The Influence of Detention Time, Flow Rate and Particle Size in the Removal of "Copper" from Water Using Limestone Filtration Technology

–Laboratory Scale—

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Abstract

The concern over increasing needs for drinking water and awareness for development of systems to improve water quality both for drinking purposes and for effluents from wastewater treatment and industrial facilities have provided incentives to develop new technologies and improve performance of the existing one. Adsorption technology has many advantages over other treatment methods such as simple design, low investment cost, limited waste production, etc. Synthetic water with a dosing of artificial copper solution (Cu No_3) was passed through a PVC column (15 cm diameter, 100 cm length) containing limestone as a filter media in three different sizes, using three different hydraulic rates, and three initial influent copper concentrations (7.04, 4.39, 1.72) ppm .For this study, three experiments have been conducted; continuous batch and field experiment. The up flow roughing filtration is the suitable technique to recover heavy metals present in aqueous solutions, without the need of adding further substances. The filtration results demonstrated that the smaller size of filter media (3.75) mm gave higher removal efficiency (93.75 – 98.80) % than larger filter media (9.50) mm which gave removal efficiency of (67.61 – 94.0) %. This is due to the large specific surface. The smaller size of limestone achieved the longer detention time (49) min, so the removal of Cu was more than (90) % for the (50) min of experiment. At lower flow rate (0.16) L/min, the removal efficiency was higher than at higher flow rate (0.77) L/min. At high flows, there is a reduced period of surface contact between the particles and copper solution. This study also involved three different batch experiments .The removal efficiency was (93- 97) % for the three types of limestone which indicates the importance of limestone media in the removal process. This also indicates that the removal efficiency was increasing with the increase of the limestone volume. Field experiment has been conducted using wastewater from Al- Dura Electric Station on the three types of limestone so that to ensure the laboratory tests. It was achieved good removal efficiency range from (87.5) % to(97.5) % at the high adsorbent dose .To calibrate the physical model, a computer program of multiple regressions is used to assess the relative importance of the predicted variables. The partial correlations indicate that influent concentration of copper, surface loading (flow rate), and detention time are the most important variables while the size of limestone is not important as others.

Keyword: Limestone, Detention Time, Particle size, Flow rate, Copper.

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تأثير وقت الاحتجاز، معدل التدفق وحجم الجسيمات في إزالة "النحاس" من المياه عن طريق تكنولوجيا ترشيح الحجر الجيري -مقياس مختبر-

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الخلاصة

ان القلق بشأن الاحتياجات المتزايدة لمياه الشرب والوعي لتطوير الانظمة لتحسين نوعية المياه لأغراض الشرب اضافة الى تحسين نوعية المياه المتدفقة من معالجة مياه الصرف و المنشآت الصناعية توفر الحوافز لتطوير تكنولوجيا جديدة وتحسين أداء التكنولوجيا الحالية.أن تكنولوجيا الامتزازتملك مزايا عديدة اكثر من طرق المعالجة الاخرى: بسيطة التصميم، كلفة استثمارها منخفضة، ومحدودة في إنتاج النفايات اضافة الى مزايا عديدة اخرى. تم امرار ماء محضر بجرعة محلول النحاس الصناعي (نترات النحاس) خلال عمود (قطر 15 سم ،طول 100سم) حاوي على حجر الكلس كوسط مرشح بثلاث احجام مختلفة(3.75mm,5.omm,9.0mm)، ثلاث معدلات لتصاريف هيدروليكية وثلاث تراكيز اولية للنحاس اولية (7,04، 4,39 و 1,72) جزء لكل مليون. في هذه الدراسة تم اجراء ثلاث انواع من الجريان: تجارب من نوع الجريان المستمرة ،جريان بأجرعة وتجارب حقلية تطبيقية. ان المرشح الخشن ذو الجريان نحو الاعلى هو التقنية الصالحة لاستعادة المعادن الثقيلة الموجودة في المحاليل المائية، من دون الحاجة الى اضافة مواد اخرى. اظهرت نتائج الترشيح ان وسط المرشح الاصغر حجما (3,75) ملم اعطى كفاءة ازالة اعلى (93,75 – 98,80) ٪ من وسط المرشح الاكبرحجما (9,50) ملم والذي اعطى كفاءة ازالة (94,0-67,61). ويعود هذا الى ان هناك مدة قليلة للتماس السطحي بين الجسيمات ومحلول النحاس عند الجريان العالي.. تضمنت الدراسة ايضا ثلاث تجارب ذو دفعات مختلفة.كل تجربة استخدمت احجام مختلفة من حجر الكلس، خلطت مع محلول النحاس بتراكيز مختلفة لكل حجم لمعاينة سلوك ازالة النحاس.. ان كفاءة الازالة تتراوح (93 - 97)٪ لكل الاحجام الثلاثة من حجر الكلس مما يشير الى اهمية حجر الكلس في عملية الازالة وان كفاءة الازالة يزداد بزيادة حجم حجر الكلس. واخيرا اجريت تجارب حقلية باستخدام مياه الصرف من محطة كهرباء الدورة على الانواع الثلاثة من حجر الكلس وذلك لتأكيد التجارب المختبرية. فقد حققت كفاءة ازالة جيدة تتراوح من (87,5)٪ إلى (97,5)٪ عند جرعة العالية للمادة الممتزة. تم استخدام برنامج حاسوبي لمعايرة الموديل الفيزيائي، من الارتدادات المتعددة لتقيم الاهمية النسبية للمتغيرات المتوقعة. الارتباطات الجزئية اشارت الى ان تركيز النحاس الاولي، الحمل السطحي (معدل الجريان) و زمن المكوث هم المتغيرات الاكثر اهمية بينما حجم حجر الكلس ليس مهم كالاخرين.

1. Introduction

Conventional water and wastewater treatment processes have been long established in removing many chemical and microbial contaminants of concern to public health and the environment,(Zhou H.(2002)). Treatment methods differ depending on the conditions of the process and properties of wastewater, (Hosseini S.N. (2010)). For drinking water treatment ,the recent technological advancements relate to primarily filtration (media filtration and membrane systems), disinfection processes, ion exchange, and carbon adsorption processes, (Berrin T.(2008)). For wastewater treatment, removal of heavy metals from wastewater is usually achieved by physical and chemical processes which include precipitation, coagulation, reduction membrane process, ion exchange and adsorption,(Norilhamiah Y. and Ahmad F. R.(2010)).

