and cadmium ions recognized by the highest values of (R^2), this model has been used successfully to describe equilibrium adsorption. Results can be compared for the three adsorbates in term of maximum bending capacity and (n) parameters: $Cu^{2+} > Cd^{2+} > Ni^{2+}$.
- The copper which has the highest affinity order for being adsorbed by the nanosrbent, has the lowest hydration Van der Waals radius while nickel ions the least favorable by the nanosrbent, has the highest hydration Van der Waals radius, **Table 2**. This coincides with the fact that less hydrated ions radius is preferably accumulated at interface **,Hawari, 2006**.

4. 1.7 Binary Component System

Binary systems are usually present in effluent from different industries. The data, for binary component systems were correlated with three models as mentioned in section (2.2). The parameters for each model obtained from non-linear statistical fit of the equation to the experimental data. The adsorption isotherms for binary component systems of Cu^{2+}, Ni^{2+} and Cd^{2+} ions onto nonabsorbent are shown in **Fig. 14 to 16**. **Table 9** represents all parameters with correlation coefficient for binary systems.

Fig.17 to 22 show a three-dimensional adsorption surface for the simulation uptake for Cu^{2+}, Ni^{2+} and Cd^{2+} ions onto nanosorbents in binary mixtures.

4.1.8 Ternary Component System

The adsorption isotherms for ternary component systems were correlated to which the best model was fitted in binary component system. The parameters for each model obtained from non-linear statistical fit of the equation to the experimental data.

The adsorption isotherms for ternary component systems of Cu^{2+}, Ni^{2+} and Cd^{2+} ions onto nanosorbent are shown in **Fig.23**.

Fig. 14 to 23 and **Tables 9 and 10** show the following:

- For each the binary, ternary and quaternary systems the Combination of Langmuir- Freundlich model seems to give the best fitting for the experimental data at highest value of R^2. It can be seen from the figures, Cu^{2+} always adsorbed more favorable onto nanosrbent than Ni^{2+} and Cd^{2+} in binary and ternary systems.
- The decrease of adsorption capacity in binary and ternary systems compared to the single metal systems observed for all metals with exception of copper, reflects the existence of a competition between the metals studied for the binding sites present in nanoparticle wall. It seems that the total metal adsorption capacity onto the nanoparticle decreases when increasing the number of metals present. This fact supports the assumed competition between metals for the nano particle binding sites and tends to decrease the relative amount of each adsorbed element. These results agreed with the results obtained by **,Nassar, 2010**.

Fig. 24 to 26 show that the metal removal efficiency of nanosorbent in single and mixed system was inhibited by the presence of the other heavy metals in the system. The removal efficiency of Cu^{2+} in single system is 100% reduced to 96.4% and 97.6% respectively in binary system with Cd^{2+} and Ni^{2+} ions respectively, while the removal efficiency of Cu^{2+} in ternary system reduced to 95% with $[Cd^{2+} + Ni^{2+}]$. The removal efficiency of Cd^{2+} in single system is 98.1% reduced to 64% and 88.6% respectively in binary system with Cu^{2+} and Ni^{2+} ions respectively, while the removal efficiency of Cd^{2+} in ternary system reduced to 47% with $[Cu^{2+} + Ni^{2+}]$. The removal efficiency of Ni^{2+} in single system is 82% reduced to 58.8% and 58% respectively in binary system with Cd^{2+} and Cu^{2+} ions respectively, while the removal efficiency of Ni^{2+} in ternary system reduced to 20.4% with $[Cd^{2+} + Cu^{2+}]$.

5. CONCLUSIONS

This study revealed the following conclusions, concerning the batch for nanosorbent Cu^{2+}, Cd^{2+}, and Ni^{2+} ions:

5.1 Batch Process for Nanosorbent

5.1.1 Single component system

1. Optimum pH was 6 for Cu^{2+}, Cd^{2+} and Ni^{2+}ions in adsorption process onto Fe_3O_4 nanoparticle (20-30 nm).
2. It can be concluded that 50 min contact time is sufficient to reach equilibrium condition for all heavy metals.
3. The equilibrium isotherm for each single component is of a favorable type and Freundlich isotherm gives the best fit model for representing the experimental data for this system.

