

**REPUBLIC OF TURKEY
FIRAT UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND
APPLIED SCIENCES**



**SINGLE AND BINARY ADSORPTION OF Cu(II) AND
Cd(II) ONTO CHITIN**

**MASTER THESIS
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SUMMARY

Single and Binary Adsorption of Cu(II) and Cd(II) Onto Chitin

The adsorption of single and binary Cu(II) and Cd(II) onto chitin was examined in the batch system. The influence of primary pH, temperature, and initial single and binary metal concentrations on the adsorption equilibrium and kinetics of every constituent, together single and binary combination were studied. The equilibrium uptakes of single and binary Cu(II) and Cd (II) were increased with increasing temperature up to 40 °C. The chitin selectively adsorbed single Cu(II), binary Cu(II) and Cd(II) ions at pH= 4.5, while single Cd(II) ions were adsorbed by the chitin at pH 5.0. The Freundlich, Langmuir, and Tempkin adsorption models were utilized for the mathematical definition of the adsorption equilibrium and isotherm constants were assessed at different temperatures (20, 30 and 40 °C). The single and binary constituent system was well defined with the Langmuir isotherm model. The maximum Cu(II) and Cd(II) adsorption capacity of chitin calculated Langmuir model were as high as 5.80 and 6.87 mg/g for single Cu(II) and Cd(II), 6.01 and 8.41 mg/g for binary Cu(II) and Cd(II), respectively. The results showed that adsorption of single and binary Cu(II) and Cd(II) onto chitin were endothermic and natural. Kinetics studies were carried out in the temperature range of 20–40 °C. The stimulation energies of the adsorption were determined as 1.34 and 2.55 kJ mol⁻¹ for single Cu(II) and Cd(II), respectively. Utilizing the thermodynamic equilibrium coefficients obtained at different temperature, the Gibbs free energy changes -3.78 kJ/mol for single Cu(II) and -4.15 kJ/mol for single Cd(II) at 40 °C, enthalpy changes 15.38 kJ/mol for Cu(II) and 20.13 kJ/mol for Cd(II) of adsorption were also determined, respectively. The pseudo-first order, pseudo-second order and intraparticle diffusion models were applied to the kinetic data. The pseudo-second order kinetic fitted well model and the presence of intraparticle diffusion mechanism was specified. Thermodynamic examined presented an endothermic, dissociative, natural and a physical adsorption operating among the metal ions and the chitin. In addition, a synergistic influence of two metals has been noticed and examined in the binary metal system. The results signify that not only the concurrent attendance of the two metals does not lessen the adsorption ability, but also improves their removal from the emanation.

Keywords: Chitin; Adsorption; Single and binary Cd(II)–Cu(II) ions; Isotherms; Activation energy; Thermodynamics; Gibbs free energy; Entropy; Enthalpy.

ÖZET

Kitin Üzerine Tekli veya İkili Cu(II) ve Cd(II) Adsorpsiyonu

Tekli ve ikili Cu(II) ve Cd(II)'nin kitin üzerine adsorpsiyonu kesikli sistemde incelenmiştir. Başlangıç pH, sıcaklık ve başlangıç tekli ve ikili metal iyon konsantrasyonlarının, her bileşenin adsorpsiyon dengesi ve kinetiği üzerindeki etkisi, tek ve ikili kombinasyon ile birlikte incelenmiştir. Tekli ve ikili Cu(II) ve Cd(II)'nin denge alım hızı sıcaklık 40 °C'ye kadar arttıkça artmıştır. Adsorpsiyon dengesinin matematiksel tanımı için Freundlich, Langmuir ve Tempkin adsorpsiyon modelleri kullanılmıştır ve izoterm sabitleri, farklı sıcaklıklarda değerlendirilmiştir. Kitin seçici olarak pH = 4.5'da tekli Cd(II) ve ikili Cu(II) ve Cd(II) iyonlarını adsorbe ederken, tekli Cd(II) iyonları ise pH = 5'te adsorbe etmiştir. Tek ve ikili bileşen sistemi, pahalı olmayan Langmuir izoterm modeli ile iyi tanımlanmıştır. Tekli ve ikili Cu(II) ve Cd(II) iyonlarının adsorpsiyon kapasitesi sırasıyla 39.06 ve 54.64 mg/g'dir. İkili Cu(II) ve Cd(II) için ise sırasıyla 37.73 ve 44.64 mg/g'dir. Sonuçlar, tekli ve ikili Cu(II) ve Cd(II)'nin çitin üzerine adsorpsiyonunun endotermik ve doğal olduğunu göstermiştir.. Kinetik model çalışmaları 20-40 °C'de çalışılmıştır. Adsorpsiyonun stimülasyon enerjileri sırasıyla tekli Cu(II) ve Cd(II) için 1.34 ve 2.55 kJ mol⁻¹ olarak tespit edilmiştir. Farklı sıcaklıklarda elde edilen termodinamik denge katsayıları kullanılarak, Gibbs serbest enerjisi sırasıyla 40 °C'de tekli Cu(II) için -3.78 kJ/mol ve tekli Cd(II) için -4.15 kJ/mol olarak bulunmuştur. Entalpi değişimi ise Cu(II) için 15.38 kJ/mol ve Cd(II) için 20.13 kJ/mol olarak bulunmuştur. Kinetik verilere yalancı birinci derece ve yalancı ikinci dereceyle beraber intrapartikül difüzyon modelleri uygulanmıştır. En uygun uyum, yalancı ikinci derece modeli ile gerçekleştirilmiş ve intrapartikül difüzyon mekanizmasının varlığı belirtilmiştir. İncelenen termodinamiğin metal iyonları ve kitin arasında çalışan bir endotermik, dissosiyatif, doğal ve fiziksel bir adsorpsiyon olduğunu göstermiştir. Buna ek olarak, iki metalin sinerjik etkisi fark edilmiş ve ikili metal sisteminde incelenmiştir. Sonuçlar, iki metalin eş zamanlı olarak katılmasının sadece adsorpsiyon kabiliyetini azaltmadığını aynı zamanda emandan çıkarmayı da geliştirdiğini gösteriyor.

Anahtar Kelimeler: Kitin, Adsorpsiyon, Tekli ve ikili Cd(II)-Cu(II) iyonları, İzoterm, Aktivasyon enerjisi, Termodinamik, Gibbs serbest enerjisi, Entropi, Toplu ısı

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NOMENCLATURE

C	: Unadsorbed heavy metal concentration in solution at any time (in milligrams per litre)
C_{eq}	: Unadsorbed heavy metal concentration in solution at equilibrium (in milligrams per litre)
C₀	: Initial heavy metal concentration (in milligrams per litre)
d_p	: Particle diameter (in centimetre)
K_b	: Adsorption equilibrium constant (in litres per milligram)
K_F	: Freundlich constant
k_L	: External mass transfer coefficient (in centimetres per minute)
K	: Intraparticle diffusion rate constant (in milligrams per gram per minute ^{0.5})
k₁	: Rate constant of pseudo-first-order sorption (per minute)
k₂	: Rate constant of pseudo-second-order sorption (in grams per milligram per minute)
n	: Freundlich constant
q	: Adsorbed heavy metal quantity per gram of adsorbent at any time (in milligrams per gram)
q_{eq}	: Adsorbed heavy metal quantity per gram of adsorbent at equilibrium (in milligrams per gram)
q_{max}	: Maximum amount of heavy metal per unit weight of the adsorbent to form a complete monolayer on the surface (in milligrams per gram)
R	: Universal gas constant (8.314 Jmol ⁻¹ K ⁻¹)
R²	: Regression correlation coefficient
t	: Time (in minute)
T	: Temperature (in kelvin in degree Celcius)
X	: Sorbent concentration (in grams per litre)
ΔG°	: Gibbs free energy change
ΔH°	: Enthalpy change of adsorption
ΔS°	: Entropy change of adsorption
SD	: Normalised standard deviation
ρ_p	: Particle density (in grams per millilitre)

1. INTRODUCTION

Heavy metal pollution is important sources of contamination. Heavy metals in industrial effluents are a main ecological hazard and environmental [1-3.] Metal contamination of water and wastewater, a tremendously environmental issue, has arisen in recent years because of growth and expansion of industries which have spread heavy metals to water [4]. Example for heavy metals, nickel, cobalt, chromium, copper, lead, and zinc ions have been distinguished in the waste inflow from mining processes, the creation of paints and colors, ammo, and earthenware, electronics, electroplating and petrochemical trades, and also in material factory items. It is considered as the possibly metals with growing toxicity for humans and different marine microorganisms [5-7, 3]. After they surpass the tolerance proportions and don't experience biodegradation. Heavy metals harmfully affect human physiology and other biological systems. On account of inadequate wastewater treatment or if the contaminated water is discharged to a channel, these metals can amass in the environment [8, 9]. The heavy metals, having dangerous impacts on health, can be dealt with wastewater by utilizing different physicochemical methods [10]. Distinctive sorts of techniques have been suggested for the cure of industrial waste water and water comprising heavy metals [11]. For example, biological cures, procedures utilizing advanced oxidation forms, a filtration membrane, electrochemical approaches and adsorption procedures have proven to be more feasible alternate because of small price of processing and instrumentation, simplicity of process and no requirement for expansive amenities [12-15, 1, 2, 16]. Among these approaches, adsorption is an exceptionally well known one and has been generally rehearsed in mechanical wastewater treatment procedures. The significant points of benefits of an adsorption system for water contamination control are less investment in terms of introductory price and land, basic design and simple operation, and no impact of poisonous substances contrasted with customary natural biological process [17]. Nevertheless, there is an expanding enthusiasm for the utilization of biomass for expulsion of liquefied metals from aqueous solutions because normal water analysis substances are moderately costly and require complex functional set-up and safety precautionary measures. An assortment of minimal price biomass has been grown and commercialized for controlling contamination from different resources. Instances for such minimal price bio-sorbents are tea leaves, farming waste,

cellulose, wool fiber, fly cinder, groundnut hull pellets, creature bones, pine barks and immobilized fungal biomass [18]. Chemical precipitation/coagulation, reverse osmosis, adsorption/biosorption, extraction, and membrane separation process are normal approaches to uptake of heavy metal from water solution [19]. Adsorption is an alternate to traditional machineries like electrochemical approaches or ion exchange [3].

From the environmental hazard and health perils purpose of perspectives, a standout amongst the most hazardous heavy metals is Cu(II). In spite of the fact that Cu(II) is a basic micronutrient, it is required by the body in little sums (20-80 $\mu\text{g/kg}$ of body weight per day). Overabundance exposure to Cu(II) can bring about serious and in addition unending impacts [20, 16, 2]. Cu(II) is especially poisonous, complexion with enzymes and other metabolic specialists associated with breathing and rendering them idle. It is an aggravation to skin bringing on tingling and mange, and may bring about keratinization of the hand and underside of the feet [4].

One of the heavy metal of impressive circumstantial and professional responsibility is Cd(II). It is broadly disseminated in the worlds' coating at a normal centralization of around (0.1) mg/kg. The top most balanced amount of Cd(II) mixes at the earth is amassed from sedimentary rocks, and sea phosphates include around 15 mg Cd/kg [21]. Chitin is a long chain polymer of N-Acetyl glucosamine, a subordinate of glucose [22] second most actually accessible material beside cellulose. It is a hard, white, inelastic, nitrogenous polysaccharide having biodegradability, biocompatibility, non-harmfulness and metal adsorption properties [23].

In this thesis, a procedure of completely adsorption focused single - binary metal ions onto chitin is portrayed. The heavy metal restricting limit of chitin is appeared with parameters such as of pH, temperature and initial metal ions concentration. The Adsorption wonders had communicated with Freundlich, Langmuir and Tempkin adsorption models and coefficients were assessed relying upon temperature. As there is no data about the active investigation of the adsorption of single-binary Cu(II) and Cd(II) by chitin. The information was additionally dissected utilizing the pseudo-first and pseudo second adsorption models and active constants were ascertained. The instruments by substantial metal adsorption onto chitin and potential ratio controlling steps were analyzed by utilizing outside mass exchange and intraparticle dispersion models.

2. WATER POLLUTION

2.1. General

The water Pollution is a conspicuous global problematic which needs incessant valuation and revision of water source approach in the all levels. It has been approved that water pollution is the foremost general cause for deceases and sicknesses [24, 25] and that it accounts the deceases of more than 14,000 society's everyday [25]. An assessed 580 individuals in India decease of water contamination linked sickness day after day [26, 27]. Notwithstanding the intense issues of water contamination in evolving nations, advanced nations furthermore preserve on strive with contamination issues. For instance, in the most current report about water quality in the United States, 44 percent of evaluated stream miles, 64 percent of surveyed lake sections of land, and 30 percent of evaluated bayous and estuarine square miles were delegated polluted [28]. As indicated by the European Community (EC), not more than 1% of the earth's water is accessible for humanoid utilization and in excess of 1.2 billion populaces on the planet make sure no entrance to protect drinking water. In addition, with a regularly expanding total population, the circumstance is required to decline sooner rather than later, particularly in thickly populated or industrial regions. These zones consume huge amount fresh water, and in the meantime deliver and discharge a lot of waste water into the environmental.