For wastewater treatment, removal of heavy metals from wastewater is usually achieved by physical and chemical processes which include precipitation, coagulation, reduction membrane process, ion exchange and adsorption,(Norilhamiah Y. and Ahmad F. R.(2010)).

However, these processes have significant disadvantages including:

-Incomplete metal removal, particularly at low concentrations.

-High operational costs and maintenance costs,(Antonio A. L.(2010)).

-Some of conventional techniques can not produce effluent that can fulfill discharge water quality regulations,(Nikola S.(2010)).

For decades, copper has been recognized as an essential trace metal for humans, but there is a range of intakes that permits optimum health. The primary effect of long-term exposure to excess copper is its accumulation in the liver, leading to structural and biochemical changes including liver cirrhosis. Copper levels greater than 5 ppm impart a bitter taste to drinking-water,

(Antonio A. L.(2010)). Potential sources of copper bearing wastes include plating baths, fertilizer industry, paints and pigments industry, and municipal and storm water runoff,(Hosseini S. N.(2010)). For wastewater treatment, a significant majority of recent developments relate to biological processes and advanced treatment technologies such as adsorption,(Berrin T.(2008)).

A number of adsorbent materials have been studied for their ability to remove heavy metals and they have been sourced from natural materials and biological wastes of industrial processes. These materials including: activated carbon, chitosan, carrageenan, lignite, kaolinite, ballclay, diatomite, coconut fiber and limestone,(Onundi Y.B.(2010)). The systems derived to the water and wastewater treatment is known as Roughing filters.

Various studies have been carried out to remove copper from adsorbent materials. The ability of activated carbon produced from coconut shell to remove mercury Hg (II), Lead Pb (II) and Copper Cu (II) from dye effluent was investigated by (Onyeji L.I. (2011)). The activated carbon was produced through chemical activation processes by using zinc chloride ($ZnCl_2$). The adsorption capacity was determined as a function of adsorbent dosage. The adsorption Isotherms of the studied metals on adsorbent were also determined and compared with the Langmair models. The activated carbon produced showed excellent efficiency in removing Hg (II) and Pb (II) with percentage removal up to 80 % at low adsorbent dosage of 2g. In contrast, only about 29 % removal of Cu (II) was achieved at adsorbent dosage of 2g. The study also showed that the adsorption of Hg (II), Pb (II) and Cu (II) by the activated carbon is dependent on the dosage of the adsorbent and the initial metal concentration. The use of coconut shell for activated carbon also helps in solving the problem of over abundance of coconut shell as agricultural waste.

The removal of copper from hazardous waste landfill leachate was investigated by (Norilhamiah Y. (2010)). Peat was used as absorbent due to its high absorption capacity for the heavy metal. To study the efficiencies of peat as an absorbent, fresh peat and dried peat which have different characteristics were used. For each peat type, three parameters that can have effect on absorbent performance were investigated, including absorbent dose, contact time and the use of hydrochloric acid. Batch kinetic study was conducted using Jar Tester to determine the optimum conditions of peat absorption for removal of copper from leachate. The highest removal of copper was obtained using 400g of dried peat that removed 95% of copper content from its initial concentration. The addition of hydrochloric acid to fresh peat and dried peat shows that the latter has higher ability to absorb copper compare to the former. The rate of copper (II) adsorption increases with the quantity of acid added. The highest percentage of removal rate by the dried peat observed was 95.96 % and 98.7 % for the fresh peat.

Granular activated carbon produced from palm kernel shell was used as adsorbent to remove copper, nickel and lead ions from a synthesized industrial wastewater (Onundi Y. B.(2010)). Laboratory experimental investigation was carried out to identify the effect of pH and contact time on adsorption of lead, copper and nickel from the mixed metals solution. Equilibrium adsorption experiments at ambient room temperature were carried out and fitted to Langmuir and Freundlich models. Results showed that pH5 was the most suitable, while the maximum adsorbent capacity was at a dosage of 1 g/L, recording a sorption capacity of 1.337 mg/g for lead, .581 mg/g for copper and 0.130 mg/g for nickel. 1 The percentage metal removal approached equilibrium within 30 min for lead, 75 min for copper and nickel, with lead recording 100%, copper 97% and nickel 55% removal, having a trend of $Pb^{2+} > Cu^{2+} > Ni^{2+}$. Langmuir model had higher R2 values of 0.977, 0.817 and 0.978 for copper, nickel and lead respectively, which fitted the equilibrium adsorption process more than Freundlich model for the three metals.

The World Health Organization (WHO) recommended a maximum acceptable concentration of Cu in drinking water of (1.5) mg/L. Table (1) summarizes copper standards in current Environmental Protection Agency (EPA) regulations. Therefore, it is essential that potable waters should be given some treatment to remove copper before domestic supply. There are many different methods for treating wastewaters.

Table (1): "EPA copper discharge limits".

EPA regulation	Limit
Toxic Release Inventory (TRI)	1 mg/L
Clean Water Act (CWA) (daily)	3.39 mg/L
Clean Water Act (CWA) (30-day average)	2.07 mg/L
Safe Drinking Water Act (SDWA)	1.3 mg/L
Superfund Amendments and Reauthorization Act (SARA)	4.5 kg/yr

The main objective of the present study is to investigate the suitability of limestone particles to be used as a filter, capable of attention of heavy metals ,especially copper (cu).The study was carried out through laboratory trials using both batch experiments and prototype filter system (column experiments) to test the limestone-based material under aerated natural water conditions, three parameters have been used in this experiments, surface loading rate, media size and influent copper concentration. Field trials with batch experiments was carried out to confirm laboratory results.

2. Materials and methods

2.1 Materials

All limestone types used in this study have been examined and prepared as in the following:

- In this study two types of limestone have been used, western red and northern white in three different sizes which are classified according to the experience of the sieve analysis conducted on them, as shown in Fig. (1).

a b c

western red no.2 northern white no.2 northern white no. 3

Fig. (1): Types of limestone, (a, b and c).