4. In this system Cu^{2+} ions was the most favorable component rather than Cd^{2+} and Ni^{2+} ions, that due to its physiochemical characteristics that make the most favorable adsorbed component, due to the lowest hydration Van der Waals radius for copper. Results for the three adsorbates in term of adsorption capacity parameters were: $Cu^{2+}>Cd^{2+}>Ni^{2+}$.There were a good matching between experimental and predicted data.
5. It can be seen that the percentage removal efficiency was not altered greatly if the concentration increase from 10-50 mg/l, this behavior due to that the nanosorbent may contain enough sites for this concentration range, but when the concentrations increase to 100 and 150 mg/l the sites will not be enough to accumulate these concentrations so that the depletion in percentage removal was obvious.
6. Adsorption of Cu^{2+}, Cd^{2+} and Ni^{2+}ions was endothermic and physical in nature.

5.1.2 Binary and ternary component system

1. For each binary and ternary component systems, combination of Langmuir-Freundlich Isotherm gives the best fit for the experimental data.
2. The behavior of the equilibrium isotherm is of favorable type.
3. For each system Cu^{2+} ions is still most adsorbed component rather than Cd^{2+} and Ni^{2+}ions.
4. Due to the competitive effect of Cu^{2+}, Cd^{2+} and Ni^{2+}ions with each other to occupy the available site(s) of the nanosorbent, Cu^{2+}ions offers the strongest component that able to displace Cd^{2+} and Ni^{2+}ions from their sites, while Ni^{2+}ions was the weakest adsorbed component.
5. Compared with their adsorption in single component system the adsorption capacity of all three metals shows obvious decreases both in the binary and ternary system.

The percentage removal efficiency of each single component was decreased as each component presented with the other(s) in the binary and ternary system. This due to the presence of more than one component will enhance the competitive struggling race for occupying a certain site.

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Table 1. Constant parameter R_L

R_L	Type of isotherm
$R_L > 1$	unfavorable
$R_L = 1$	linear
$R_L = 0$	irreversible
$0 < R_L < 1$	favorable

Table 2. Main physicochemical properties of the metals tested **Wikipedia,2014**

Properties	**Copper**	**Nickel**	**Cadmium**
Formula	Cu^{2+} from $Cu(NO_3)_2$	Ni^{2+} from $Ni\ (NO_3)_2$	Cd^{2+} from $Cd(NO_3)_2$
Appearance	blue crystals	Emerald green solid	white crystals
Molar mass ($g{\cdot}mol^{-1}$)	241.6	290.79	236.42
Standard atomic weight	63.546	58.6934	112.414
Solubility in water g/100 ml	137.8 (0°C) 1270(100°C)	94.2 (20°C) 158 (60°C)	325 (15°C) 156 (25°C)
Melting point	114.5 °C	56.7 °C	59.5 °C
Boiling point	170 °C	136.7 °C	132 °C
Atomic Radius(pm)	128	124	151
Van der Waals radius(pm) *	140	163	158
Electronegativity (Pauling scale) **	1.9	1.91	1.69
Electrical resistivity nΩ·m(20 °C)	16.78	69.3	72.7(22 °C)
Magnetic ordering	diamagnetic	Ferromagnetic	diamagnetic
Density (g/cm^3)	2.32	2.05	2.455
Charge	2	2	2
Company	BDH (England)	Fluka (Switzerland)	RIEDEL-DE HAEN AG (Germany)

* pico meter $=10^{-12}$ m.

**Pauling Scale: A dimensionless quantity, on a relative scale running from around 0.7 to 3.98 (Hydrogen was chosen as the reference, its electronegativity was fixed first at 2.1, later revised to 2.20).

Table 3. The main physical properties of the Nanosorbent(manufactural reported)

Physical Properties of the Nanosorbent, Iron Oxide (Fe_3O_4)	
Purity	98+%
Average Particle Size	20-30 nm
Surface Area	40-60 m^2/g
Color Dark	Dark Brown
Morphology	spherical
Bulk Density	0.84 g/cm3
True Density	4.8-5.1 g/cm3

Table 4. Certificate of Analysis --% Iron oxide Nanoparticales (manufactural reported)

Certificate of Analysis --% Iron oxide Nanoparticales (Fe_3O_4)				
Ca	**Cr**	**K**	**Mn**	**SiO2**
0.02290<	0.0016<	0.0012<	0.086<	0.142<

Table 5. Characterizations of Fe_3O_4 nanosorbents considered in this study**.**

Manufacturer reported surface area (m^2/g)	Specific surface area (m^2/g)	External surface areas(m^2/g)
40-60	63	61

Table 6. Major experimental parameters that varied in batch experiments

	Parameter	Range	Purpose
Batch	pH	3, 4, 5 ,6 and 7	To find the optimum pH of removal efficiency.
	Nanosorbent weight	0.05, 0.1, 0.2, 0.4, 0.6,0.8, 1,1.2, and 1.4 g	To plot the equilibrium isotherm curves.
	Temperature	20, 35, and 50 °C	To study the thermodynamic parameters of adsorption.
	Initial conc.	10, 50, 100, and 150 ppm	To study the effect of initial conc. on the adsorption.