Water contamination is generally very much characterized as any chemical, physical or natural change in water quality that adversely influences dynamic living beings. In the several feel, contamination can be characterized by means of the exchange of several materials toward the environment. Nevertheless, there is a resistance confine aimed at every contaminant, meanwhile zero-level contamination is financially and technically impractical. The greatest critical sorts of water characteristic decay are the accompanying.

- Thermal contamination
- Biological contamination by oxygen-demanding wastes
- Contamination by determined organic chemicals (POPs)
- Eutrophication by nitrates and phosphorus
- Toxic pollutants

In Table 2.1, the direct delivery of the most significant contaminates inside water are displayed in relationship with the relating principle manufacturing source. Aimed at reasons for examination, it is valuable now to review that street transportation and explosion establishments, fundamentally of the vigor area, are the greatest vital sources of air contaminates. On account of water forms, it is apparent that farming and the metal manufacturing, in addition to the exercises in the generation of not organic chemicals and manures, comprise the main real polluters.

Table 2.1. The arrivals of the fundamental contaminants charged straightforwardly to water in the industrial area in Europe 2001 [29].

Compound	t/yr	Main source
Phenols	1,419,344	Basic inorganic chemicals or fertilizers (47%)
Total organic carbon (TOC)	246,524	Industrial plants for pulp from timber or other fibrous materials, and paper or board production(70%)
Nitrogen	22,317	Basic inorganic chemicals or fertilizers (29%)
Phosphorus	1662	Basic inorganic chemicals or fertilizers (25%)
Chromium (Cr)	864	Metal industry (87%)
BTEX	82.5	Basic organic chemicals (56.1%)
Nickel (Ni)	71.5	Metal industry (45%)
Copper (Cu)	45.8	Metal industry (23%)
Lead (Pb)	41.7	Metal industry (40%)
Cadmium (Cd(II))	8.1	Metal industry (74%) hydrocarbons
Arsenic (As(II))	5.1	Metal industry (22%)
Mercury (Hg(II))	0.5	Metal industry (23%)
Polycyclic aromatics	1 0 . 3	Metal industry (74%) hydrocarbons

2.2. Heavy Metal Pollution in Waters

Acids/bases, metals and nonmetals discharged by characteristic of people exercises seriously decay water feature, meanwhile they are harmful even at consolidation of effort of (ppm). It must be noticed that heavy metals are intensely hazardous for human health and safety and water lifetime. In any case, what is more regrettable is that there is no cycle

of normal treatment of these materials. Unavoidably, heavy metals stay in place in the environment, and lastly they are collected in the food series (bioaccumulation). If it has been made the correct course of move, issues related with both characteristic of water will be experienced, even in districts that appear to have adequate measures of fresh water nowadays. Afterward the conflicts and wars on the ownership of oil before, water might be the following clash region among contiguous nations, even in Europe. 20% of totally superficial water in the European Union is genuinely undermined with contamination according to the EC. Besides, water is a long way from existence uniformly conveyed in Europe and this is one noteworthy explanation behind exchequer issues [30].

2.3. Heavy Metal Toxicities

The toxic heavy metals include mercury, copper, chromium, nickel, lead, zinc, and cadmium trigger serious effects on the aquatic environment, both humans and animals [31]. Metals and their "free radicals" are exceedingly receptive assaulting other cellular structures. The capacity of metals to upset the capacity of vital biological molecules, for example, enzyme, DNA and protein, is significant reason for their toxicity. Dislocation of specific metals critical for cell by a comparative metal is adding reason of harmfulness [32].

2.3.1. Cupper (Cu^{2+})

Cu(II) is amongst heavy metals found in city and industrial waste waters. Cu(II) is especially harmful, complexion with enzymes and other metabolic agents associated with breathing and rendering them inactive. Furthermore Cu is an aggravation to skin creating tingling and dermatitis, and may bring about keratinization of the hand and soles of the feet [4]. However, it gets to be distinctly poisonous at high focuses [33]. If permitted to enter the environment, Cu(II) can bring about genuine potential health problems. Indeed, even at low focuses, Cu(II) might be dangerous to people [34]. Moreover, binding of Cu(II) to aromatic amino acid remnant from enzyme molecules, could be trigger oxidative destruction of proteins by introduction of oxidative strain related with the manufacturing reactive oxygen kinds include superoxide radicals or hydroxyl [35].

2.3.2 Cadmium (Cd^{2+})

Cd(II) has been revelation experienced in color industries, metal plating, a few plastics, and batteries. Cd(II) contamination can bring about noteworthy humanoid contact to Cd (II) through the ingestion of polluted fodder, particularly grains, cereals, and verdant vegetables. Acute high-dose exposures can bring about serious respiratory disturbance. Word related levels of Cd(II) presentation are a hazard feature for constant lung malady and testicular degeneration and are still under scrutiny as a hazard figure for prostate cancer [36, 37]. Cd(II) is application for a long time utilized as a part of different industrial exercises. The main industrial utilizations of Cd(II) incorporate the generation of alloys, colors, and batteries [38]. Despite the fact that the utilization of Cd(II) in batteries has indicated significant development as of late, its business utilize has declined in developed nations because of environmental working. In the United States such as, the day by day Cd (II) admission is around ($0.4\mu\text{g/kg/day}$), not as much as partial of the U.S. EPA's oral reference dosage [28]. This decrease has been connected to the presentation of rigid waste bounds in the coat with metallic material works and, all the greater as of late, to the presentation of commonly limitations on Cd utilization in specific nations.

2.4. Adsorption

Adsorption is a standout amongst the most proficient strategies for remove heavy metal particles from wastewater. This procedure likewise gives an alluring option treatment, particularly if the biosorbent is inexpensive and promptly accessible [39]. The bond of atoms, particles, and molecules from a gas, fluid, or broke down strong to a surface is defined the adsorption [40]. Adsorption is a surface-based process while absorption consists of the entire size of the substantial. Adsorption is by and large favored technique to dispose of environmental contamination due to relatively low price and simplicity of the procedure. In adsorption procedures, the contaminants are exchanged starting with one medium then onto the next at which they are focused. In the treatment of wastewater, activated carbon, clay minerals, metals, organic and inorganic films are for the most part utilized as adsorbents. Among these adsorbents, utilization of mud minerals particularly Na-montmorillonites as sorbents to eliminate pollutants has been progressively focused on due to they are less expensive than different materials, for example, actuated

carbon. Muds are broadly connected in abundant fields of science and technology to instance, the evacuation of fluid contaminates and cleansing of gasses such a wide helpfulness of muds is a consequence of their high particular surface range, high chemical steadiness, and an assortment of surface and operational possessions. The chemical nature and pore construction for the most part decide the sorption capacity of mud. Because of the presence of lasting positive and negative charges on their planar superficial, big particular superficial region, the swelling proprietary and big cation exchange capacity (CEC), these materials have extraordinary adsorption proprietary [41].

By way of deliberated before, adsorption has risen out as compelling, inexpensive and eco-friendly treatment method. It is a procedure sufficiently powerful to satisfy water recycles commitment and high emanating guidelines in the productions. Essentially a mass exchange operation by which a entity is exchanged in the fluid stage for the surface of a hard is adsorption, and gets to be distinctly bound by physical as well as synthetic associations [42]. It is a partition procedure in which couples of parts of the fluid stage are moved to the external of the strong adsorbents. All adsorption techniques are dependent on strong fluid equilibrium and on mass exchange rates. The adsorption methodology can be batch, semi-bunch and ceaseless. At atomic level, adsorption is predominantly because of alluring interfaces between a surface and the gathering being ingested. Contingent on the sorts of intermolecular appealing powers adsorption could be of taking after sorts:

2.4.1. Physical Adsorption

Physical adsorption is an overall occurrence and happens in every strong/fluid or strong/gas system. It is a procedure in which official of adsorbate on the adsorbent surface is brought on by Van der Waals strengths of fascination. Van der Waals powers start from the communications between initiated, constant or transient electric dipoles. Commercial adsorbents use physical adsorption for its surface binding. The procedure of physisorption could be routinely turned by warming or reducing the physical drive of the adsorbate (as on account of gasses) in light of the fact that the forces of fascination are not solid [43, 44].

2.4.2. Chemical Adsorption

Chemical adsorption is a kind of adsorption which incorporates a chemical reaction between the adsorbent and the adsorbate. Substance adsorption is in like manner eluded as instituted adsorption. The adsorbate can shape a monolayer. It is utilized as a part of reactant operations. Inside mass trade by pore spreading from outer surface of adsorbent to the inner surface of permeable structure. Adsorbate of adsorption the dynamic goals of the pores of adsorbent. The general ratio of adsorption is picked by either film improvement or intra particle dispersal or both as the last walk of adsorption are quick when stood out from the remaining two phases. The disposal of substantial metals by using insignificant exertion adsorbent is seen to be moreover consoling in extended terms as there are a couple of materials existing locally and plentifully, for instance, common materials, green wastes or mechanical by-things which can be utilized as straightforwardness adsorbents [45]. Models are used to depict and sum up exploratory adsorption information. Nevertheless, in using adsorption models for interpretative Intention, it is well to examine the advice that the adherence of trial adsorption data to a particular adsorption condition gives no proof of the genuine instrument of an adsorption system. The Freundlich and Langmuir conditions have truly been used, and are so far being used, by authorities in many fields. Surface complexation models have starting late ended up being by and large used as a piece of various logical orders. Each one of these models either unequivocally or certainly summons the mass movement law; in this manner, these models are actually related [46]. The examination of the adsorption equilibrium begins with the order of the isotherms. This arrangement is basic for the displaying of adsorption wonders and for different practical reasons.

2.5. Calculations and Kinetic Procedure

The harmony, motor and thermodynamic outcomes are assumed as elements of adsorbed metal particle focus at balance $C_{ad,eq}$; mg/L, adsorbed metal particle amount per gram of chitin and unabsorbed metal particle fixation in arrangement in the balance, individually q_{eq} ; mg/g, C_{eq} ; mg/L gotten from the incline of q against time (min) plot at $t=0$. Ad%; characterized as the proportion of adsorbed amount of Cd(II) and Cu(II) particle

per gram of the chitin at harmony to the underlying measure of metal particle and figured from Eq. (2.1).

$$Ad\% = \frac{q_{eq}X}{C_o} 100 \quad (2.1)$$

Where X: is the chitin concentration (g/L).

In building up the methodology to get a system and potential ratio restricting stride, models active had been utilized to exam trial information [47-50]. The chitin is utilized. The impact of film dispersion on adsorption ratio could be thought to be not noteworthy from an all-around fomented clump framework. Hence, measured fixations are equivalent for cell superficial focuses.

Of the exploratory information, it is demonstrate that the underlying adsorption ratio is relative for the principal energy to the underlying metal particle focus at decrease mass metal particle fixations and at bigger metal particle focuses, the degree ends up noticeably autonomous of introductory metal particle focus. It could be utilized to depict the ratio of the adsorption precisely in the together of these circumstances. This ideal forecasts the adsorption conduct over the entire considered fixation scope of metal particle and was from concurrence with an adsorption system being the ratio ruling stride [51, 52]. The temperature reliance of the particular adsorption response ratio steady k_1 could be related by a condition of the sort;

$$k_1 = A_o \exp\left(\frac{-E_a}{RT}\right) \quad (2.2)$$

Eq. (2.2) recognized as the Arrhenius condition, A_o consist of recurrence calculate, E consist of initiation vitality at sorption. At the point at that time $\ln k_1$ was plotted against $1/T$, a conventional line with slant $-EA/R$ is gotten. The extent of actuation vitality may give a thought regarding the sort the sorption. Adsorption happens by two distinct procedures; chemisorption and physical adsorption. Physical adsorption is like buildup. The warmth of adsorption is generally little, existence on the request of 4.2 kJ mol^{-1} . The powers of fascination among the atoms and the strong superficial are week. From chemisorption the adsorbed atoms are hung at first glance by valence constrains so the

enactment vitality for concoction adsorption is of an indistinguishable size from the warmth of compound responses. Two sorts of chemisorption are experienced, enacted and non-activated. Initiated synthetic adsorption implies that the rate changes with temperature as indicated by the limited actuation vitality from Arrhenius condition $8.4-83.7 \text{ kJ mol}^{-1}$. Nonetheless, in a few frameworks chemisorption happens quickly, proposing the initiation vitality is close to zero. This is named non-activated chemisorption [49].