As a result of the sieve analysis tests conducted on the limestone, the adopted three sizes of diameter of limestone are (3.75) mm western red and (5.0, 9.5) mm northern white respectively which were used in this study. Common grades of media used in roughing filters are provided by(Wegelin

(1996))and shown in Table (2). Due to this table, the limestone used in this research has been considered as fine grade limestone. The porosity ,void ratio and density of three types of limestone are listed in Table(3).

Table (2): Different sizes of roughing filter media (Wegelin(1996)).

Roughing Filter Description	First Compartment (mm)	Second Compartment (mm)	Third Compartment (mm)
Course	24- 16	18-12	12-8
Normal	18-12	12-8	8-4
Fine	12-8	8-4	4-2

Table(3): Physical properties of limestone.

Rock Type	Western Red No.2	Northern White No.2	Northern White No.3
porosity	0.365	0.39	0.45
Void ratio	0.575	0.639	0.818
Density(Kg/m^3)	1889.8	2008.2	2000

- ASTM C568 (American Society for Testing and Materials) classifies limestone into three categories based on the bulk density of the limestone as shown in Table (4).

Table (4): Standard Specification for Limestone Dimension Stone (ASTM C568)

Classification No.	Consistency Degree	Density (kg/m^3)
Class I	Low-density	1760 – 2160
Class II	Medium-density	2160 – 2560
Class III	High-density	greater than 2560

As a result of the density analysis test conducted on the chosen limestone and compare it with ASTM C-568 “Standard Specification for Limestone Dimension Stone” it is shown that the used limestone has been within the limited standard (low density).

- Chemical characterization of the limestone used in the copper removal process used in this study was described in Table (5). The determination of carbonate content can be used to classify chemical-grade limestone, Table (6). The classification of limestone used in this study is as a medium purity for northern white limestone and low purity for western red limestone. Many industrial applications of limestone constrains on the levels of specific impurities (such as SiO_2, MgO and Fe_2O_3), and therefore chemical analysis of limestone raw material are necessary to assess the grade of the stone.

Table (5): Chemical characterization of the limestone used in the present study

Components	Western Red	Northern White
Lime (CaO) %	46.28	53.00
Silica (SiO_2) %	6.88	2.12
Alumina (Al_2O_3) %	0.88	0.44
MgO %	4.2	1.0
Fe_2O_3 %	0.45	0.35
Loss on Ignition (LOI)* %	40.64	41.91
Purity	88.47	96.53

Table (6): Classification of limestone by calcium carbonate content

Category	Percentage $CaCO_3$
Very high purity	More than 98.5
High purity	98.5 – 97.0
Medium purity	97.0 - 93.5
Low purity	93.5 – 85.0
Impure	Less than 85.0

- Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas . The FTIR analyses of limestone before filtration process for western red and northern white limestone are shown in Fig. (2) and (3) respectively. FT-IR result shows that limestone has different functional groups and has characteristic bands of carboxylic, amine, amide acid groups which are able to react with copper molecules in aqueous solution.

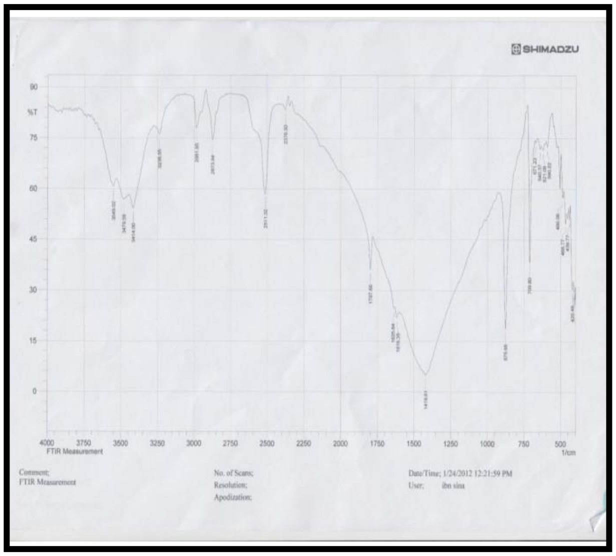


Fig. (2): FTIR spectrum for western red Limestone

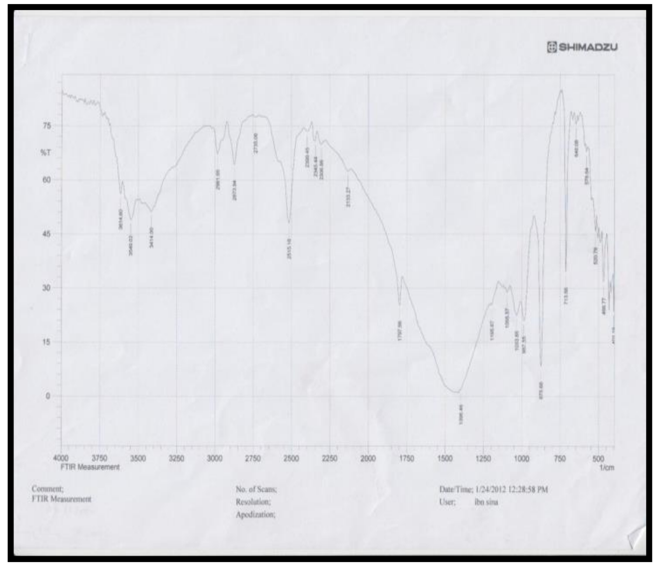


Fig. (3): FTIR spectrum for northern white Limestone

- A synthetic water has been prepared by mixing the effluent from the water tank with the highest solubility Copper compound (copper nitrate) in three different concentrations (40 mg/L, 24 mg/L and 8 mg/L). A synthetic wastewater has been prepared by dissolving (1, 3, and 5) g of Copper nitrate into (125) litter of water tank and mixed well for a homogeneous solution and to ensure melting of copper nitrate in water.

