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Aeration, Alum, and Kaolin Ore for Nutrient and Heavy Metal Removal from Urban Wastewater for the Purpose of Reuse and Conservation

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ABSTRACT

Domestic and industrial wastewater contributed to some urban wastewater, which requires specific processing before being disposed into surface waters or reused for irrigation. This paper aimed to employ kaolin as an adsorbent to remove heavy metals from wastewater, as well as aeration and alum to remove nutrients. Experiment were conducted in three parts: first, involved using the aeration method to determine the ideal amount of time to remove or minimize the nutrients. Second, involves treating the solution with potassium alum using various alum doses at the obvious times to eliminate or minimize the nutrients, while third step involves treating the solution with kaolin ore with a size of < 63 µm at various doses, pH, and contact times to remove heavy metals. The findings showed that the aeration method completely removed CO3, OH, PO4, NO3, Ca, and Mn ions after contact time equal 120, 24, 192, 24, 120, and 48 hrs, respectively. Applaying alum treatment method can remove completely CO3, OH, PO4, NO3, and Mn, after contact time 120, 24, 120, 24, and 24 hrs, respectively. When Kaolin ore used as adsorbent, the removal efficiency of Fe, Cd, Cr, Cu, Sr, Mn, and Zn were; 92, 100, 100, 100, 94, 100, and 88 % ,respectively in 24 hours contact time. The experiment succeeds in treatment of industrial wastewater that was within the range of specified limitations for disposing into surface water or reuse in irrigation field as stated by Egyptian standard code using the three successive treatment techniques.

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INTRODUCTION

Water scarcity is a major issue worldwide, particularly in arid and semi-arid regions. Researchers should go find and work on Non-conventional water resources, especially since many activities do not require fresh water. As a result, reuse of treated wastewater became a reality, which serve too the concept of sustainability. Water pollution is responsible for a destructive effect on public health and cause a destroy of aquatic environment (Mridul, et al., 2022). Water pollution was mostly caused by wastewater, particularly urban wastewater. Municipal wastewater from homes, hospitals, and commercial applications, as well as industrial and agricultural wastewater, are some of the sources of urban wastewater. This effluent pollutes surface water by including inorganic pollutants such heavy metals and nutrients. Consequently, numerous research was conducted to remove or minimize these pollutants before they were discharged or used for irrigation (Soliman, 2020). A nutrient is a substance used by an organism to survive, grow, and reproduce that include mainly nitrogen and phosphours components. The potential