2.5.1. Equilibrium Parameters of Adsorption

Freundlich, Langmuir and Tempkin isotherms model of adsorption could be applied to explain in speech the equilibrium among heavy metal in solution and adsorbed metal. An isotherm adsorption is distinguish with sure constant worth, which precise the superficial possessions and nearly of the adsorbent.

2.5.1.1. Langmuir Isotherm

In Langmuir isotherm, numerous visible feature of the adsorption mechanism were presumed in the derivation. The assumptions most importance is;

- (a) has the same activity for adsorption all the surface of the catalyst,
- (b) there is no interplay between adsorption occurs and adsorbed molecules with the alike system [49].

Langmuir model as given below is legal the adsorption monolayer to a superficial with a limited several of equal locations. The expression of the Langmuir model is given by Eq. (2.3)

$$q_{eq} = \frac{q_{max} KC_{eq}}{1 + KC_{eq}} \quad (2.3)$$

where K is the adsorption equilibrium constant containing the nearly of binding location, q_{eq} and C_{eq} are adsorbed metal ions on the sorbent at equilibrium and unadsorbed metal ions in solution, respectively. q_{max} is the highest quantity of metal ion for each unit weight of adsorbent to in a complex monolayer on the surficial mg/g. characterizes a applied

determine adsorption capability while the surficial is completely hidden by heavy metal. $q_{\max}$ and K could be limited at the linear plot of (C_{eq}/q_{eq}) against C_{eq} . [53,49].

2.5.1.2. Freundlich Isotherm

Freundlich isotherm equation intended for perfect adsorptions on heterogeneous and polluted solid surfaces, and it is a semi-experimental equation. The experimental Freundlich equation based on sorption on a heterogeneous superficial is given by Eq. (2.4)

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2.4)$$

where K_f and n are the Freundlich constants correlated to the adsorption capability and adsorption density of the sorbent, correspondingly. The Freundlich equation can be linearized by constants and taking logarithms can be determined [54- 56].

2.5.1.3. Tempkin Isotherms

Tempkin isotherms is linearly represented as Eq. (2.5) and usually used in this form:

$$q_s = B \ln A + B \ln C_s \quad (2.5)$$

where A and B are the Tempkin isotherm constant (L/g) and heat of sorption (J/mol) respectively. B is the Tepmkin isotherm constant linked to the energy parameter, R is the gas constant (J/mol/k), B , as put on display on equation:

$$b = RT/B \quad (4) \quad (2.6)$$

T the absolute temperature in kelvin (K).

2.5.2. External Mass Transfer Model

The film dissemination outside mass exchange is a crucial rate-controlling stride and limit model was utilized as a part of this thesis (Eq. 3). As per this model, the adjustment in color focus regarding time is identified with the liquid–solid mass exchange coefficient (outside mass exchange coefficient) k_L . [57, 58].

$$\frac{dC}{dt} = -k_L S(C - C_s) \quad (2.7)$$

where C is the fluid stage solute convergence of color at once t , C_s the fluid stage solute focus at the molecular surface; and S the particular surface range for mass exchange. With these suspicions Eq.(2.8) can be streamlined as

$$\frac{d(C/C_o)}{dt} = -k_L S \quad (2.8)$$

Accepting the adsorbent particles are round, S is ascertained from Eq. (2.9);

$$S = \frac{6X}{d_p \rho_p} \quad (2.9)$$

D_p the normal molecule breadth and ρ_p is the thickness of the sorbent where X is the sorbent fixation in the arrangement. By considering C/C_o against t , the estimation of k_L might be resolved from the incline at $t=0$.

2.5.2.1. Intraparticle Mass Transfer Diffusion Model

In the Intraparticle Mass Transfer Diffusion Model, the ratio of intraparticle dispersion is a component of $t^{0.5}$ and can be contributed by the accompanying condition [59,60].

$$q = f\left(\frac{Dt}{r_p^2}\right)^{0.5} = Kt^{0.5} \quad (2.10)$$

where r_p is the molecule sweep, D the powerful diffusivity of solutes inside the molecule, and K is the intraparticle dissemination steady. In another way, some different

components alongside intraparticle dispersion are likewise included. K qualities can be dictated by linearizing the bend $q=f(t^{0.5})$.

2.6. Kinetic Modeling

The analyses of adsorption kinetics describe the adsorbate take-up ratio and clearly this rate controls the habitation time of adsorbate at the strong/fluid interface[61]. Kinetic models have been proposed to elucidate the mechanism. In order to examine the mechanism of heavy metals adsorption onto chitin, pseudo-first order and pseudo-second order model were considered.

2.6.1. The Pseudo-First Order Model

The pseudo-first order equation is commonly expressed as:

$$\frac{dq}{dt} = k_1(q_{eq} - q) \quad (2.11)$$

Where k_1 is the constant rate of pseudo-first order sorption (min^{-1}). Merge this equation for border conditions

$$\log(q_{eq} - q) = \log(q_{eq}) - \frac{k_1}{2.303} t \quad (2.12)$$

A plot of $\log(q_{eq}-q)$ opposite of t must give a linear relation with the slope of $K_1/2.303$ and intercept of $(\log q_{eq})$. Though the principles of $\log(q_{eq}-q)$ are linearly related with t , the plot of $\log(q_{eq}-q)$ in compared with t will give a linear connection from which (k_1) and (q_{eq}) can be compelled from the slope and intercept of the graph, respectively.

2.6.2. The Pseudo- Second Order Model

The pseudo-second order equation which is expressed as:

$$\frac{dq}{dt} = k_2(q_{eq} - q)^2 \quad (2.13)$$

Where K_2 is the rate constant of pseudo-second order sorption's ($\text{g mg}^{-1} \text{ min}^{-1}$). For the Like boundary situations the integrated form of Eq (2.5) becomes.

If second order kinetic equation is useful, the plot of t/q against t of Eq. (2.6) must give a linear connection. The and k_2 , q_{eq} can be driven from the slope and intercept of the plot. This kinetic model articulates the response on the surface named.

Where the subscripts 'exp' and 'cal' show the experimental and calculated values, repectively and N is the number of data points [62].

$$SD(\%) = 100 \times \sqrt{\frac{\sum ((q_{t,\text{exp}} - q_{t,\text{cal}}) / q_{t,\text{exp}})^2}{N - 1}} \quad (2.14)$$

2.7. Adsorption Thermodynamic

In engineering exercise thermodynamics of adsorption, both the ΔG° factors and entropy must be measured so as to drive whether it will happen instinctively. Thermodynamic parameters, for example, ΔH° , the ΔG° and ΔS° can be supposed using temperature with equilibrium constants change. ΔG° of the adsorption response are given by the following Eq. (2.15)

$$\Delta G^\circ = -R.T.\ln K \quad (2.15)$$

Where R is the ideal gas constant [8.314 J/mol K] and T is the absolute kelvin (K) temperature [56, 63].

The equilibrium constant may be uttered in terms of enthalpy alter of adsorption as a meaning of temperature as follows:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (2.16)$$

In the Eq. (2.16), the temperature effect on the equilibrium constant (K) is persistent by the evidence of ΔH° . Thus when ΔH° is positive, i.e., when the adsorption is endothermic and growth in T results in a growth in K .

The change with temperature of the free energy change and the equilibrium constant can be characterized as follows

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (2.17)$$

Eq. (2.17) can be written as:

$$-RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ} \quad (2.18)$$

or

$$\ln K = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (2.19)$$

where values of ΔH° and ΔS° can be determined from the slope and the intercept of the plot between $\ln K$ versus $1/T$ [56].

2.8. Chitin

Chitin or (poly) β -(1 $\rightarrow$ 4)-N-acetyl-D-glucosamine is a polysaccharide renewable and biodegradable polymer, the second best bountiful normal polymer later cellulose most important, first discovered in the 1884 (Fig 2.1). Biopolymers are synthesized by colossal numeral of active organisms and it belongs to the most plentiful normal polymers, cellulose after. In the state native, happen chitin as well-ordered microfibrils crystalline which form skeletal constituents in the exoskeleton of arthropods, protozoa/fungi on the walls, and yeast nematodes are a lot pathogens in other sorts [64,65,50,66]. Chitin ((C₈H₁₃O₅N)_n) is a chain-long polymer of an N-acetylglucosamine, a derivative of glucose, and is bring into being in several places all through the nature globe. It is a distinctive constituent of fungi the cell walls, the exoskeletons of arthropods like crustaceans (such as lobsters, shrimps and crabs) and insects, the beaks and the radulae of mollusks, and internal shells of cephalopods, including octopuses and squid and on the scales and lissam phibians other soft tissues of fish [67]. The chitin structure is worthy of comparison to the polysaccharide cellulose, creating crystalline nanofibrils or whiskers. In terms of role, it may be compared to the protein keratin. Chitin has proven useful for a number of industrial, medicinal and biotechnological aim therefore chitin can be used in wastewater

cure for the removal of heavy metal ions. Chitin have most important one of them it is ability to remove metal ions from wastewater.

Chitin can be used in some industry processes for examples of the hidden uses of chemically altered chitin in food processing like the forming of edible films and as an additive to thicken and stabilize foods [68]. Chitin in the systems to size and strengthen paper employ [69,70] have been used chitin and chitosan by academic research sets to create scaffoldings in investigated of how tissue develops and how wounds rectify, and in efforts to invent more excellent bandages, surgical thread, and materials to application in all transplantation [67]. Sutures made of chitin been explored for several years but as of 2015 none exist in the market; their lack of elasticity and difficulties application them to produce thread have prevented of marketing growth [65].

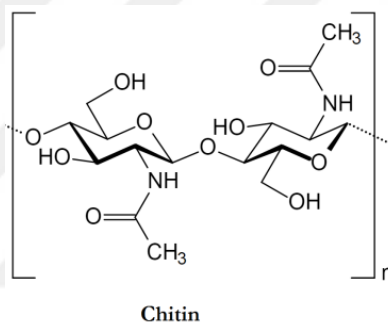


Figure 2.1. Chemical structure of chitin

2.9. Literature Review

Over whelming metals are on the forefront of scholarly and administrative stress; since a huge number of huge amounts of water hold harmful substantial metals are create yearly from various metals handling production and released to nature. Metals released into water bodies are not biodegraded but rather experiences substance or microbial finish change, creating huge impact on the earth and general constitution. Respectively, expanding mindfulness is quickly becoming over general and one of the branches of it is treatment and expulsion of overwhelming metals from such effluents as far as possible before releasing into normal streams and waters [32].

Kamal Rana et al. [71], studied that adsorption execution of Cu(II) outside of drainage has been inspected in view of this paper utilizing bagasse. Cu(II) is amazingly poisonous metal particle and seen as a compromise contaminant liberated from various synthetic businesses incorporate battery fabricate, refining, electroplating blending exercises, and so forth. In the existing paper, the test comes about done in clump adsorption prepare utilizing safeguarded bagasse with manufactured examples prepared in lab were given. It was discovered that the adsorption data were fitted strong in Langmuir isotherm. The Langmuir adsorption capacity was assumed at 4.75 mg/g for Bagasse. The greatest removal of Cu(II) is over 93% at pH 5 in 100 ppm Cu(II) concentration.

Aydin et al., [72], has considered Cu(II) removal from wastewater by low-estimated adsorbents. The use of cheap adsorbents was inspected as a swap for present day costly strategies for expelling metals from fluid arrangement. Cu(II) removal outside of waste by different adsorbents like as covering of grain, lentil, and rice was inspected. The balance adsorption adjusted was obtained as an element of the arrangement pH, beginning adsorbate focus, adsorbent measurements, contact time, and temperature. Adsorption isotherms of Cu(II) on adsorbents were obtained and associated with shared isotherm conditions incorporate Langmuir and Freundlich models. The thermodynamic parameters, ΔG° , ΔH° and ΔS° for the adsorption of Cu(II) was ascertain to figure the way of adsorption system. The energy and the components regulating the adsorption procedure were additionally deliberate. Regionally pertinent adsorbents were observed to be low-valued and assuring for the removal of Cu(II) from wastewater.

Shaliza et al. [73], show that the adsorption procedure is in effect broadly utilized by various scientists for the removal of substantial metals from wastewater and activated carbon has been by and large used as an adsorbent. The objective of this review is to provide in the scan for less exorbitant adsorbents and their utilization potential for different agrarian waste side effects like, sugarcane bagasse, oil palm shell, coconut shell, coconut, husk rice husk, and so forth for the end of substantial metals from wastewater. At an adsorbent dosage of 0.8 g/50 mL is sufficient to evacuate 80–100 percent Cr(VI) from watery arrangement having an underlying metal grouping of 20 mg/L at a pH estimation of 1. The most extreme removal acquired 99.8 percent at pH 2. The information for adsorbents fit well to the Freundlich isotherm.