2.2 Methods

Two filter columns each with 150mm diameter were used ,Fig.(4). The upflow filtration model includes the following components:

*Three Tanks of water for the following purposes:

- Ground tank: mixing water with a salt of copper.
- Top tank: providing a continuous discharge of the system without interruption during the work.
- Middle tank: it placed at about 1.25m above the top of the filter column to achieve a Constant head (a hydraulic conductivity of (10-2-10-4) cm/sec was used for the limestone).

*Water motor to pump water from the ground tank to top tank.

*Pipes with 1/2 inch and two flowmeters.

*Two filtration tube column with length of (1) meter, diameter of (15) cm made of the PVC material.

Effluent water has been sampled regularly every 15 min for one hour. Five sets of 250-ml samples have been collected for each try. The mean of them have been adopted in subsequent calculations. The pH of the effluent water is measured, and samples are analyzed by the atomic absorption spectrophotometer for copper concentration. The procedure has to be repeated for 27 attempts with 5 effluent samples, so the sums of the all experiments are 135 samples. Details of the design of Cu filter are given in Table(7).

Fig.(4): The physical model (filter columns).

Table(7): design data for Cu removal in filtration experiment

Parameter	Unit	Value		
Media		Limestone		
Type		western red no.2	northern white no.2	northern white no.3
Density	Kg/m3	1889.8	2008.2	2000
Particle size	mm	3.75	5.00	9.50
Cu concentration	ppm	7.04	4.39	1.72
Input pH		8.0	7.7	7.4
Flow rates	L/min	0.16 0.235 0.40	0.18 0.322 0.47	0.23 0.39 0.77
Surface loading rate	m3/m2/day	13.05 19.16 32.61	14.68 26.25 38.32	18.75 31.80 62.78
Retention time	min	49.0 33.3 19.6	43.6 24.3 16.7	34.1 20.1 10.2

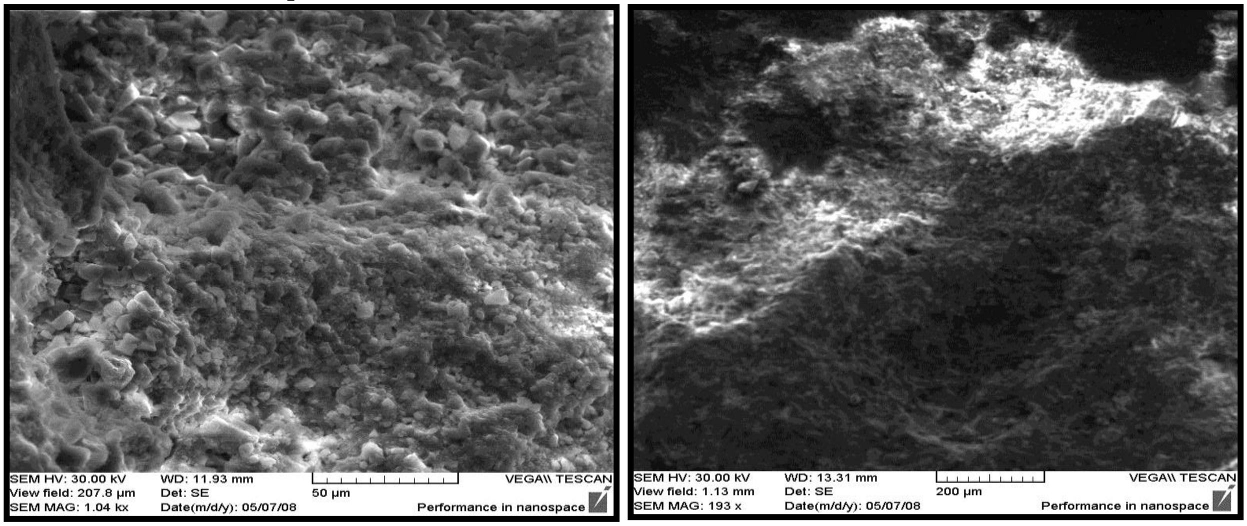
The batch study has been conducted to establish the removal pattern of heavy metals using limestone. In this experiment, different volumes of limestone calculated based on the weight (20, 60, 100, 140, and 180) g are used in a specific volume of heavy Cu solution (125 ml of synthetic Cu solution) which are kept in polyethylene bottles. The experiment has been conducted at different Cu concentrations (40, 24, and 8) mg/L, which is shaken by an orbital shaker at 300 rpm for 60 min, which it allows for all the surface area of the adsorbent to come in contact with the model water containing heavy metals. Afterwards, the solution has then been left to settle for 90 min before testing Cu concentration by an atomic absorption spectrophotometer.

A field study of copper removal is conducted on a fresh wastewater which was taken from (Department of Water Treatment Unit in Dora Power Station-Iraq) . The initial copper concentration of this wastewater was measured and it was 0.4 ppm. A batch study has been conducted for verification purpose.

3. Results and discussion

3.1 Physical and chemical characterization of adsorbent

The image of limestone particle cross section analyzed by SEM before and after the experiment is illustrated in Fig (5). The SEM image reveals the porous structure of the limestone surface. It can be observed that some Cu has been adsorbed onto the surface of media and some are penetrated through the media due to absorption.



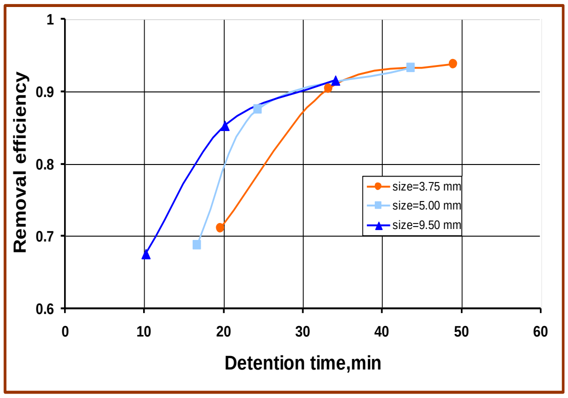
(a) before filtration. (b) after filtration.

Fig.(5): Scanning electron image of media.