Table 7. Thermodynamic constants of adsorption obtained for Cu^{+2}, $Cd^{+2}$and Ni^{+2} ions sorption onto nanoadsorbent.

Metal	Temperature (K)	ΔG^0 ($kj.mol^{-1}$)	ΔH^0 ($kj.mol^{-1}$)	ΔS^0 ($j.mol^{-1}K^{-1}$)	R^2
Cu^{+2}	293	-2.23055	12.8	0.051	0.964
	308	-3.26050			
	323	-3.77921			
Cd^{+2}	293	-0.9404	10.59	0.039	0.977
	308	-1.69034			
	323	-2.12666			
Ni^{+2}	293	-0.0359	7.119	0.024	0.999
	308	-0.41427			
	323	-0.7686			

Table (8). Parameters of single solute isotherm for Cu^{2+}, Ni^{2+} and Cd^{2+} ions for nanosorbent

MODEL	PERAMETER	SINGLE		
		Cu^{+2}	**Cd^{+2}**	**Ni^{+2}**
Langmuir $q=\frac{bq_mC_e}{1+bC_e}$ **Lin and lai, 2006**	q_m(mg/g)	9.4223	11.698	5.7933
	b(l/mg)	0.4247	0.0613	0.0639
	R^2	0.8143	0.865	0.86
Freundlich $q=KC_e^{1/n}$ **Öztürk *et al.*,2004**	K, $(mg/g)(mg/l)^{(1/n)}$	3.544	1.8751	0.9446
	n,-	3.6695	2.4836	2.4801
	R^2	0.899	0.9217	0.8816
Redlich–Peterson $q_e=\frac{K_{RP}C_e}{1+a_{RP}C_e^{\beta_{RP}}}$ **Maurya *et al.*, 2006**	k_{RP}(mg/g)	0.2138	0.1569	1.562e13
	a_{RB}(l/mg)	-0.2283	-0.3198	1.913e13
	ß,-	0.00002	0.000006	0.556
	R^2	0.5604	0.768	0.8807
Sips $q_e=\frac{K_sC_e^{\beta_s}}{1+a_sC_e^{\beta_s}}$ **Sips, 1984**	k_s, (l/g)	0.46034	0.5227	0.05114
	ß	0.02268	0.0498	0.00684
	a_s,(l/mg)	-0.8729	-0.772	-0.963
	R^2	0.877	0.902	0.865
Khan $q_e=\frac{q_{max}b_kC_e}{(1+b_kC_e)^{a_k}}$ **Khan *et al.*, 2006**	q_m (mg/g)	0.6502	0.25353	0.34003
	b_k,(l/mg	513.204	139.262	12.7709
	a_k	0.728	0.596	0.59743
	R^2	0.8887	0.9015	0.8714
Toth $q_e=\frac{q_{max}b_TC_e}{\left[1+(b_TC_e)^{\frac{1}{n_T}}\right]^{n_T}}$ **Vijayaraghavan and Yun, 2008**	q_m (mg/g)	102.994	227.12	44.5025
	b_T	736.78	1.8023	0.4606
	n_T	8.789	7.443	5.2311
	R^2	0.8908	0.913	0.877

Table 9. Parameters of binary systems solutes isotherms for copper,nickel and cadmium ions onto nanosorbent

Binary system							
Cd^{+2},Ni^{+2} system		Cu^{+2},Ni^{+2} system		Cu^{+2},Cd^{+2} system		Parameter	Model
Ni^{+2}	Cd^{+2}	Ni^{+2}	Cu^{+2}	Cd^{+2}	Cu^{+2}		
1.856	5.822	2.537	8.939	3.311	7.7233	q_m (mg/g)	**Extended Langmuir Eq.(8)**
0.1	0.1	0.1	0.1	0.1	0.1	b (l/mg)	
0.804	0.881	—	0.724	—	0.699	R^2	
17.98	0.908	144.54	0.008	12.99	0.0034	a,-	**Redlich-Peterson Eq.(9)**
18.12	0.6575	161.69	1.823	0.269	2.064	ß,-	
—	0.885	—	0.785	0.941	0.866	R^2	
3.218	0.299	4.9336	1.603	6.71	0.9228	q_m (mg/g)	**Combination of Langmuir-Freundlich Eq.(10)**
0.1	2.3173	0.1	1.895	0.1	3.0821	b (l/mg)	
1.5657	1.5246	1.6444	2.962	1.894	3.1127	n	
0.956	0.897	0.983	0.912	0.938	0.936	R^2	