The Co(II) sorption of two fleece powders was considered using its radioisotope ^{57}Co ($T_{1/2}=271.8$ days and $\gamma=122.1$ and 136.5 keV) as a tracer. The impacts of kind cushion,

the connection time, the pH esteem, the underlying convergence of Co(II) on the sorption lead of fleece powders, Co(II) liberating aptitude of fleece powders and the re-utilization of fleece powders were explored. In this learned at pH 8 in phosphate support and pH 10 in ammonium sulfate cushion found. The ideal sorption of Co(II) by the powders happened. Fourier-change infrared spectroscopy (FTIR) was utilized to concentration the modifications in chemical construction of the fleece after presentation to both cushion arrangements. Contrasted with the untreated fleece fiber, the fine fleece powders displayed expedient sorption extent and awesome sorption capacity for Co(II). Co(II) particles were recuperated in the wake of uncovering the Co(II) stacked fleece to HCl (0.1 M) and cushion at pH 3-7 (glycine/sodium chloride). Subsequent to liberating Co(II) particles from fleece powders, the ability of fleece powders re-used to sorb Co(II) was 80 percent of that of the new fleece powders. It is objective from this examination that fleece powder can be utilized as an adroit sorbent to evacuate and discharge Co(II) from solution [74].

Reynel et al. [75], show that utilizing chicken quills evacuation of Cd (II) from fluid arrangements. The goal of this review was to evaluate the take-up of Cd (II) from watery arrangements by chicken plumes in a clump framework. In this paper energy, the isotherms, and thermodynamics of Cd(II) sorption by this fowl waste were prevailing. The impacts of introductory metal focus, pH, contact time, and temperature on sorption were contemplated. Adsorption information was fitted in the direction of various motor and harmony sorption models. Decided optimum circumstances for Cd(II) particle adsorption by utilizing chicken quills have been perceive. For the tried situations, the Cd(II) take-up capacity of this waste gone from 0.86 to 4.61 mg/g. In succinct, the outcomes exhibit that chicken quills are another sorbent for the treatment of effluents pollute by Cd(II) particles.

Nacar Kocer et al. [66], studied adsorption of zinc(II) particles by chitin. Results showed that the capacity of Zn(II) particles to adsorb onto chitin was explored in this study utilizing a group procedure. It was watched that the underlying pH value of the watery arrangement, the temperature and the underlying Zn(II) particle fixation all showed an extensive impact on the adsorption limit of the sorbent. The ideal pH esteem was obtained as 4.5. It was found that, for introductory Zn(II) particle focuses up to 300 g/L, adsorption expanded with temperature up to 40 °C. The Langmuir and Freundlich adsorption models were connected to the harmony information acquired for the adsorption of Zn(II) particles onto the sorbent. The outcomes got demonstrated that the information for the adsorption procedure was better fitted by the Langmuir show over the fixation range and temperatures

considered. The pseudo-first-order and pseudo-second-order dynamic models were utilized to dissect the test information, with the outcomes acquired showing that the pseudo-second-order condition gave the better connection to the adsorption information.

Douglas et al. [76], reported that take-up of Cu(II) particles from fluid arrangement by soybean frames. Their objective was to concentrate the ability of expelling Cu(II) particles from CuCl₂ arrangement utilizing soybean bodies. The study was separated into two offers. In the initial segment, soybean frames were changed with citrus extract by arrange the soybean structures first in 0.1N NaOH and after that in 0.6 M citrus extract. Around then they have decided an opportunity to warm the changed soybean structures. In other piece of the concentrated the element influencing Cu particle take-up by utilizing soybean bodies were resolved as pH of the arrangement and introductory fixation, proportion of soybean structures to Cu chloride focus in arrangement and size of the soybean frames. The aftereffects of the examined they have chosen that the ideal conditions at an underlying arrangement pH of 4.8 for warming were an hour and a half. The soybean structures proportion to arrangement comprise of ten grams for each 1 liter. The soybean structures size was 602 micrometers and the underlying convergence of Cu chloride arrangement was 50 ppm. The Cu particle removal capacity utilizing soybean frames was 97.68 percent under these circumstances and the centralization of Cu particle has been decreased beneath the modern standard of 2.0 mg/L.

Uslu et al. [77], show that bioaccumulation of copper(II), lead(II) and chromium(VI) by developing *Aspergillus niger*, from fluid arrangement was researched. Metal bioaccumulation was reliant on the pH and starting metal particle focus. Albeit, all convergences of copper(II), lead(II) and chromium(VI) particles brought about restraint of the development of the microorganism, it was exceedingly impervious to Cu(II) lead(II) and could collect these metal particles at exceptional returns. The present study demonstrated that *A. niger* gives off an impression of being valuable as a living biosorbent for expelling overwhelming metal particles from wastewaters. A more entire review ought to be performed on the agent parameters, for example, temperature, biomass fixation, unsettling, and so on.

Sheffield et al. [78], has considered adsorption of Cu(II) particles by fleece. The removal of Cu(II) onto fleece from wastewater of Cu(II) sulfate was inspected as a task of cure time and temperature, measure of Cu(II) particles utilized, and pH. They set up that more extended warming circumstances and higher temperatures prompt expanded

adsorption: one hour close to the bubbling temperature gave ideal outcomes. Raising the measure of utilized Cu(II) particles expanded the aggregate adsorption, however, the piece of utilized Cu(II) particles brought up diminished with the sum utilized. As pH was expanded, Cu(II) adsorption expanded directly with pH up to a pH of almost 6; above pH 6, strong Cu salts were rush. The attainability of specific cradle intruding with Cu^{2+} adsorption was discussion over with another.



3. MATERIALS AND METHODS

3.1. Adsorbent

Chitin from smashed crab shells (Sigma–Aldrich Co., Ltd., Dorset, U.K.) was utilized to expel substantial metal arrangement from wastewater in this study. The shells were filtered to isolate the material into distinct molecule estimate ranges. Past studies demonstrated that the 147–300 μm molecule measure extends gives an appropriate size to adsorption tests.

3.2. (BET) Surface Area

Surface area is identified with the adsorption limit of an adsorbent. The BET covering region was resolved at nitrogen isotherms utilizing a Micromeritics Flow Sorb (II-2300) Superficial Part Analyzer. The deliberate BET surface area for chitin was $6.667\text{ m}^2\text{ g}^{-1}$.

3.3. Chemicals

The test solutions single and binary Cu(II) and Cd(II) ions were prepared by dissolving 1 g/L of stock solution of Cu(II) and Cd(II) to the desired concentrations. Stock solution of Cu(II) and Cd(II) were obtained by dissolving or dissolving exact quantities of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in 1 g/L of double-distilled water, respectively. The pH of the each solution was adjusted to the required value with the addition of dilute or concentrated HNO_3 and NaOH solutions before mixing with the chitin. Since negligible changes in the final equilibrium pH were observed during this procedure, the uptake pH was assumed to remain constant during the adsorption experiments.

3.4. Heavy Metal Analysis

Cu(II) and Cd(II) analysis in the solutions were made by using Perkin Elmer Analyst 800 model atomic absorption spectrophotometer.

3.5. Batch Adsorption Experiments

The factors that affect the adsorption uptake capacity of the adsorbent were examined in a batch system. Single cadmium(II) and copper(II) ions and binary cadmium(II)–copper(II) ions adsorption studies were performed at various initial concentrations, adsorbent dosage, pH and temperatures at constant 150 rpm shaking glass flasks of 0.25 L containing of 0.15 L metal ion solution at desired concentration including 0.5 g chitin using a rotabit shaker from Selecta. Samples of 5 mL were taken before mixing the adsorbent solution and single cadmium(II)/copper(II) ions and binary cadmium (II)/copper(II) ions bearing solution, at 5 min intervals at the beginning of adsorption and 15–30 min intervals after reaching. Before analysis, samples were filtered by using blue type whatman filter paper and supernatant fluid was analyzed for the remaining metal ions. During the biosorption studies the pH values were measured at the different interval and it was observed that the pH of the medium changed a bit, the difference was always less than 0.5 pH degree for single and binary metal ions, so pH change did not cause metal ion precipitation. All the experiments were carried out in duplicates and average values were used for further calculations.

4. RESULTS AND DISCUSSION

Concurrent adsorption of Cu^{+2} and Cd^{+2} by chitin was examined and adsorption of single and binary metal ion onto chitin was studied as a connected to pH, temperature and initial metal concentration.

4.1. Single Cu (II) and Cd (II) Adsorption onto Chitin

4.1.1. Effect of Contact Time

An important parameter is Contact time because this factor determines the adsorption kinetics of an adsorbate at a given initial concentration of the adsorbate. The effect of contact time on the Cd(II) and Cu(II) ions adsorption onto chitin was investigated for 120 min. Fig. 4.1 and Fig 4.2 displays the adsorption of Cu(II) and Cd(II) onto chitin as a meaning of the time of contact at 40 °C. The adsorption ability increased with increasing contact time and a greater amount of Cu(II) and Cd(II) were removed by chitin at first 15 min of the time of contact. The equilibrium was established in 30–60 min at the end of a rapid adsorption for all temperatures investigated. After an equilibrium time of 120 min, no more Cd(II) was adsorbed. The adsorption of Cu(II) and Cd(II) were endothermic, by increasing temperature the range of adsorption is increased. The sorption of Cu(II) and Cd(II) ions by chitin may involve not only physical but also chemical sorption. This effect may be due to the fact that at greater temperatures an increase in active sites occurs due to bond rupture.

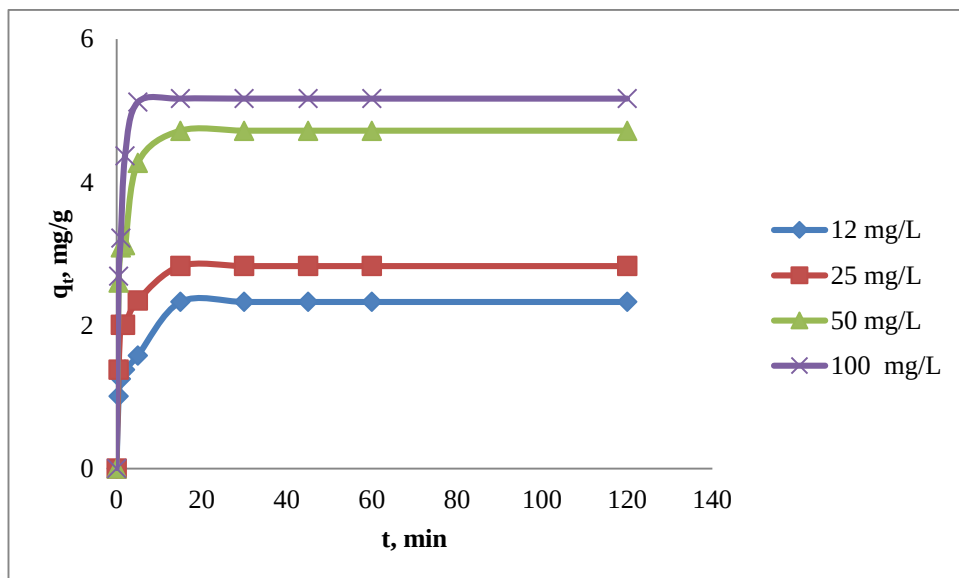


Figure 4.1. The influence of time of the adsorption of Cu(II) onto chitin in different initial Cu(II). (pH = 4.5, T = 40 °C, X₀ = 3.33 g/L, agitation rate = 150 rpm).

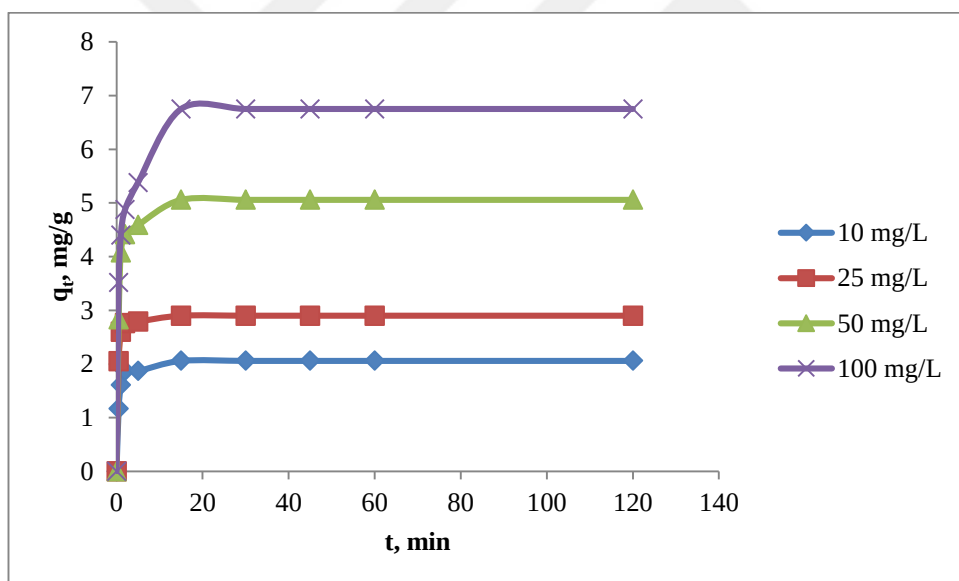


Figure 4.2. The influence of time of the adsorption of Cd(II) onto chitin in different initial Cd(II), (pH = 5, T = 40 °C, X₀ = 3.33 g/L, agitation rate = 150 rpm).