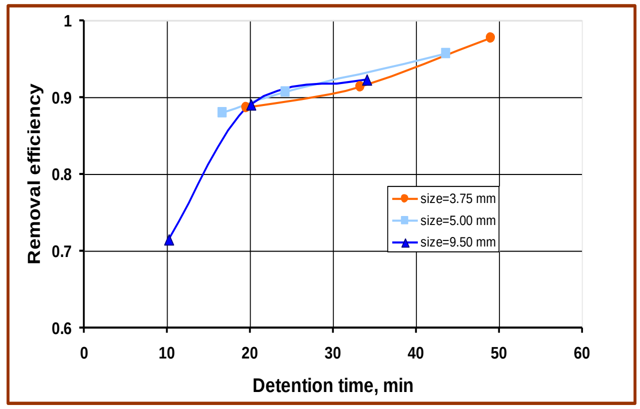
3.2 Column Experiment Methodology

a- The effect of detention time on removal efficiencies for different types of limestone and for different influent concentrations of copper (7.04, 4.39 and 1.72) mg/L are as shown in Figure (6). The removal efficiency increased with the increase of the detention time for all types of limestone as a result of providing the sufficient time for removal process. It can also be noted that the smallest size of limestone (western red no.2) with the diameter of (3.75) mm achieved the longer detention time (49) min because of its small particles. The smaller a particle size the larger its specific surface. The specific surface is a good indication of the relative influence of electrical forces on the behavior of the particle. Also it achieved the higher efficiency about (93.75% – 98.80%) especially at the longer detention time provided to it. The results indicated that (68% – 94%), (72% - 98%) and (78% - 99%) of cu can be removal based on cu concentration of (7.04, 4.39 and 1.72) mg/L respectively.

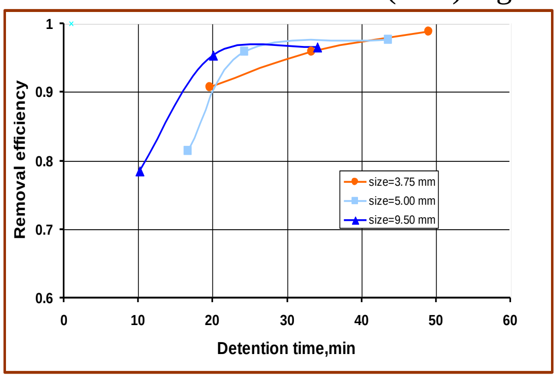
b- The effluent Cu concentrations for influent concentration of copper equal to (7.07, 4.39 and 1.72) mg/L are decrease with the increase of detention time for all types of limestone, as shown in Figure (7). that is because of providing the sufficient time for the limestone to hold the particles form the solution, so the effluent concentration of copper will be at least about (0.44, 0.10 and 0.02) ppm respectively for the detention time of (49) min. Also, it was shown that the smallest size of limestone achieved the minimum effluent concentration of cu because of its high efficiency. The surface charge of limestone is predicated to be a contributing factor for the removal of cu also, the adsorption phenomenon. It is noted that at high flows (low detention time), there is a reduced period of surface contact between the particle and the copper solution as well as higher velocity of flow through the media increasing the sloughing of precipitate from the media. The removal of cu was more than (90%) for the (50) min of experiment.



a- influent concentration of CU(7.04) mg/l

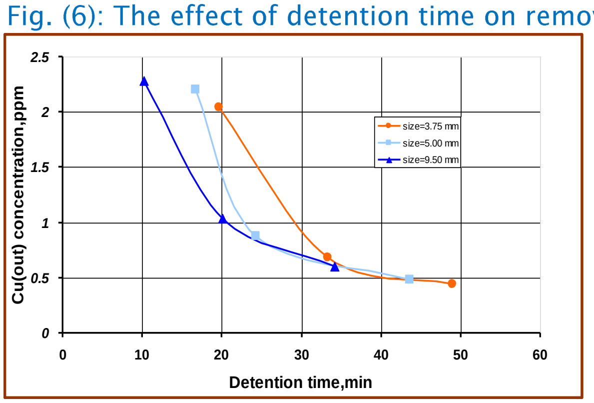


b- infl. concentration of CU(4.39) mg/l

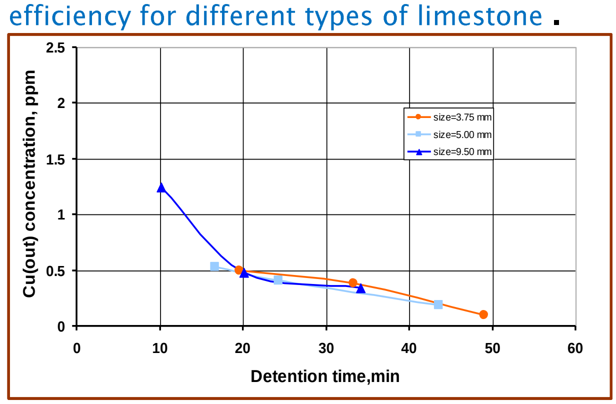


c- influent concentration of CU (1.72) mg/l

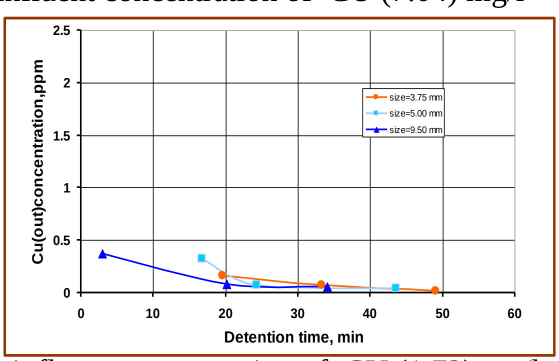
Fig. (6): The effect of detention time on removal efficiency for different types of limestone .