Table10. Parameters of ternary system solutes isotherms for copper,nickel and cadmium ions onto nanosorbent

Ternary system				
Model	**Parameters**	**Cu^{+2},Cd^{+2}, Ni^{+2} system**		
		Cu^{+2}	**Cd^{+2}**	**Ni^{+2}**
Combination of Langmuir-Freundlich Eq.(10)	q_m (mg/g)	0.746	1.78	0.622
	b (l/mg)	2.482	0.098	0.103
	n	1.999	1.065	1.124
	R^2	0.95	0.874	0.833

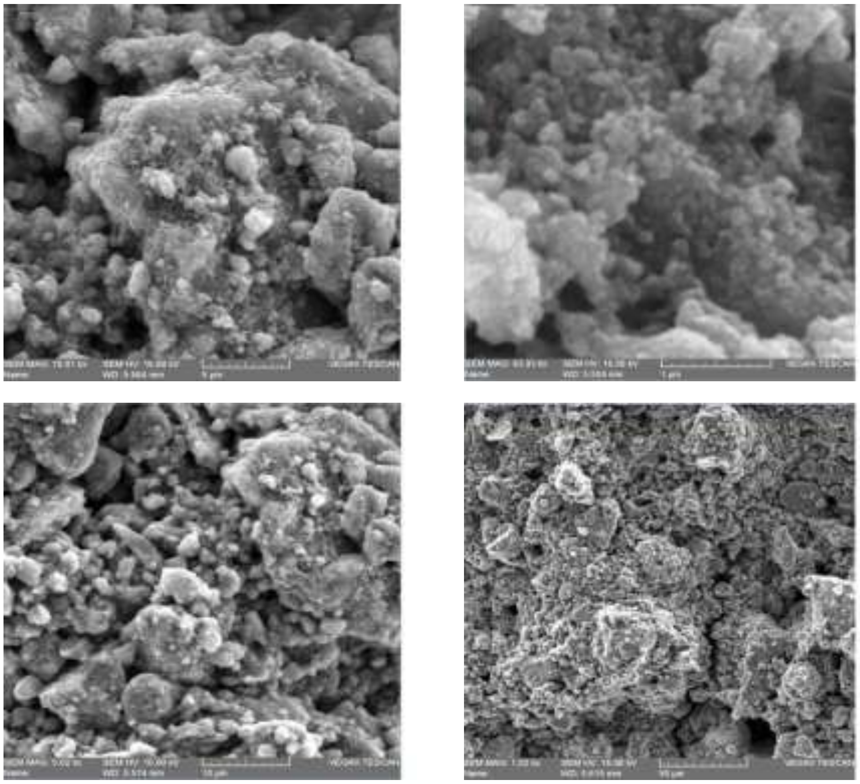

Figure 1. Scanning electron micrographs for nanosorbent

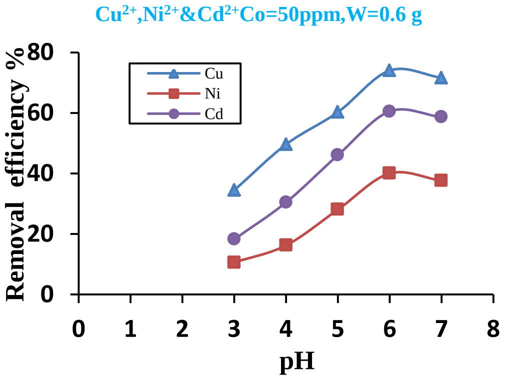

Figure 2. Effect of different pH values on copper, nickel and cadmium ions uptake by nanosorbents, $C_{nanosorbents}$= 6g/l, $C_{o(Cu,\ Ni\ and\ Cd)}$=50 mg/l.