4.1.2. Effect of Initial pH on Cu (II) and Cd (II) Adsorption

Previous investigations have displayed that initial pH is a very important parameter in the treatment of heavy metals by sorbents. The influence of initial pH on the equilibrium uptake ability of chitin towards cadmium was examined over the pH range 3.5–5.5 for Cu(II) and Cd(II) employing an initial metal ion concentration of 100 mg/L and the difference of adsorption initial concentration by initial pH was given in Figure 4.3. The maximum adsorption capacity was get at pH= 4.5, and 5.0, for Cu(II) and Cd(II), respectively. An increase or decrease of the pH from these optimum pH resulted by a decrease in the adsorption of metal ions. Little adsorption acquired place to pH a smaller in the 3.5. Functional groups such as phosphate, amino groups and carboxyl was noticed to be accountable to adsorption of the heavy metals.

The variation of the equilibrium uptake of Cu(II) and Cd(II) with the initial pH value is depicted in Figure 4.3, which shows that the highest adsorption ability of chitin towards Cu(II) ions was 5.17 and 6.75 mg/g at a pH value of 4.5 and 5.0, respectively. The pH value chiefly influences the grade of ionization on metal ion and surface possessions of the chitin. This can be due to the construction of soluble hydroxyl ions. For Cu(II) and Cd(II), the start of the metal precipitation and hydrolysis begins in the pH>6. Such hydrolysis happen via the substitute of metal ligands in the internal co-ordination circle through hydroxyl groups later removal of the external hydration sphere.

Indeed, adsorption cannot be connected straight to the hydrolysis to the metal ion, but rather to the formation of the internal hydration sphere that precedes hydrolysis (Kocer at all, 2008). It was been advised that, at small pH worth, the cell ligands would be approximately correlate with H_3O^+ ions which would confine admission to the ligands with metal ions of consequence of offensive forces. The pH worth overhead the isoelectric point, the cell surface carries a net contradictory charge and ionic situation of ligands like carboxyl, amino groups and phosphate would be like that response by metal ions would be advanced, hence leading to a rapid binding efficiency. During this process, increases the hydrogen ion concentration if the pH value is low (< 3.5), leading to modest adsorption among H^+ ions and Cu(II) and Cd(II) ions.

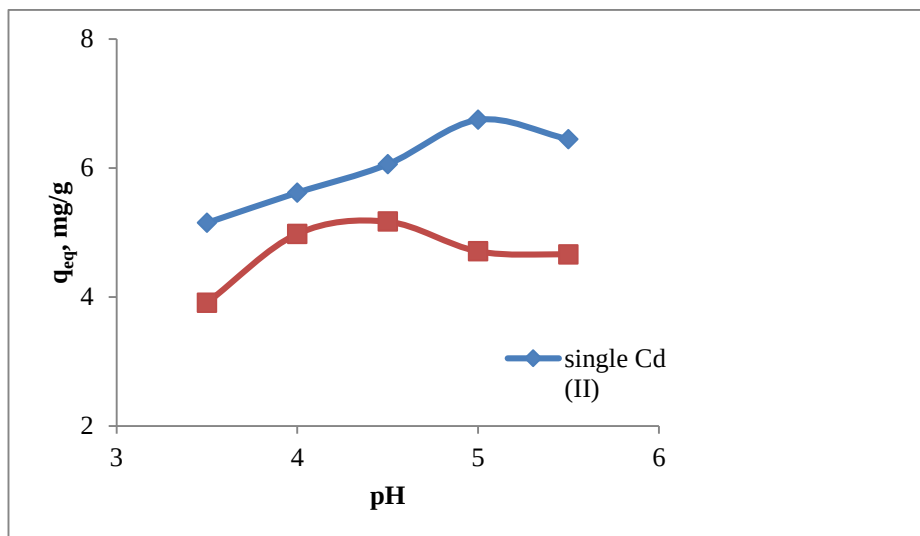


Figure 4.3. The effect of pH on the single Cu(II) and Cd(II) ions adsorption (C_o = 100 mg/L, pH= 4.5 for Cu(II), pH= 5 for Cd(II), X_o = 3.33 g/L, T = 40 °C, agitation rate= 150 rpm).

4.1.3. The Effect of Adsorbent Dosage

The effect of adsorbent dosage of effects on adsorption and equilibrium uptake is represented in Figure 4.4. The addition in adsorbent dosage since 0.1-1.0 g/L consequence in an rise at % 30.27-% 33 and %19.47-% 35.13 in adsorption of Cu(II) and Cd(II), respectively, in the 100 mg/L. Additional increase in adsorbent dosage did not reason important development in adsorption.

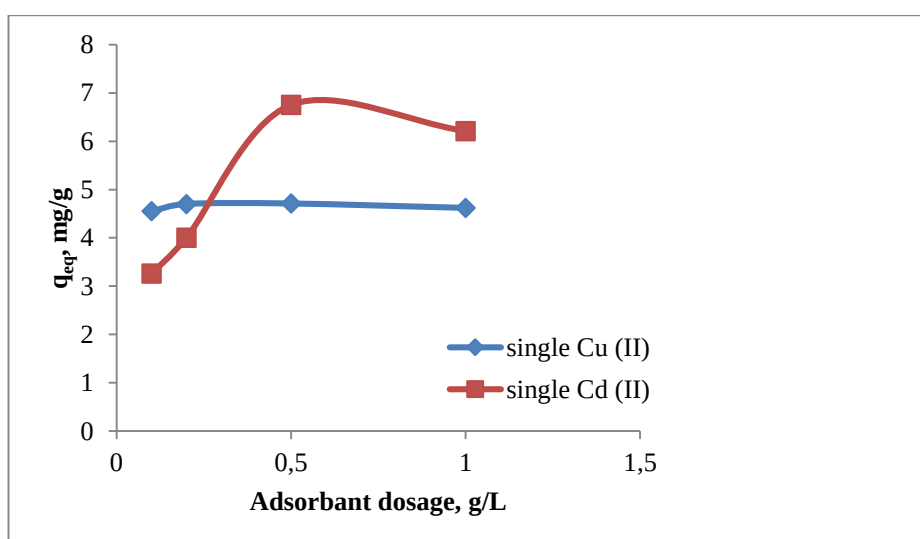


Figure 4.4. The Effect of adsorbent dosage and equilibrium uptake on the single Cu(II) and Cd(II) (C_o = 100 mg/L, T = 40 °C, pH= 4.5 for Cu and 5.0 for Cd, X_o = 3.33 g/L, agitation rate= 150 rpm).

4.1.4. The Influence of Initial Cu(II) and Cd(II) Concentration on Temperature Dependent Adsorption

Influence of initial Cu(II) and Cd(II) concentration is examined in the ratio 1-100 mg /L at 20, 30 and 40 °C. The equilibrium uptake of Cu(II) and Cd(II) ion was influenced with temperature and increased by increasing temperature up to 40 °C. This designates endothermic nature of the adsorption procedure. Figure 4.5 show that, the equilibrium sorption capability of the sorbent increased with an increase of initial Cu(II) and Cd(II) concentration up to 100 mg /L. Providing an significant driving force to overwhelmed altogether mass transfer resistance. The increase of loading capability of chitin with increasing initial Cu(II) and Cd(II) concentration may also be due to greater interplay among heavy metal and chitin. As chitin give a finite number of surface binding sites, Cu (II) and Cd(II) adsorption displayed a satiation trend at higher initial Cu(II) and Cd(II) concentration.

The equilibrium uptake concentration of Cu(II) and Cd(II) with chitin are also influenced by temperature. The effect of temperature on the equilibrium sorption capacity of chitin was also presented in Figure 4.5 and 4.6 for Cu(II) and Cd(II), respectively. It is indicate that Cu(II) concentration adsorption ability increased with a increase of teamperature from 20 to 40 °C. The maximum equilibrium uptake were determined as 35.71 to 43.6% for Cu(II) ion and 37.90 to 47.70% for Cd(II) at 100 mg /L initial metal ion concentration for 20 to 40 °C, respectively. Similar results were observed to Cd(II) and Cu(II) ion concentration yield adsorption of chitin and the adsorption yields increased by increasing temperature. The increase of the adsorption yield and adsorption capability at increased temperature showed that the sorption of heavy metal on chitin is in endothermic natural and may include not just physical but also chemical sorption. This influence can be ascribing to the expansion of whole size or formation of any new active sites on the adsorbent surface owing to bond breach.

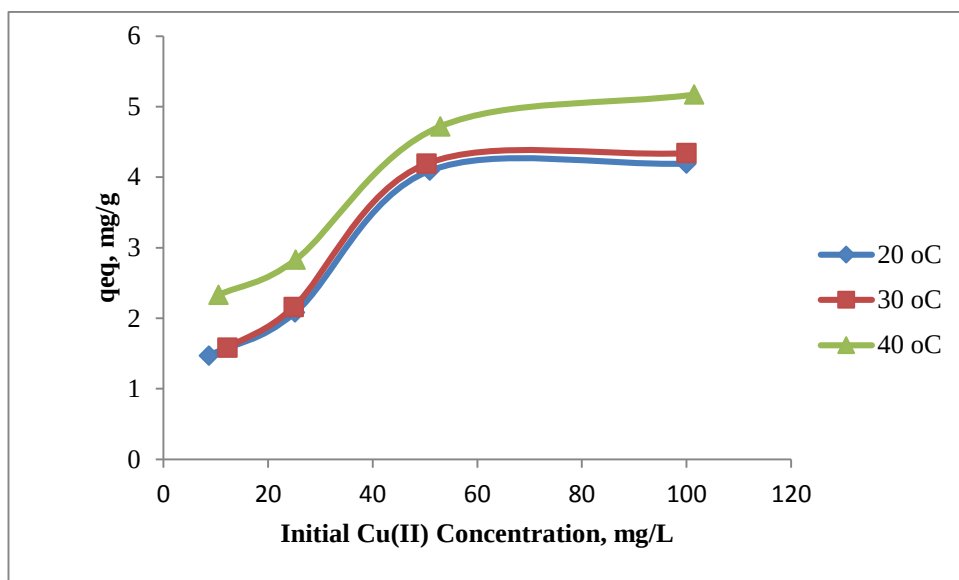


Figure 4.5. The influence of initial Cu(II) concentration on the adsorption (pH= 4.5, X_0 = 3.33 g/L, agitation rate= 150 rpm).

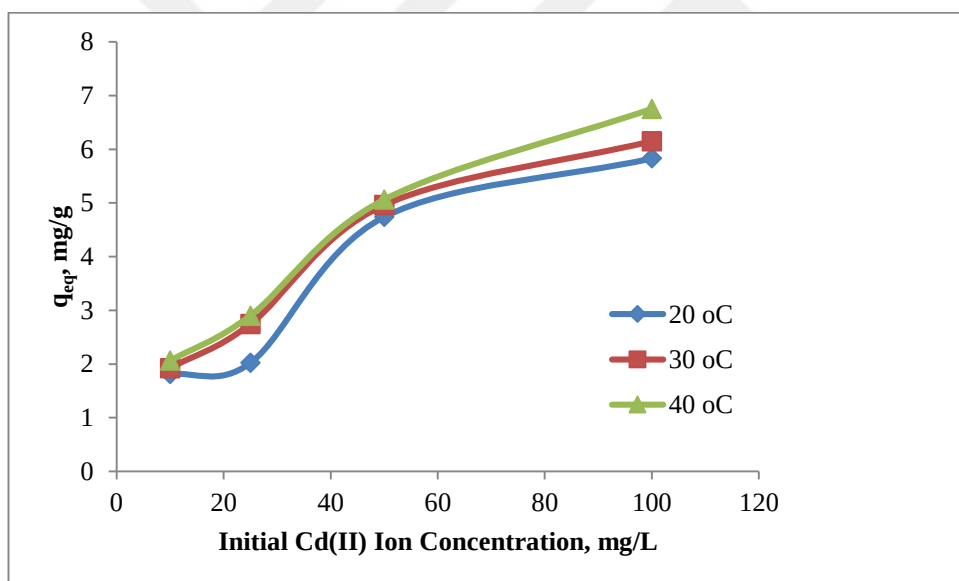


Figure 4.6. The effect of initial Cd(II) concentration on the adsorption (pH= 5, X_0 = 3.33 g/L, agitation rate= 150 rpm).