a- influent concentration of CU (7.04) mg/l



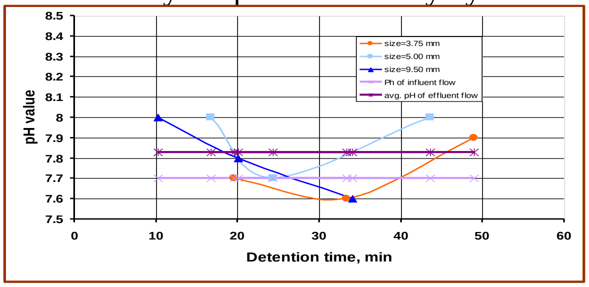
b- infl. concentration of CU(4.39)mg/l



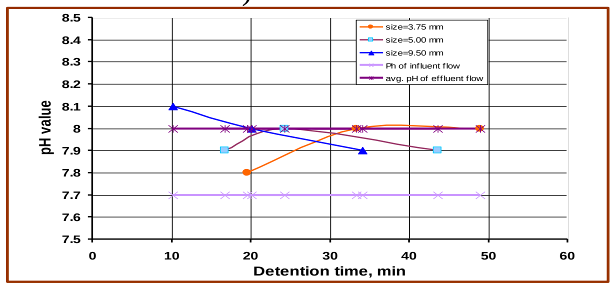
c- influent concentration of CU (1.72) mg/l

Fig (7): The Effect of detention time on the effluent cu concentrations for different types of limestone

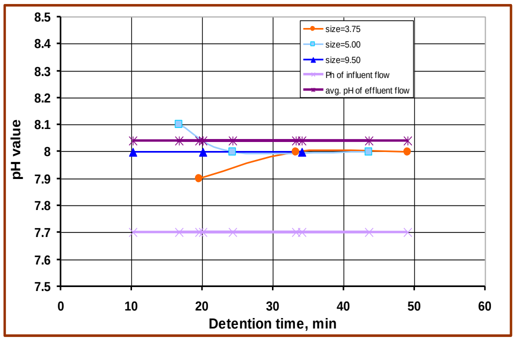
C- the influent pH was set constant at (7.7) for all experiments with a dosing of artificial copper solution from (CuN03). It can be observed from Figure (8) that the average pH of the effluent increased by range from (7.83) to (8.04) for different cu concentrations, this is due to the presence of CO_3 in limestone and the amount of limestone has been increased further (alkaline condition). It can be observed that the increase in metal removal is related to the increase in pH. The removal of cu is influenced by the pH and not only by the media (limestone and its size).



a- influent concentration of CU (7.04) mg/l



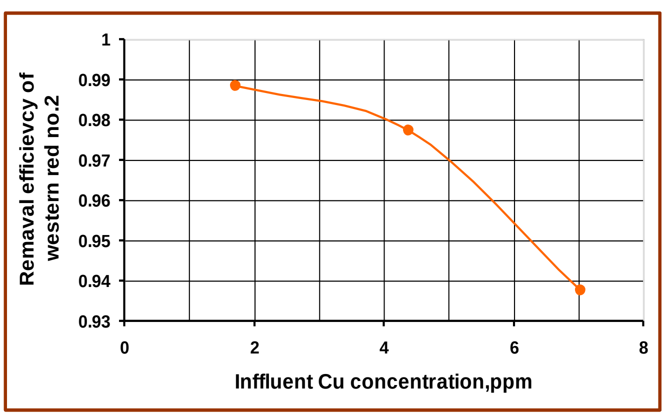
b- infl. concentration of CU(4.39) mg/l



c- influent concentration of CU (1.72) mg/l

Fig (8): pH values vrs. detention time for different types of limestone .

d- it was noted that the western red no.2 with 3.75 mm diameter is the most effective type stone with removal efficiencies of (93.75, 98.77 and 98.83)% and the least value of the effluent copper concentration (0.44, 0.10 and 0.02) ppm respectively. The higher removal efficiency (98.83) % has been at the lowest influent concentration (1.72) ppm as shown in Fig. (9). The lowest effluent copper concentration (0.02) ppm is at the lowest influent copper concentrations (1.72) ppm as shown in Fig. (10). The percentage removal of cu increases with the decrease in the particle size of limestone, this is due to the good surface contact between the particle and cu solution.



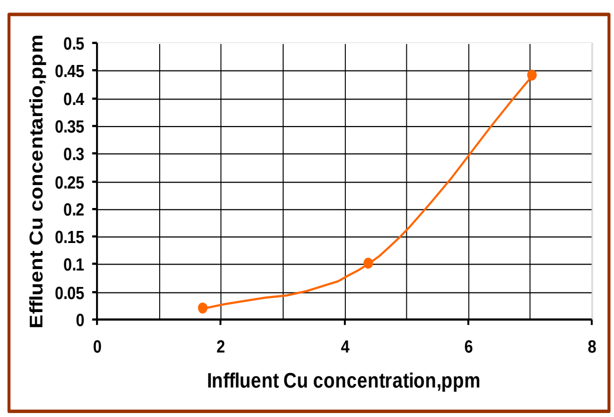
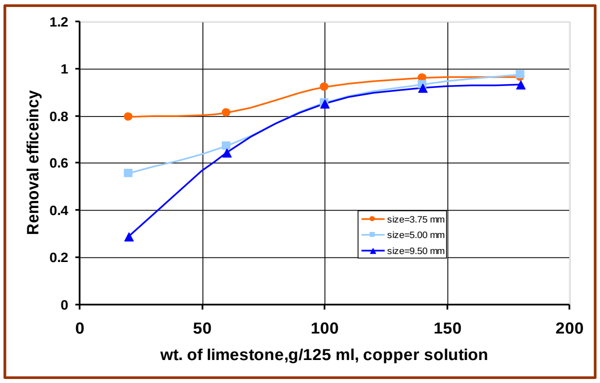


Fig (9):The relationship between the removal efficiency and the influent copper concentrations .