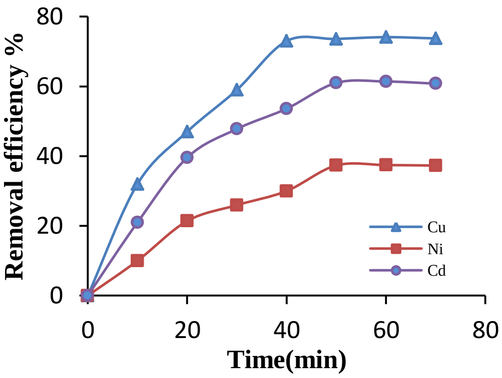

Figure 3. Adsorption efficiency for nanosorbent with different contact time, C_o=50 ppm, pH=6, $W_{nanosorbent}$=0.6 g, 200 rpm

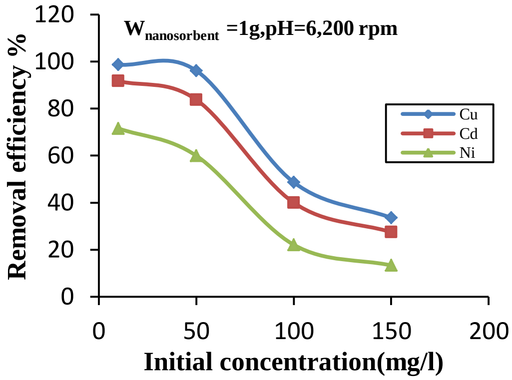

Figure 4. Percentage of removal adsorption efficiency with variation of initial concentration, contact time 50 min and 200rpm

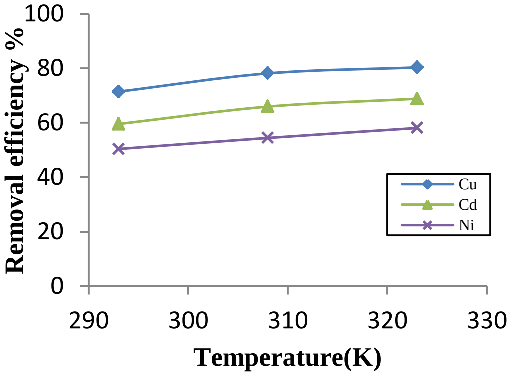

Figure 5. Variation of percentage removal with solution temperature, C_o=50 ppm, contact time 50min.,$W_{nanosorbent}$=0.6g, and 200rpm

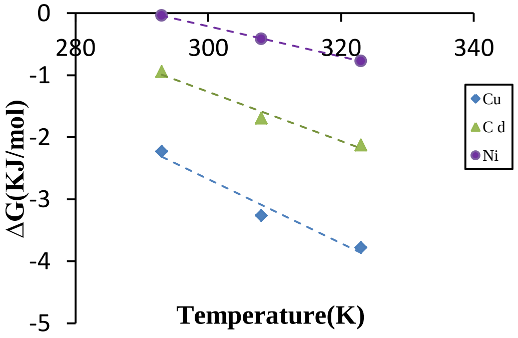

Figure 6. Change in free energy with temperature for the adsorption of Cu^{2+}, Ni^{2+} and Cd^{2+} ions by nanosorbent at initial concentration of 50 mg/l, and pH 6.