4.1.5. Equilibrium Modeling in Batch System at Different Temperatures

Adsorption isotherms are suitable for description of adsorbate distribution among the liquid and solid phases at equilibrium. Useful information such as adsorption mechanism, favorability of adsorption process as well as adsorbate affinity for adsorbent can be obtained. Investigation of equilibrium statistics is significant to growing an equation that

can be applied arrangement meaning. Freundlich, Langmuir and Tempkin adsorption isotherms was applied to express the sorption mechanism of Cu(II) and Cd(II) onto chitin. The Langmuir, Freundlich and Tempkin isotherm constant of adsorption of Cu(II) and Cd(II) obtained at temperatures of 20, 30 and 40 °C are given in Table 4.1. Table 4.1 presents the comparison of the calculated equilibrium parameters according to the isotherm models to Cu(II) and Cd(II) adsorption onto chitin. The Langmuir adsorption isotherm model assumed homogeneous binding sites on the adsorbent surface, equivalent sorption energies, and no interactions among the adsorbed species. Q^0 signifies the adsorption capacity while the surface is completely provided by cover with metal ions. The adsorption capability of chitin increased by increasing the temperature and highest Q^0 value determined as 5.80 mg/g for Cu(II) and 6.86 mg/g for Cd(II) at 40 °C. A highest K value displays the affinity to binding of metal ions. The maximum value of K is find at 40 °C to Cu(II) and Cd(II).

Table 4.1. Langmuir, Freundlich and Tempkin isotherm constants for single Cu(II) and Cd(II) adsorbed onto chitin.

Temperature	Langmuir			Freundlich			Tempkin		
	Cu(II)								
	Q°, mg/g	K, L/mg	R²	K _f , mg/g	n	R²	b _T , J/mol	A _T , L/g	R²
20	5.48	0.001	0.988	0.832	0.35	0.990	44.18	1.81	0.987
30	5.68	0.015	0.989	0.878	0.40	0.831	54.39	2.74	0.892
40	5.80	0.017	0.999	1.286	0.46	0.935	59.075	15.26	0.935
Cd(II)									
	Q°, mg/g	K, L/mg	R²	K _f , mg/g	n	R²	b _T , J/mol	A _T , L/g	R²
20	6.60	0.016	0.88	1.52	0.42	0.708	37.69	0.25	0.816
30	6.75	0.023	0.89	1.92	0.58	0.782	58.10	0.31	0.869
40	6.86	0.024	0.99	2.07	0.62	0.985	72.58	8.58	0.997

The calculated R_L value to the chitin-Cu(II) ions was in the series of 0 and 1, confirming that the Cu(II) adsorption onto chitin was agreeable. Comparing the K values it can be stated that the affinity of Cu(II) for the chitin was higher. The value of R_L shows the isotherm form to be unfavorable $R_L > 1$, favorable $0 < R_L < 1$ and irrevocable $R_L = 1$. The R_L values were >1 , which approve that the Cu(II) and Cd(II) adsorption onto chitin is disapproving below these situations application Langmuir isotherm to every temperature examined (Table 4.2). In addition, the R_L values of chitin followed the order of Cu(II) >

Cd(II), implying that the adsorption is more favorable to Cd(II) than Cu(II) ions. Moreover, the optimal adsorption temperatures for single Cu(II) and Cd(II) were 40 °C.

Table 4.2. The value of R_L of chitin for Cu(II) and Cd(II).

C_o , mg/L	R_L					
	Cu (II)			Cd (II)		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
10	0.086	0.070	0.070	0.061	0.061	0.051
25	0.047	0.044	0.040	0.032	0.033	0.025
50	0.028	0.026	0.022	0.018	0.018	0.014
100	0.015	0.013	0.012	0.009	0.009	0.007

However, the Freundlich isotherm model described the systems under discussion with insignificantly higher values of the determination coefficients. The Freundlich model assumed heterogenous surface of adsorbent and multilayer coverage of adsorbate as well as no well-defined adsorption limit and distribution of adsorption heat. From Table 4.1, it is find that the Freundlich coefficient n and Freundlich constant K_F increased by the increase from temperature. The values of K_F increased from 0.83 to 1.29 for Cu(II) and 1.52 to 2.07 for Cd(II) by increasing temperature from 20 to 40 °C. In all value was found high ample to adsorption >1.0 . Depending on the $1/n$ values obtained since the Freundlich isotherm, the adsorption can be classified as irreversible when $1/n$ is equal to 0 ($1/n = 0$), favorable when $1/n$ is higher than 0 but lower than 1 ($0 < 1/n < 1$) and unfavorable when $1/n$ is higher than 1 ($1/n > 1$).

The Tempkin isotherm assumed the linear logarithm decrease of adsorption heat with coverage while ignoring extremely low and high concentrations. It also established unchanging distribution of bonding energy up to any highest value [79, 80]. The values of b_T increased from 44.18 J/mol to 59.08 J/mol for Cu(II) and from 37.69 J/mol to 72.58 J/mol for Cd(II) with increasing temperature since 20 to 40 °C onto chitin. The A_T values related to the maximum binding energy were found to be 1.81 L/g to 15.26 L/g for Cu(II) and 1.81 L/g to 8.59 L/g for Cd(II) at 20 to 40 °C (Table 5.1).

In vision of the results obtainable in Table 4.1, the isotherms seemed to follow the Langmuir model extra closely than the further models at completely the temperatures investigated. Though, the Freundlich and Tempkin adsorption models also appear to acknowledge fine with the empirical data in view of that percentage mistake value were

lesser than 1.77 K_F . It has been one of the Freundlich constants usage as a respective amount of adsorption capability, the other constant Freundlich is not to connect to adsorption intensity.

4.1.6. Thermodynamic Parameters of Adsorption in Batch System

Thermodynamic parameters include ΔG° , ΔH° , and ΔS° may be supposed by applying constants equilibrium by temperature. It was given back the practicability and unprompted nature of the operation. The standard Gibbs free energy of Cu(II) and Cd(II) system exist appraised applying K worth gotten the optimum temperatures in the Langmuir model and existing in Table 4.1. The negative values of ΔG° affirm the practicability of the practicability and unprompted nature of metal ions adsorption through big choice of Cu(II) and Cd(II) for chitin. The usual the entropy changes and enthalpy of adsorption operation existed determined since the $\ln K$ versus $1/T$ plots (Table 4.3). The enthalpy values ΔH° to the adsorption onto chitin were found as 1.34 KJ/mol for Cu(II) and 2.55 KJ/mol for Cd (II). As seen from the table, the positive values of ΔH° proposed the endothermic nature and of adsorption likely strong bonding among Cu(II) and Cd(II) and sorbent. The positive values of ΔS° affirms the increased randomness from the solid–solution border throughout adsorption.

Table 4.3. Thermodynamic parameters obtained for Cu(II) and Cd(II) adsorption.

Cu (II)				Cd (II)		
Temperature, °C		- ΔG , kj/mol	ΔS , kj/molK		- ΔG , kj/mol	ΔS , kj/molK
20	$\Delta H=1.34$ KJ/mol	3.24	15.66	$\Delta H=2.55$ KJ/mol	3.50	20.73
30		3.39	15.61		3.73	20.67
40		3.79	15.38		4.15	20.13

4.1.7. Kinetic Parameters of Adsorption

Different kinetic models that is to say the Lagergren's intraparticle diffusion models and pseudo-first order and pseudo-second order have been applied for the legitimacy through the examined at adsorption process for Cu(II) and Cd(II) onto chitin. Of the average shake rapidity of 150 rpm, it is expecting to proposal no mass transfer opposition

to the complete adsorption operation. The plot of linearised from pseudo-first order equation was displayed in Table 4.4. The results presented that, the relationship coefficient for the pseudo-first order kinetic model gotten 20-40 °C was exact short and they increased by increasing temperature for Cu(II) and Cd(II). The experiment $q_{eq,cal}$ value found in this model did not gave sensible values particularly from the small temperature so pseudo-first order model could not define the results adsorption of Cu(II) and Cd(II) onto chitin. Table 4.4 displays the linearized from the pseudo-second order model for Cu(II) and Cd(II), respectively. The value of second order adsorption ratio constant, k_2 , obtained. Theoretical and experimental q_{eq} and connection coefficients are too given Table 4.4. In the perspective of these consequences, it can be said that the pseudo-second order kinetic model providing a good connection for the adsorption of Cu(II) and Cd(II) onto chitin in compare for the pseudo-first order model.

Table 4.4. Change of the pseudo- first and second order response ratio constants with temperature for Cu(II) and Cd(II).

Concentration, mg/L	Pseudo First order kinetic model				Pseudo Second order kinetic model			
	Cu (II)							
	k _{1,ad} (min ⁻¹)	R ²	q _{eq,cal} mg/g	q _{eq} , mg/g	K _{2,ad} (min ⁻¹)	R ²	q _{eq,cal} mg/g	q _{eq} , mg/g
10	-0.044	0.7568	1.175	2.33	0.015	0.9971	3.39	2.33
25	-0.013	0.7263	2.282	2.83	0.0023	0.9421	6.78	2.83
50	-0.066	0.9088	3.225	4.72	0.0083	0.9779	5.30	4.72
100	-0.137	0.9742	4.605	5.17	0.0054	0.9960	9.05	5.17
	Cd (II)							
	k _{1,ad} (min ⁻¹)	R ²	q _{eq,cal} mg/g	q _{eq} , mg/g	K _{2,ad} (min ⁻¹)	R ²	q _{eq,cal} mg/g	q _{eq} , mg/g
10	-0.049	0.6123	1.168	2.06	0.153	0.9996	2.36	2.06
25	-0.004	0.5125	2.38	2.90	0.073	0.9957	4.62	2.90
50	-0.015	0.5927	2.67	5.06	0.083	0.9978	6.44	5.06
100	-0.021	0.8752	4.25	6.75	0.039	0.9903	10.06	6.75

The consequence presented that the correlation coefficients (R^2) for the pseudo-second-order kinetic model were greater than those for the pseudo-first-order kinetic model; and the (q_e) values calculated since the pseudo-second-order kinetic model were

very close to the experimental data. In addition the ratio constant k_2 was found to decrease by an increase in primary concentration, which also provides the evidence at pseudo-second order model [81].

4.1.8. Intraparticle Mass Transfer Diffusion Model

In the model developed by Weber and Morris, the rate of intraparticle diffusion is a function of $t^{1/2}$ and can be given by the following equation [49,50]:

$$q_t = k_d t^{1/2} + C \quad (4.1)$$

where (k_d) is the intraparticle diffusion ratio constant $\text{mg/g min}^{1/2}$ and C is the intercept. Intraparticle diffusion ratio constant k_d and q_{eq} are calculated through the intercept and slope of the plot and are too registered in Table 4.5 along with the consistent connection coefficients. It is noticed that the relationship coefficients exist not pleasing. The primary linear share is ascribing to the border layer diffusion influence and the last linear portion may be due to the intraparticle diffusion influence [82].

The obtained results indicate of the intraparticle diffusion is not the ratio determine phase and some other mechanisms can control Cu(II) and Cd(II) sorption on chitin. Deviation from the linearity was observed and C_i values were larger than zero which denotes that the Cu(II) and Cd(II) adsorption may be affected by the boundary layer diffusion to some extent. The determination coefficients were found to be in the range 0.29-0.74 for Cu(II) and 0.15 to 0.78 for Cd(II) at 10 to 100 mg/L onto chitin confirming non-linearity.

The intraparticle diffusion is the ratio warning stage, formerly the plot of q_t against $t^{1/2}$ permits from the ancestry. The primary linear share pursue the border coating diffusion pursue by extra linear section which signifies the intra particle diffusion. This display that the adsorption operation exist not alone by intraparticle diffusion but the film diffusion too have fun a function together the noticed operation [83].

Table 4.5. Intraparticle diffusion model of Cu(II) and Cd(II) Ions.