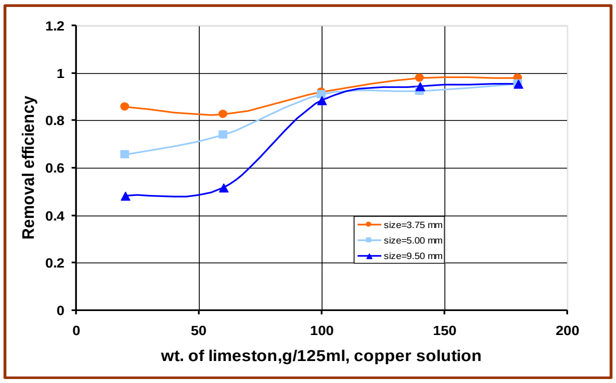
Fig (10): The relationship between the effluent copper concentration and influent copper concent

3.3 Batch Experiment Methodology

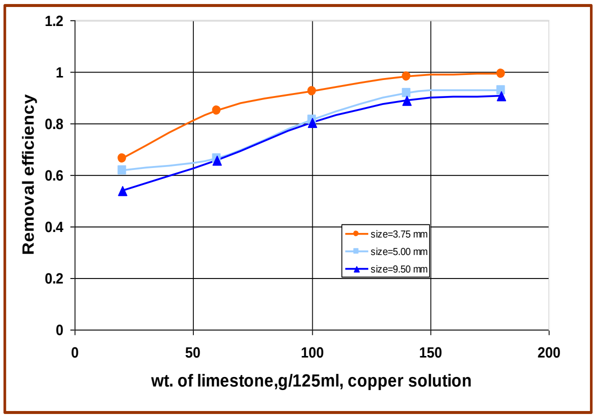
The removal efficiency is increased with the increase of the volume of limestone (calculated based on the weight) within constant volume solution (125) ml ,Fig.(11). This indicates that the removal of copper has been influenced by the media specific area (surface area). A trend of increment in efficiency capacity with increment in adsorbent dosage is observed, the maximum efficiency is at weight of (180) g used in this experiment. The increment in adsorption capacity with increase in adsorbent dosage has been expected, since number of adsorbent particles increases and thus more surface areas were available for metals attachment. It is plausible to suggest that with higher dosage of adsorbent, there would be great availability of exchangeable sites for metal ions.



a-influent concentration of CU(7.04) mg/l



b-influent concentration of CU(4.39) mg/l



c- influent concentration of CU (1.72) mg/l

Fig (11): The Effect of volume of limestone on removal efficiency of copper .

3.4 Effective Size of Limestone in Batch Studies

It has been noted that the western red no.2 limestone with diameter of 3.75 is the most effective size for removal of copper from synthetic solution, Table (8). Also it is noted that the behavior of the three types of limestone within the three different influent copper concentrations have not been the same and range from(90)% to (99)%, this means there is a direct correlation between metal ion concentration and removal efficiency. So there is a significant difference in removal rate with decreasing copper concentration from (7.04) ppm to (1.72) ppm.

Table (8): Ranges of removal efficiency for different size of limestone and influent copper concentrations.

Dia. (mm)	Influent Copper Concentration (mg/L)		
	7.04	4.39	1.72
3.75	79.68%-96.44%	85.64%-97.94%	66.27%-99.41%
5.00	55.53%-97.44%	65.37%-95.21%	61.62%-93.02%
9.50	28.97%-93.32%	48.06%-95.16%	54.06%-90.69%

3.5. Field Experiment Methodology

The applicability of the filtration technique process for actual wastewater is validated by treating an industrial effluent sample, collected from (Department of Water Treatment Unit in Dora Power Station-Iraq). For a constant influent copper concentration, the removal efficiencies have been increased as the increased of the limestone weight for the three types of it, that was confirmed by the field test conducted for these purpose, as shown in Fig. (12).

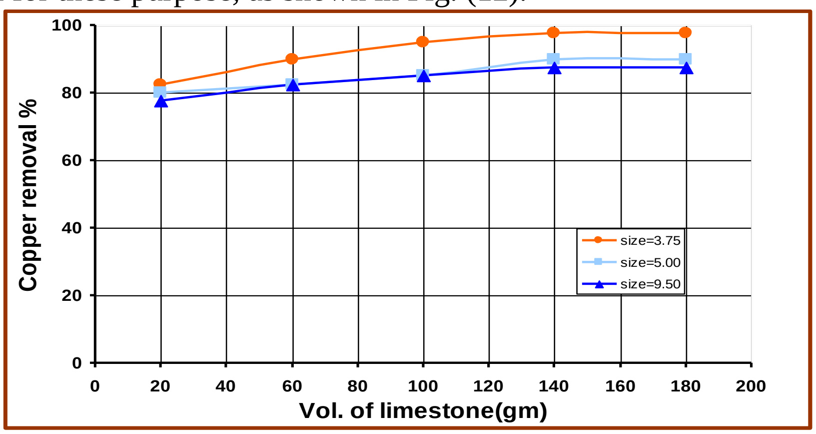


Fig. (12): Effect of volume of limestone on the copper removal for different sizes of limestone, Al-Dura Electrical Station-Iraq.

3.6. Effect of the Variables on Cu Concentration

In the physical model calibration, a computers program of multiple regressions is used to obtain a set of coefficients for a linear model, also it is used to assess the relative importance of the predictor variables (C^{in}, D^{L}, S^{L} and R^{t}) and how well dose the linear model represent the observed data. The following regression models are derived for the Cu concentration of the effluent flow.

$$C_{OUT} = C_{in}^{1.68} * D_{L}^{-0.2} * S_{L}^{0.28} * R_{t}^{-1.22} \qquad (1)$$

Where:-

C_{OUT} : Effluent copper concentration, C_{in} : Influent copper concentration, D_{L} : Media size, mm, S_{L} : Surface loading, m3/m2/day, R_{t} : Retention time, min.

The coefficients of determination, R^{2}, standard error of estimate are 0.972 and 0.306 respectively. There are good agreements between the predicted and measured values of the C_{OUT} of the copper, Fig.(13). The partial correlations indicate that C_{in}, S_{L} and R_{t} are the most important variables while D_{L} is less important than the others, Table (9).

Table (9): Statistical information for prediction (copper concentration).