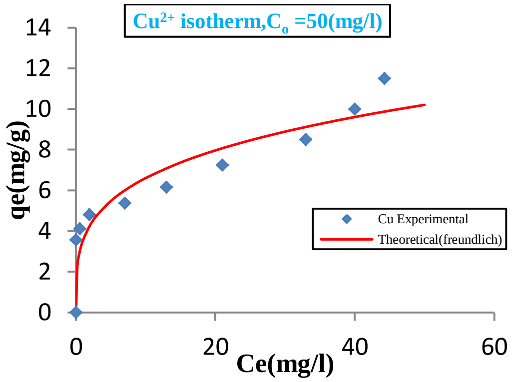

Figure 7. Adsorption isotherm for copper ions onto nanosorbent

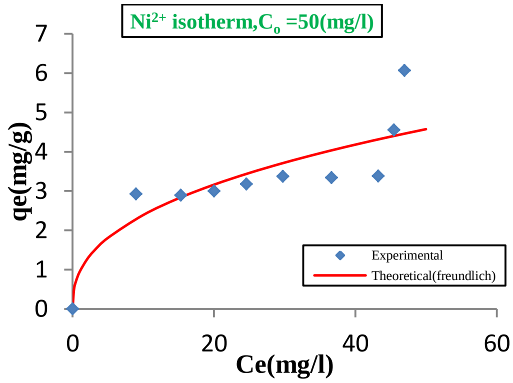

Figure 8. Adsorption isotherm for nickel ions onto nanosorbent

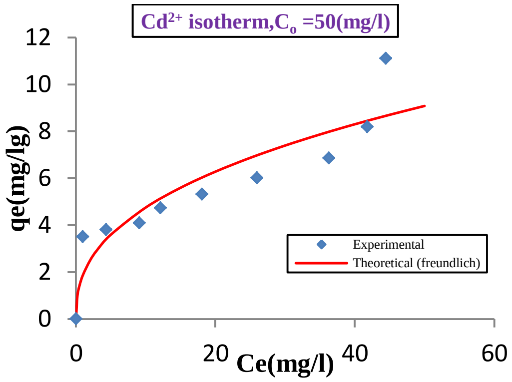

Figure 9. Adsorption isotherm for cadmium ions onto nanosorbent

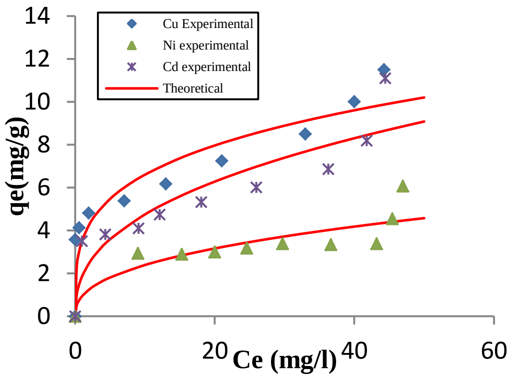

Figure 10. Adsorption isotherms of Cu, Ni and Cd ions as single solutes onto nanosorbent

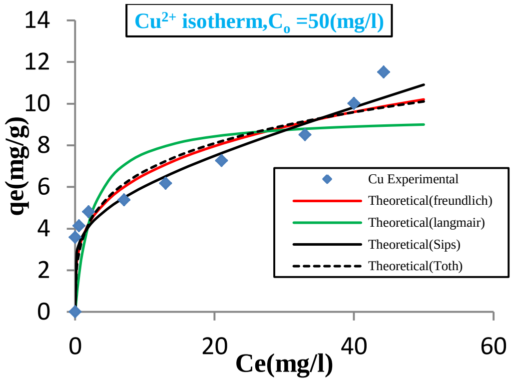

Figure 11. Comparison of some selective models applied in single system for copper ions onto nanosorbent

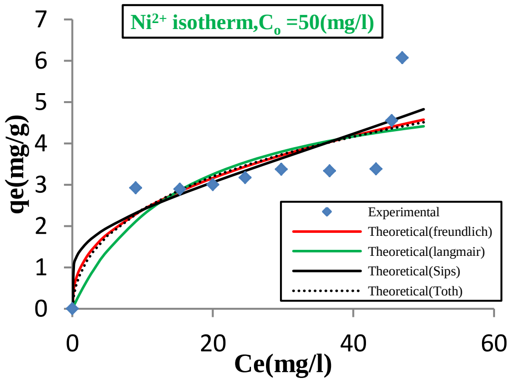

Figure 12. Comparison of some selective models applied in single system for nickel ions onto nanosorbent

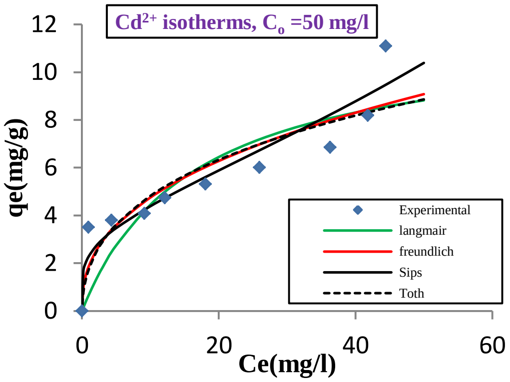

Figure 13. Comparison of some selective models applied in single system for cadmium ions onto nanosorbent