Concentration, mg/L	Intraparticle diffusion model for Cu (II)				Intraparticle diffusion model for Cd (II)			
	K_p (g/mgd ^{0.5})	R^2	$q_{eq,cal}$ mg/g	q_{eq} mg/g	K_p (g/mgd ^{0.5})	R^2	$q_{eq,cal}$ mg/g	q_{eq} mg/g
10	0.29	0.84	3.39	2.33	0.15	0.534	2.36	2.06
25	0.57	0.96	6.78	2.83	0.34	0.7105	4.62	2.90
50	0.55	0.85	5.30	4.72	0.43	0.6355	6.44	5.06
100	0.74	0.99	9.05	5.17	0.78	0.8399	10.06	6.75

4.2. Binary Component Adsorption in the Batch System

Therefore distant, the adsorption of a single metal on the adsorbent own been investigate. Nevertheless, in industrialized emanation, it is mutual exercise to have a blend of dissimilar metals. It is necessary to explore the instantaneous removal efficacy of the adsorbent for Cu(II) and Cd(II). In the most of the circumstance, the adsorbents commonly have less capability in the multi-component systems than the single-component systems perhaps due to the obstruction influence of one metal ion on the others. Also, the summed adsorption capacity of the material in the binary system is greater than the respective capability for all metal ion in a single-component solution which display that there is a synergistic influence of together metal ions in the adsorption operation. The binary adsorption systems, consisting of Cu(II)-Cd(II), were examined and the consequences were fitted with Langmuir, Freundlich and Tempkin competitive model. The binary metal ion systems were equimolar with concentration variable at the 10 to 100 mg/L.

4.2.1. Effect the Contact Time for Binary Cu (II) and Cd (II) Adsorption

The contact time is significant parameter to find the equilibrium condition. At equilibrium there was no altering in concentration of adsorbate of the surface from adsorbent as well as from solution. Equilibrium time for Cu(II) and Cd(II) was found to 15 min and 5 min, respectively. Figure 4.7 and Figure 4.8 shows that initially both Cu(II) and Cd(II) were adsorbed onto the surface of chitin very rapidly after that it is adsorbed gradually and then becomes constant. It could be due to fact that initially there existed

great concentration grade among the bulk liquid and adsorbent surface after concentration gradient decreases [16].

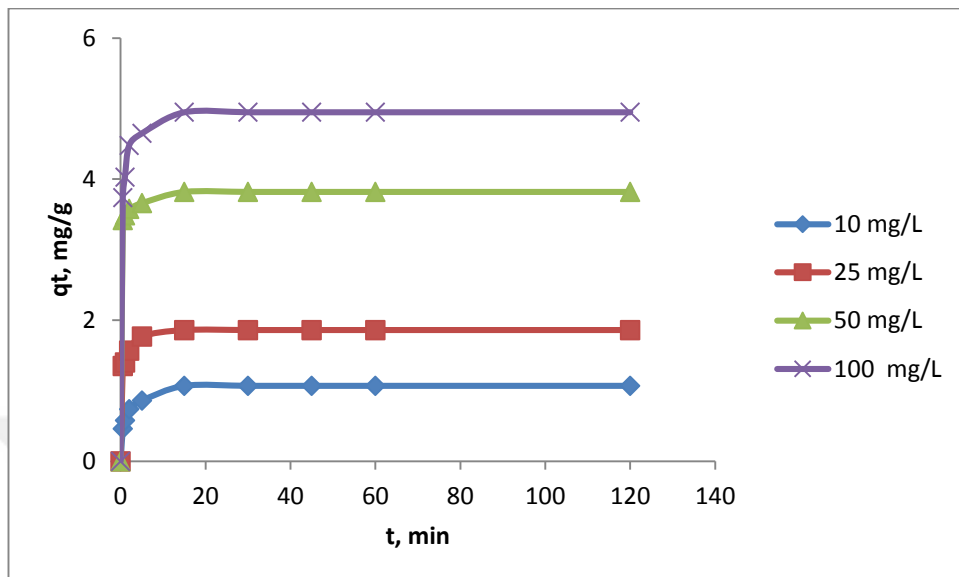


Figure 4.7. The influence the time of contact on the adsorption of binary Cu(II) ions on chitin in various initial Cu(II) concentration (pH = 4.5, $X_0 = 3.33$ g/L, T= 40 °C, agitation rate = 150 rpm).

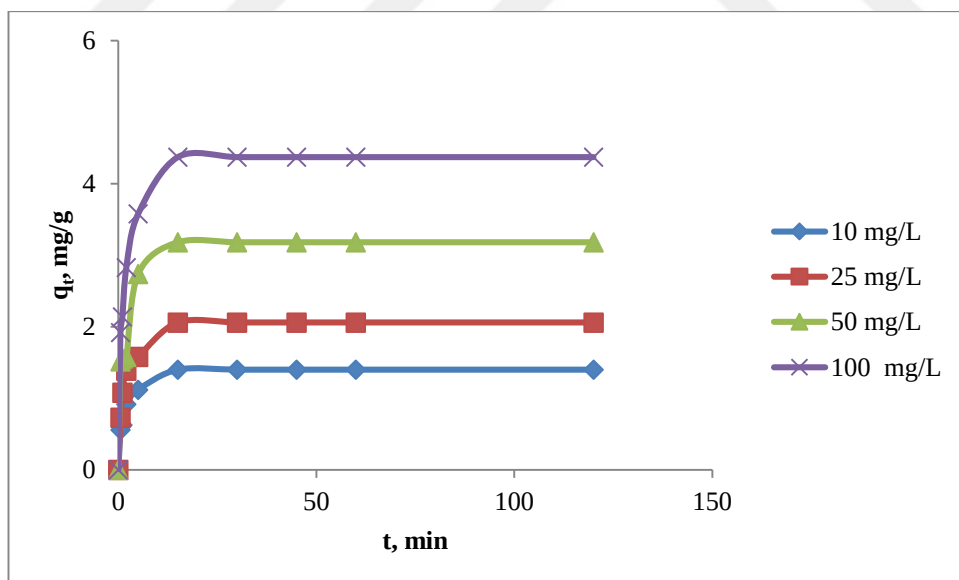


Figure 4.8. The influence the time of contact of the adsorption the binary Cd(II) onto chitin in different initial Cd(II) concentration (pH = 4.5, T= 40 °C, $X_0 = 3.33$ g/L, agitation rate = 150 rpm).

4.2.2. Effect of pH to Binary Cu(II) and Cd(II) Adsorption

One of the greatest significant reasons in the adsorption of metal ions unto adsorbents as it influence the surface charge of the adsorbent and the grade of ionization and spec of the adsorbate is the initial pH of solution [16, 84]. The influence of initial pH on binary Cu(II) and Cd(II) ions uptake capability of chitin was studied among pH 3.5–5.0 at 50 mg/L initial concentration. pH has been known to be necessary active effect on the adsorption of heavy metals onto different adsorbents. Fig. 4.9 depicts the pH influence on the adsorption of Cu(II) and Cd(II) onto chitin. The pH optimum of adsorption for Cu(II) and Cd(II) onto chitin in the binary system was achieved at pH=4.5. For chitin in single system, the pH optimum for adsorption of Cu(II) was pH= 4.5 while to Cd(II) was pH= 5. In binary adsorption process, the optimum pH for chitin was 4.5 for binary Cu(II) and Cd(II). Slight change in the optimum pH of binary adsorption process for chitin and that surface charge of chitin has a quite significant role in the binary adsorption, as discussed previously that chitin has good stability at the various condition of pH. The same pH binding profile for binary solution of Cd(II) and Cu(II) could be due to the behavior of chemical interaction of every component with chitin. At small pH big hydrogen ions contest with metal ions at binding site resulting in little uptake; therefore optimum pH for utmost percentage removal of both components was usually between 3.5 and 5. In contrast to binary Cu(II) and Cd(II) adsorption was due to van der Waals forces and π - π interaction between phenyl ring and adosorbent [85].

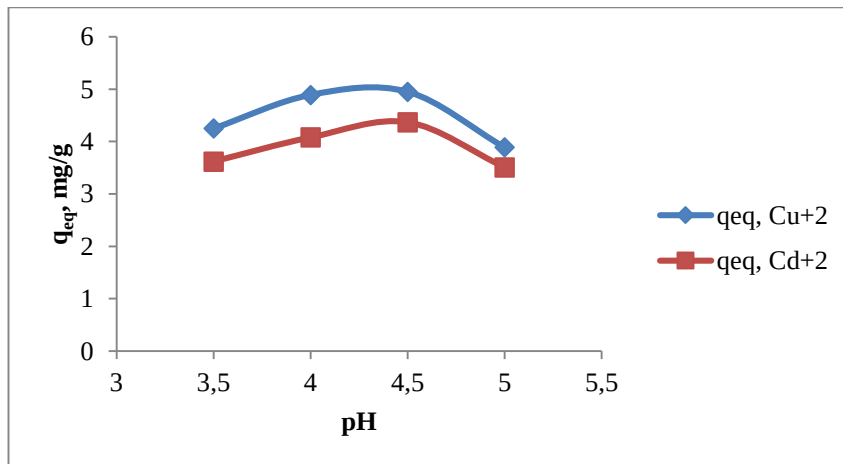


Figure 4.9. Influence of pH on the adsorption of binary Cu(II) and Cd(II) (C_o = 50 mg/L Cu(II) and Cd(II), T = 40 °C, X_o = 3.33; pH= 4.5, agitation rate= 150 rpm).

4.2.3. Effect of Adsorbent Dosage

The influence of adsorbent dosage on the equilibrium uptake of together metal ions in is exposed in Fig. 4.10. It is notice because as the weight in chitin increased at 0.1 to 0.5g a conforming increase in the equilibrium uptake were get to together metal ions. The maximum equilibrium uptake were determined as 2.95 mg/g to 4.95 mg/g for Cu(II) ion and 2.72 to 4.37 for Cd(II) at 50 mg /L initial metal concentration at 40 °C, respectively. The principally was due to an addition in the adsorptive surface zone and the obtainability of higher effective binding sites on the superficial of the adsorbent by increase in adsorbent dosage [84].

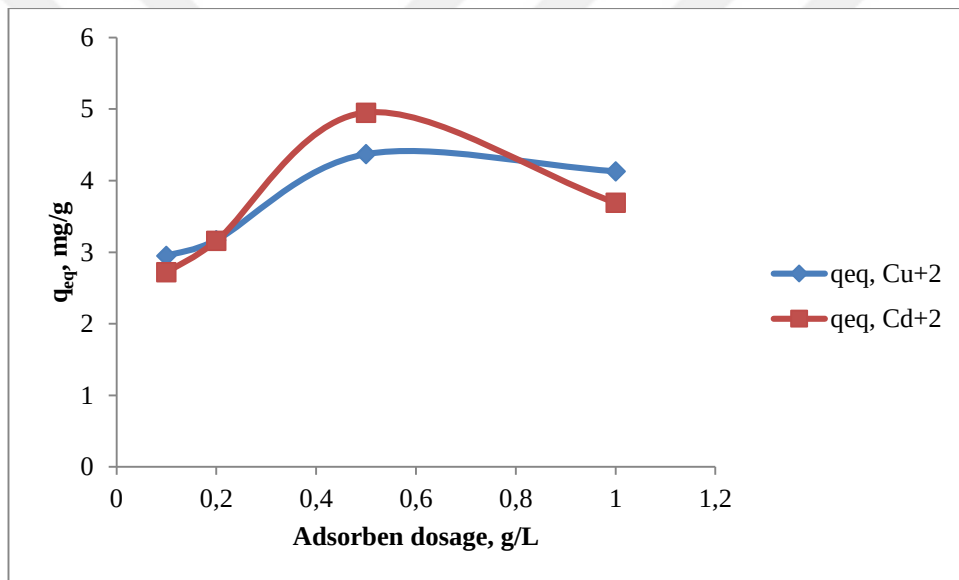


Figure 4.10. The effect of adsorbent dosage on equilibrium uptake on the binary Cu(II) and Cd(II) ions adsorption ($C_o = 50$ mg/L Cu(II) and Cd(II), $T = 40$ °C, $pH = 4.5$, $X_o = 3.33$ g/L, agitation rate = 150 rpm).

4.2.4. Influence of Initial Binary Cu(II) and Cd(II) Concentration on Temperature Dependent Adsorption

The adsorption ratios of the metal ions on adsorbents are a role of the initial concentration of the metal ions that creates it a significant cause to be limiting to an active sorption. In binary metal ion system, the adsorption of both Cu(II) and Cd(II) ions was also studied. The adsorption capacity of chitin was found different in binary metal system. The results of binary Cu(II) and Cd(II) adsorption in binary metal system are shown in Fig.