	C_{in}	D_L	S_L	R_t	C_{OUT}
C_{in}	1.00	0.00	0.00	0.00	0.80
D_L	0.00	1.00	0.40	-0.40	0.19
S_L	0.00	0.44	1.00	-1.00	0.55
R_t	0.00	-0.44	-1.00	1.00	-0.55
C_{OUT}	0.80	0.19	0.60	-0.60	1.00

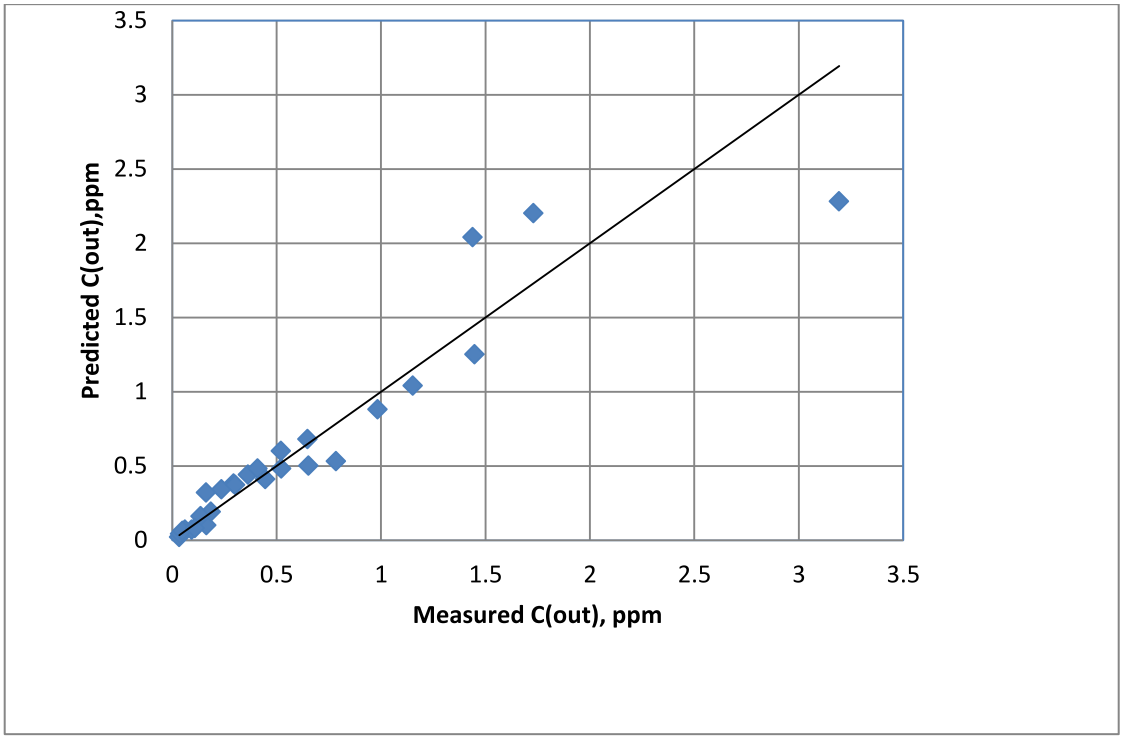


Fig.(13): Comparison between the Predicted and Measured C(out) in ppm

4. Conclusions

Based on the preliminary results, it can be concluded that :

- The batch experiments show that limestone removed about more than (90) % of copper with shaking and settling times of (60) and (90) minutes, respectively. The increase in adsorbent dosage increases the percentage removal of copper due to increase of the volume of limestone (the weight equal to 180 g).
- In the upflow column, the experimental data showed that lower flow rate resulted in higher removal efficiency. This is due to the increase in a contact period to surface between the particle and copper solution. This was further proven in the filtration experiment whereby above (90) % removal of Cu was achieved at retention time of (49) min, surface-loading rate of (13.05) m3/m2 per day.
- During the test it was notice that a decrease in particle size corresponds to an increase in surface area and therefore an increase in available active sites, suggesting an overall increase in metal removal that must be investigated.

- Utilization of limestone for the treatment of water and wastewater containing heavy metals is gaining attention as a simple, effective and economical method of treatment. Limestone is plentiful, inexpensive and readily available. The obtained results showed that limestone is good adsorbing medium for metal ions and had high adsorption yields for the treatment of wastewater containing copper ions. Adsorption process was among the mechanisms involved during the removal process.
- When the physical model is calibrated, the partial correlations indicate that influent concentration of copper, surface loading (flow rate) and detention time are the most important variables while the size of limestone is not important than the others.
- The smallest particle size (3.75) mm showed the best removal efficiency for all adsorbents, which is probably because of the larger surface area available, and the increase in the external surface area of the sorbent available for adsorption.
- The average pH at the effluent increased by a range from (7.83) to (8.04) for different Cu concentrations, due to the present of CO_3 in limestone and the amount of limestone was increased further.
- Compared to the removal from synthetic solutions, the removal rates of the studied metal from wastewater seem to be the same. The higher removal efficiency (97.5) % was achieved by the western red no.2 limestone.

References

António A. L. S. Duarte, João M. D. Machado and Paulo J. Ramisio (2010), "Efficiency Removal Copper from Potable Water Using a Pine Bark Porous Media", Recent of Researches in Environment, Energy Systems and Sustainability, Isbn: 978-1-61804-088-6.

Berrin T. (2008), " New Technologies for Water and Wastewater Treatment: A Survey of Recent Patents", Recent Patents on Chemical Engineering, pp. 17-26.

Hosseini S.N. and Mirbagheri S.A.(2010), "Pilot Plant Investigation on Petrochemical Wastewater Treatment for the Removal of Copper and Chromium with the Objective of Reuse".

Nikola Stanić (2010), "Critical Review on the Adsorptive Removal of Heavy Metals by Iron Oxides Based Media", UNESCO-IHE Institute for Water Education, Delft, the Netherlands.

Norilhamiah Y. and Ahmad F. R.(2010), "Copper Removal from Hazardous Waste Landfill Leachate Using Peat as an Adsorbent", Health and Environmental Journal, Vol. 1, No.2.

Onundi Y.B., Mamun A.A., Al Khatib M.F. and Ahmed Y.M.(2010), " Adsorption of Copper, Nickel and Lead Ions from Synthetic Semiconductor Industrial Wastewater by Palm Shell Activated Carbon", Int. J. Environ. Sci. Tech., 7 (4), pp. 751-758.

Onyeji, L. I.; Aboje, A. A. (2011), "Removal of Heavy Metals from Dye Effluent Using Activated Carbon Produced from Coconut Shell", International Journal of Engineering Science and Technology (IJEST), Vol. 3 No.12 .

Zhou H. and Smith D.W.(2002), "Advanced Technologies in Water and Wastewater Treatment", J. Environ. Eng. Sci. 1: 247–264.-