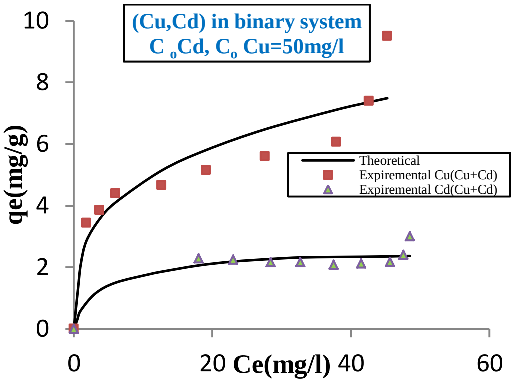

Figure 14. Adsorption isotherms of copper and cadmium ions onto nanosorbent

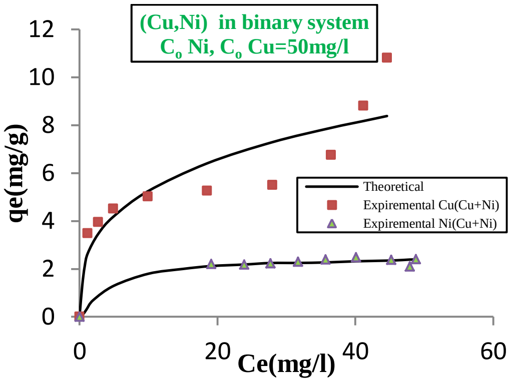

Figure 15. Adsorption isotherms of copper and nickel ions onto nanosorbent

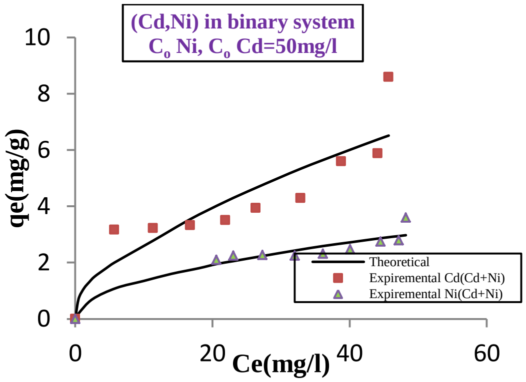

Figure 16. Adsorption isotherms of cadmium and nickel ions onto nanosorbent

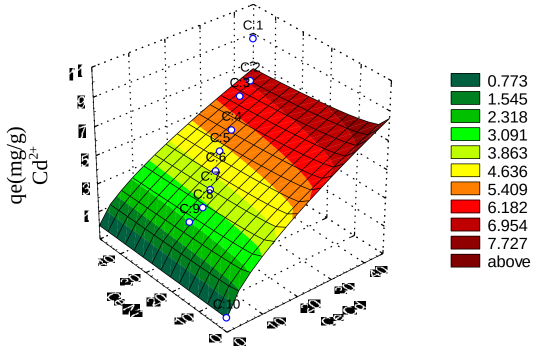

Figure 19. A three-dimensional adsorption surface for the simultaneous uptake of Cd ions onto nanosorbent from Cd ions and Ni ions binary mixtures

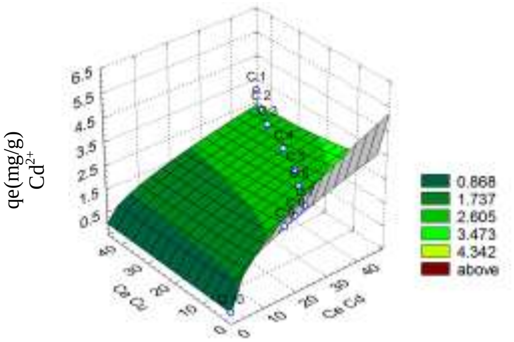

Figure 17. A three-dimensional adsorption surface for the simultaneous uptake of Cd ions onto nanosorbent from Cd ions and Cu ions binary mixtures

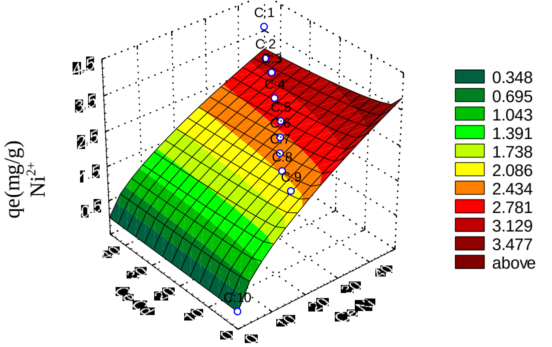

Figure 20. A three-dimensional adsorption surface for the simultaneous uptake of Ni ions onto nanosorbent from Ni ions and Cd ions binary mixtures

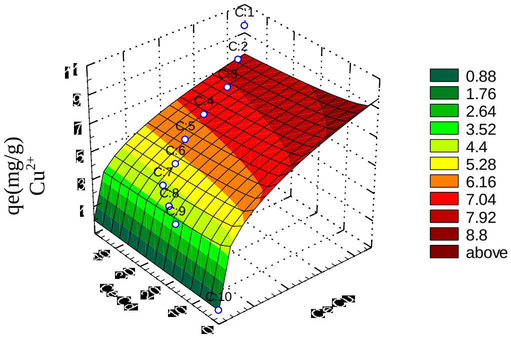

Figure 18. A three-dimensional adsorption surface for the simultaneous uptake of Cu ions onto nanosorbent from Cu ions and Cd ions binary mixtures