4.11 and 4.12, respectively. The influence of initial binary Cu(II) and Cd(II) ion concentration was examined in the ratio 10-100 mg/L at 20, 30 and 40 °C. The increase of loading capacity of chitin by increasing primary Cu(II) and Cd(II) ion concentration can also be due to higher interaction among heavy metal and chitin. As chitin obtainable a finite numeral of superficial binding sites, Cu(II) and Cd(II) ion adsorption presented a saturation trend at greater initial Cu(II) and Cd(II) ion concentration. The equilibrium uptake of Cd(II) lowers habitually by higher Cu(II) ion concentration. Lower in the uptake of Cd(II) in attendance of the Cu(II) ions appears easy to clarify. The attendance of the other constituent evolves a rivalry for the adsorption location on the superficial and any places are employed by the second constituent. As a result, the initial constituent has a lesser and its uptake is lower. The bigger the complete metal concentration, the greatest active was the modest lead uptake because of a stout driving force or a big variation from concentration among adsorbent superficial and metal solution. In together single and binary do not Cu(II) and Cd(II) ion mechanism, not yet important increase in the adsorbed extents and announcement of metal ions after the equilibrium phase was noticed. The optimum adsorption temperature for binary Cu(II) and Cd(II) were selected to be 40 °C, owing to the effect of physical adsorption. The consequence showed that an higher of the temperature in the interim 20–40 °C bargain by an higher in the equilibrium uptake capability of chitin to single and binary Cd(II) ions and single and binary Cu(II) ions. At below temperature, the binding of heavy metal ions onto chitin happen by a physical adsorption operation. Thus, the initial adsorption rates decreased with increasing temperatures on 40 °C, for Cu(II) and Cd(II), respectively. At 50 mg/L, while the binary Cu(II) and Cd(II) concentrations higher at 1.4 to 4.37 mg/g and 1.07 to 4.95 mg/g for 20 to 40 °C, respectively. Results showed that the higher adsorption yields occurred for binary Cu(II) and Cd(II) at the higher temperature. The increase of the adsorption yield and adsorption capability at increased temperature designated that the sorption of Cu(II) and Cd(II) onto chitin is endothermic in nature and may include not alone physical but further chemical sorption. This effect may be ascribe to the expansion of pore size or create of few recent effective location on the adsorbent surficial due to bond break.

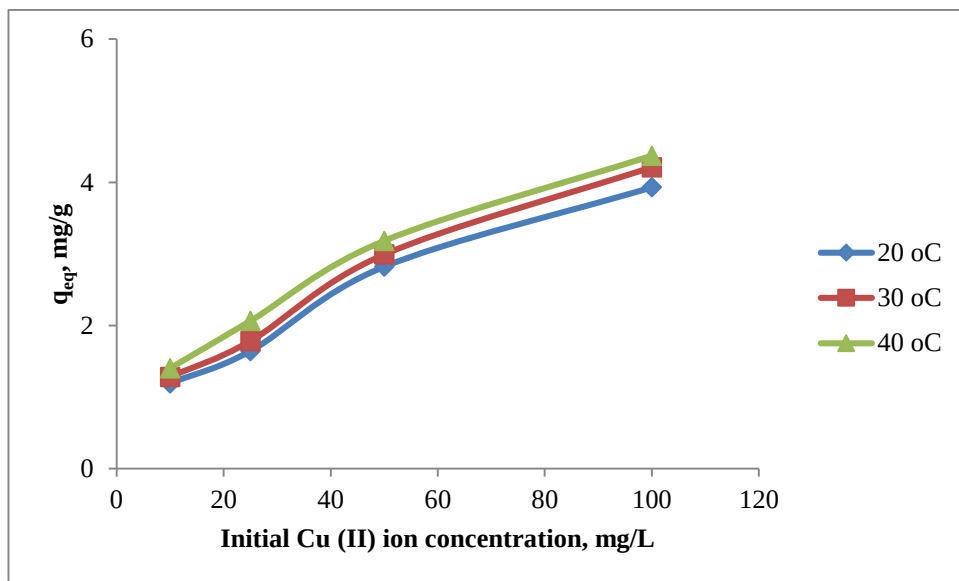


Figure 4.11. The effect of initial Cu(II) concentration on the adsorption (pH=4.5, $C_o = 50$ mg/L Cd(II), $X_o = 3.33$ g/L, agitation rate= 150 rpm).

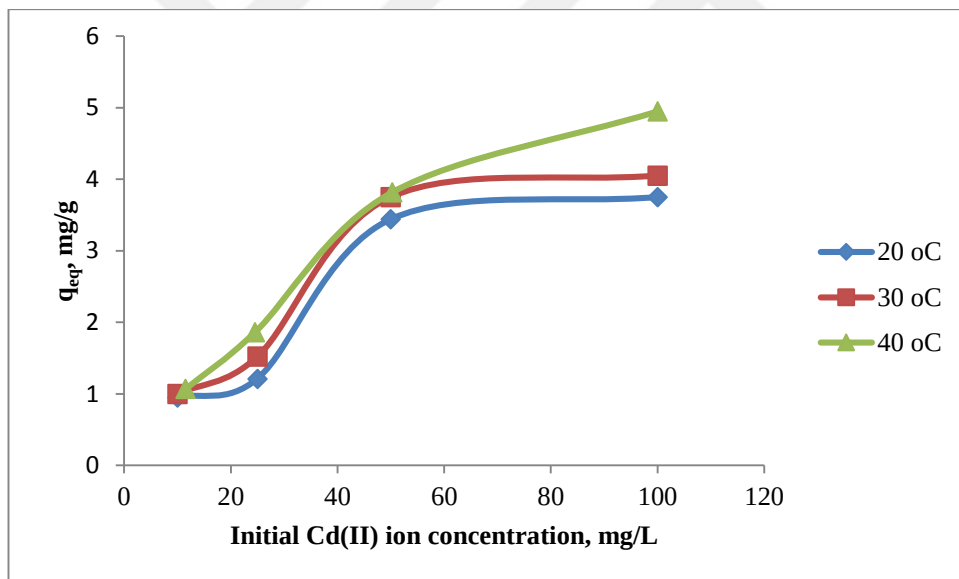


Figure 4.12. The effect of initial Cd(II) concentration on the adsorption (pH= 4.5, $C_o = 50$ mg/L Cu (II), $X_o = 3.33$ g/L, agitation rate= 150 rpm).

4.2.5. Equilibrium Modeling for Binary Cu(II) and Cd(II) Ions in Batch System

Adsorption isotherms assert the connection among the quantity of adsorbate removal from the liquid phase by unit mass of adsorbent at not change temperature. Adsorption isotherms are elementary necessity for the sketch of adsorption systems. An accurate numerical characterization of equilibrium adsorption capability is high significant to

trustworthy forecast of adsorption parameters and measurable resemblance of adsorption conduct for various adsorbent systems. The information of equilibrium isotherms generally gives beneficial knowledge on sorption instrument, surficial possessions and nearly of the adsorbent. It was respectively valuable to limit the greatest acceptable relationship of equilibrium arcs in instruction to enhance the situations for designing adsorption mechanism [86]. In this study, the Freundlich, Langmuir, and Temkin isotherms were experienced to examine the equilibrium knowledge, and the consequences are displayed in Table 4.6. Like can be perceived at Table 4.6, the value of the connection coefficient R^2 is 0.993 for binary Cu(II) and Cd(II) at 40 °C for Langmuir adsorption isotherm. The capacity monolayer adsorption for Cu(II) and Cd(II) remove by chitin are 6.14 mg/g and 8.41 mg/g at 40 °C, respectively. Adsorption ability of chitin increased by increasing the temperature and highest Q^0 value was obtained as 6.09 mg/g for binary Cu(II) ions and 8.41 mg/g for binary Cd(II) ions at 40 °C. high K_b value display the nearly for binding of metal ions. The maximum value of K_b was founded at 40 °C for binary Cu(II) and Cd(II).

From Table 4.6, the size of K_F and n ; the constants of Freundlich, display simple uptake of metal ions from waste sewage with in height adsorptive ability of chitin, particularly nat single and binary Cu(II) and Cd(II) at 40 °C. Thus the Freundlich isotherm gave a more excellent fit to the data than the Langmuir isotherm model for together metal ions. Moreover, the value of n lies among 1 and 10, it shows a suitable adsorption [85]. The value of n gotten is 0.48 and 0.29 for Cu(II) and Cd(II) ions at 40 °C, correspondingly, showing a favorable adsorption process also shows so n is bigger than unity, signifying that the heavy metal ion is agreeable adsorbed by dehydrated biomass from every the temperature prepared.

The model isotherm Temkin different the Freundlich and Langmuir isotherms income for account of interplay among adsorbents and heavy metal ions to be adsorbed and is based on the supposition so that of the free energy of sorption is a role of superficial treatment [87]. The rectilinear of Temkin isotherm model is assert [85]: The values of b_T increased from 1.02 J/mol to 1.21 J/mol for binary Cu(II) ion and from 1.69 J/mol to 1.90 J/mol for binary Cd (II) by increasing temperature from 20 to 40 °C onto chitin. The A_T values related to the maximum binding energy were found to be 1.05×10^{-6} L/g to 0.012 L/g for binary Cu(II) and 0.32×10^{-12} L/g to 0.32×10^{-10} L/g for Cd(II) at 20 to 40 °C (Table 4.6).

The adsorption ability for the heavy metals appeared to be lesser in the binary mix cases than the single section system. In vision of the results offered in Table 4.6, the

isotherms seemed to trail the model Langmuir most strictly than the other models from complete temperatures examined for single and binary systems. Nevertheless, the Tempkin and Freundlich adsorption models also appeared to decide well with the investigational data considering. One of the Freundlich constants is K_F has been applied as a comparative amount of adsorption ability, Freundlich constant was connected to intensity of adsorption.

Table 4.6. Langmuir, Freundlich and Tempkin isotherms constants for binary Cu(II) and Cd(II) adsorption onto chitin.

Temperature	Langmuir			Freundlich			Tempkin		
	Binary (Cu+Cd) Cu (II)								
	Q°, mg/g	K, L/mg	R ²	K _f , mg/g	n	R ²	b _T , J/mol	A _T , L/g	R ²
20	4.01	0.010	0.975	0.53	0.34	0.999	1.02	1.05x10 ⁻⁶	0.981
30	4.87	0.016	0.978	0.95	0.41	0.977	1.13	0.25x10 ⁻⁴	0.955
40	6.01	0.027	0.993	1.59	0.48	0.965	1.21	0.012	0.997
Binary (Cu+Cd) Cd (II)									
	Q°, mg/g	K, L/mg	R ²	K _f , mg/g	n	R ²	b _T , J/mol	A _T , L/g	R ²
20	3.94	0.009	0.994	0.49	0.19	0.982	1.69	1.05x10 ⁻¹²	0.929
30	4.99	0.012	0.982	0.51	0.27	0.986	1.76	0.32x10 ⁻¹¹	0.946
40	8.41	0.013	0.993	0.76	0.29	0.966	1.90	1.05x10 ⁻¹⁰	0.976

5. CONCLUSION

In this master thesis, the adsorption of Cu(II) and Cd(II), in single and binary systems was investigated utilizing chitin in the batch system. The consequence pointed out that, adsorption ability of the sorbent is impressed by pH, temperature and initial metal ions concentration. The chitin selectively adsorbed binary Cu(II) ions and single at pH= 4.5, while single and binary Cd(II) ions were specially adsorbed with the chitin from pH 5.0 and 4.5, respectively and at 30 °C.

The Freundlich, Langmuir, and Tempkin adsorption models were utilized for the mathematical explanation of the adsorption equilibrium single and binary Cu(II) and Cd(II) removal onto chitin dependent on the isotherm coefficients appraise and temperature from the isotherms existed applied to liken the adsorption ability of the chitin for single and binary systems. It is view that the isotherms constants increased by cumulative temperature up to 20 and 40 °C to Cu(II) and Cd(II) ions, correspondingly. The consequence acquired displayed that the adsorption equilibrium data fitted the Langmuir model in the examined concentration series at altogether the temperatures investigated for single and binary systems.

The negative value of ΔG° settled the natural adsorption procedure. The positive value of ΔS° presented the increased randomness at the solid–solution interface for the duration of adsorption and the positive value of ΔH° displayed the adsorption operation was endothermic. The consequence also displayed that single and binary Cu(II) and Cd(II) adsorption procedure by chitin was endothermic.

It might be finished that chitin may be utilizing as a small-cost, usual and plentiful source for the heavy metal ions removal of and it can be an alternate to large costly methods such as solvent extraction, chemical oxidation and active carbon adsorption for removal of single and binary combination heavy metal of waste stream. This effort could empower to infer the forecast of adsorption equilibrium of the single and binary system if investigational ages are not available to a sure balanced of bio solute concentrations.

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CIRRUCULUM VITAE

My name is Marewan Mohammed Ahmed, I was born in 21/2/1989, I graduated in Sulaimany University, in department science soil and water, The year grade was 2010-2011, I worked from in both Environmental and Agriculture field, I liked completing study and obtained higher certificate such as master degree for increasing experience specially in area of environmental and weathering because is very important my country and to serve in Iraq and turkey state and all humanity.