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for nutrient removal and recovery from nutrientrich wastewater to aid in sustainable development has recently attracted a lot of interest (Kamilya, et al., 2022). The biological nitrogen removal processes have been widely adopted as the famous method used for removal of nitrogen from wastewater in recent years (Anjali, et al, 2016 a and Weißbach et al.,2016). The conventional biological nitrogen removal process includes nitrification under the aerobic condition followed by denitrification under the anoxic condition (Zhu, et al., 2016). Numerous treatment systems have been put into place to deal with nutrient-rich wastewater, but their applicability have been severely constrained by problems including high cost, poor adaptability to changing organic loading, and poor effluent quality. On the other hand, Constructed wetlands (CWs) are reliable, economical technologies that effectively remove and recycle large amounts of nutrients (Kamilya, et al., 2022). Nutrient removal from natural wastewater sources by electrochemical method and its impact on water quality has been tested by (Laszl et al., 2022). Heavy metals are generally defined as metals with relatively high densities, atomic weights, or atomic numbers. Heavy metals have bad side effect on environment and work on its removal from wastewater became very urgent and requires recent years. Different effective techniques to remove heavy metals from wastewater are currently available (Saleh and Ali, 2018). Heavy metal removal processes, including but not limited to; adsorption, photocatalysis, chemical precipitation, flotation, remediation, ion exchange, electrochemical treatment, coagulation/flocculation, and membrane technologies (Tawfik et al., 2022). These procedures represent cutting-edge technology with high industrial productivity and practical viability. The cost involved, the wastewater's properties, and the process's applicability are generally the most important considerations when choosing the best method for treating wastewater. Kaolin has received considerable recognition as an adsorbent because of its high adsorption capacity. It is generally referred to as clay that is mainly composed of kaolinite and a lower amount of minerals such as quartz and mica etc . Kaolinite with the chemical formula $Al_2[Si_2O_5]\ (OH)_4$ is a dioctahedral 1:1 phyllosilicate formed by superposition of silicon tetrahedral sheets and aluminum octahedral sheets. Adjacent layers are linked by van der Waals forces and hydrogen bonds. The most reactive functional groups in kaolinite are hydroxyl groups, which are capable of taking part in many chemical reactions as well as ion exchange processes (Cheng et al., 2010). Kaolin has been used in the field of wastewater treatment by different ways. According to Qian et al. (2022) who used the pyrolyzed sewage sludge / kaolin / zeolite composite to improve the immobilization of heavy metals in pyrolytic carbon. Guanjie et al. (2022) studied the removal Pb from wastewater by kaolinite / oxalic acid–activated phosphate rock. El-Sheikh et al. (2020) prepared nanokolinite from kaolin and used it for the removal of P-nitrophenol. Alum is a material that is used to treat water, and man has known this for a very long time. Yang et al., 2022 used iron and aluminum electrocoagulation for removal of phosphate in secondary effluent from municipal wastewater treatment plant and studied its Efficiency and mechanism. Aluminum sludge composition and its structure has been tested by (Alia et al., 2022) for its valorization as an alternative natural material for removal of heavy metals from wastewater for further reuse as treated water in variant applications. To remove heavy metal ions from aqueous solutions, kaolin is utilised as an adsorbent However, the lower heavy metal adsorption capacity of kaolin limits its practical application. Calcium alginate immobilised kaolin (kaolin/CA), a novel substance , was created utilising the sol-gel technique (Li et al., 2011). Also, Lin et al. (2014) used kaolin as adsorbent for cgromium removal. Alum is an inorganic substance made up of sulphates, additional metals besides aluminium, and water molecules. In its hydrated state, it is a double salt. It comes in a variety of forms, including potash, soda, ammonium, and chrome alum. The general chemical formula for Alum is $XAl(SO_4)_2 \cdot 12H_2O$**.** Potasium Alum (potassium aluminium sulphate) [$KAl(SO_4)_2.12H_2O$] usually consisting of aluminum sulfate, water of hydration, and the sulfate of potassium and it is widely used for water treatment (Peter, 2006). Mankind has known for a very long time that alum can be used to treat water. Yang et al., 2022 investigated the effectiveness and mechanism of iron and aluminium electrocoagulation for the removal of phosphate in secondary effluent from municipal wastewater treatment plants. Blending alum with plant-based *Cactus Opuntia* and *Moringa oleifera* extracts as natural polymeric coagulants displayed high turbidity reduction potential (Maiti et al., 2021).

This study aims to apply three continuous treatment procedures to urban wastewater that collected from the Kima drain, which receives wastewater from homes, hospitals, and fertilizer factories and is thought to be a point source of pollution in the Nile River. These procedures include: Aeration process for nutrient reduction or removal, Alum (potassium aluminium sulphate) [$KAl(SO_4)_2.12H_2O$] is used as a treatment to remove or reduce both remaining nutrients and heavy metals, and Heavy metal removal utilizing kaolin ore, which is found in significant quantities in Aswan (South of Egypt).

The innovation and the main target of this study is using local materials (Alum and Kaolin ore) exist with resonable price, and apply low cost technique to treat urban wastewater. The treated wastewater will reuse in some activities that not require fresh water like; irrigation of non-food agriculture of landscape or at least recharge the ground water. after matching its characteristics with standards of Egyptian specification code. By applying this concept, the meaning of sustainability can be achieved.

MATERIALS AND METHODS

All chemicals used were analytically grade and purchased from Sigma-Aldrich . Potash alum (aluminium potassium sulfate dodecahydrate, Molar Mass: 258.192 g/mol (anhydrous) 474.37 g/mol (dodecahydrate) , Density1.725 g/cm^3, and deionized (DI) water with resistivity > 18 M.

BDH Company in the UK provided certified atomic absorption spectroscopic standard solutions for Cd, Cr, Cu, Mn, Pb, and Zn (1000 ppm). By dilution the stock solution, working standard solutions 10, 8, 4, and 1 ppm were created.

All the experiments were carried out in Pyrex conical beaker (100 ml) at room temperature under mechanical stirring (150 rmp), the solution pH was adjusted with (1N) NaOH or HCl.

Samples of the wastewater were retrieved from the Kima drain. Pre-cleaned glass reactors were dipped into the drain stream to collect wastewater samples, which were then placed in a 20-L plastic container. Coolers were used to carry samples to the laboratory.

Five kilograms of kaolin ore samples were taken from the Kalabsha area (80 km south of Aswan city, Egypt). A mechanical crusher and a ball mill were used to crush the ore. After that, use an electric agate mortar to grind. The ore was sieved through a sieve measuring < 63 µm.

For experiment using aeration and alum, two glass reactors held 20 liters of wastewater samples each (40x40x40 cm). Every 24 hours, up to 192 hours, 50 mg/l of alum (potassium aluminium sulphate) was added to one reactor while air was injected into another reactor. In the alum reactor, samples were analysed after each addition, and in the aeration reactor, they were examined at predetermined intervals of 24, 48, 120, and 192 hours.