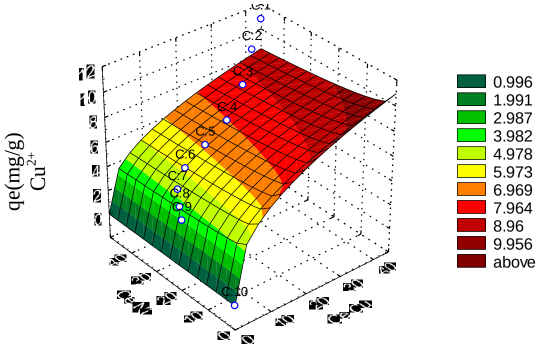

Figure 21. A three-dimensional adsorption surface for the simultaneous uptake of Cu ions onto nanosorbent from Cu ions and Ni ions binary mixtures

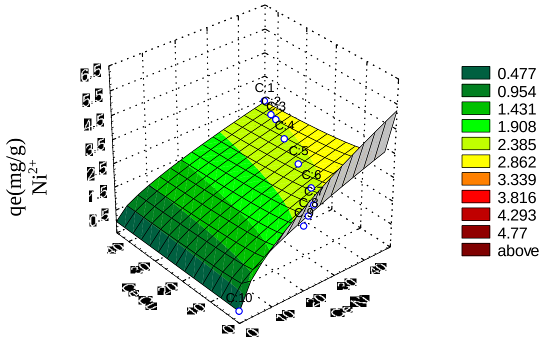

Figure 22. A three-dimensional adsorption surface for the simultaneous uptake of Ni ions onto nanosorbent from Ni ions and Cu ions binary mixture.

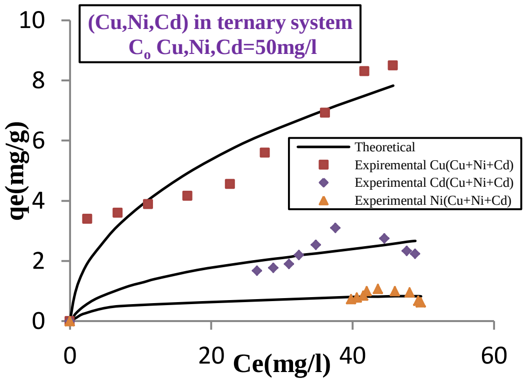

Figure 23. Adsorption isotherms of copper, cadmium and nickel ions onto nanosorbent

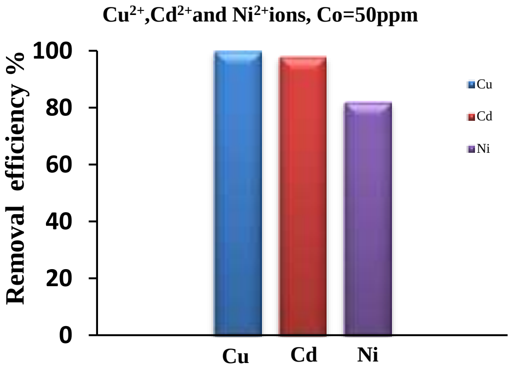

Figure 24. Adsorption of copper, nickel and cadmium ions, when used in single system

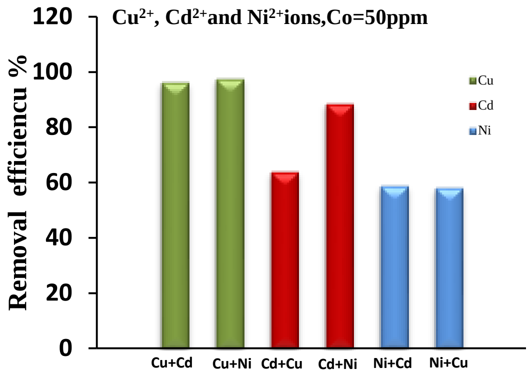

Figure 25. Adsorption of copper, nickel and cadmium ions, when used in binary system

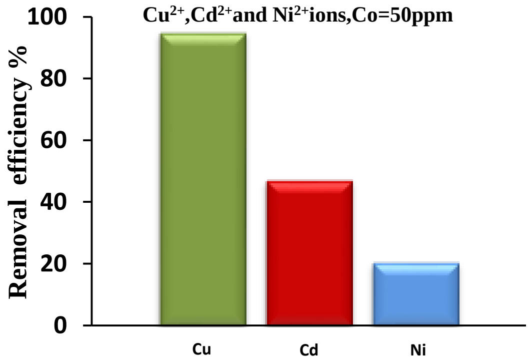

Figure 26. Adsorption of copper, nickel and cadmium ions, when used in ternary system