For experiment using kaolin ore, one gm of kaolin (63 µm) sample was mixed with 50 ml 10 ppm mixed standard solution (Cu, Mn, Cd, Cr, Zn, and Pb) in a conical flask. The solution was continuously stirred for 24 hours, filtered using a Whatman 0.45 µm cellulose nitrate membrane , and washed with bidistilled water . The studied heavy metals were measured in the filtrate using atomic absorption spectrophotometer (SP1900 Pye Unicam). The known total amount of additional adsorbate was used to compute the concentration of adsorbed metal ions.

To study the influence of concentration, one gm of kaolin (63 µm) was mixed with 50 ml of each concentration of heavy metal standards (1, 2, 4, 8,and 10 ppm) in a conical flask for 24 hours. When equilibrium was reached, the flask's contents were filtered using a filter paper Whatman 0.45 µm, and metal ions were then determined using an atomic absorption spectrophotometer (AAS). The adsorption removal percentage was determined.

To study the influence of pH on adsorption process, 50 ml of a 10 ppm heavy metal standard combination was used to treat one gm of the kaolin sample, and after that, 0.5 M NaOH or 0.5 M HCl was used to adjust the pH of the adsorption mixture to a range of pH values (3, 5, 7, and 9). After 24 hours, the metals concentrations were determined, and the adsorption capacity was computed.

To study the influence of kaolin ore dosage, 50 ml of a 10 ppm standard combination was used to treat 0.25, 0.5, 1, and 2 gm of kaolin. AAS was used to estimate the final concentration of the metals after 24 hours, and the adsorption capacity was computed.

After establishing the ideal aeration time and alum dose, a kaolin (63 $_{\mu}$m) experiment was conducted on a wastewater sample to determine the ideal pH, dose, and treatment time.

According to standard methods, the conductivity, pH, PO_4, SO_4,SiO_2, NO_3, OH,CO_3, Cl, F, Ca, Mg, Na, and Fe of the original wastewater sample and the samples obtained from each treatment were examined. The Atomic absorption spectrophotometer, SP1900 Pye Unicum, was used to analyse the metals Cr, Co, Cu, Sr, Mn, Pb, Cd, and Zn.

RESULTS AND DISCUSSIONS

The results of the aeration method for treatment of the wastewater sample showed high efficiency (100%) after 120 hours for completely removing CO_3, OH, and Mn ions, while it decreased the concentrations of pH, Ca, Cl, NO_3, SiO_2, PO_4, Na, and Fe at various times (Table 1). NO_3 decreased from 42 to 34 mg/l and Ca from 44.8 to 42.4 mg/l after 48 hrs, SiO_2 17-8.5 mg/l and Cl 76.5-6.3 mg/l after 120 hrs. The elimination of chloride was accomplished by some metal chlorides adhering to the precipitate. After 48 hours, the effectiveness of removing nitrate reduced, and with time nitrate concentration increased. This might be because the nitrification process caused free ammonia to be converted from nitrite to nitrate (Haipeng et al., 2022). Groundwater nitrate levels were lowered by adding 315-mish iron and being buffered at pH 8.8 (Cheng et al, 1997). After 192 hours, PO_4 was eliminated (with a 100% removal efficiency), possibly as a result of Ca and Al phosphate precipitation or phosphate adsorption on the hydrous iron oxide (Furumal and Ohgakl , 1989; Biao et al., 2021). After 120 hours, the maximum

Table 1. Efficiency of treatment (%) of the study items in the wastewater.

Time.	24 hr			48 hr			120 hr		192 hr	
Treatment Methods	I	II	III	I	II	III	I	II	I	II
Ions	Treatment Removal Efficiency %									
pH	3.51	5.04	-	6.68	9.09	-	12.2	12.9	24.6	23.7
CO_3	27.7	44.45	-	55.5	86.1	-	100	100	100	100
OH	100	100	-	100	100	-	100	100	100	100
Cl	83.6	83.6	-	91.6	91.6	-	91.6	91.6	91.6	91.6
PO_4	22.6	62.7	-	47.9	75.8	-	96.5	100	100	100
NO_3	100	100	-	80.9	100	-	100	100	100	100
SiO_2	31.7	58.8	-	43.9	18.2	-	50	48.2	48.2	32.9
Ca	96.4	96.4	-	94.1	96.4	-	100	100	100	100
Na	66.3	64.1	-	63	66.3	-	63	59.9	63	58.7
Fe	5.75	5.75	92	3.45	21.8	93	82.7	69.9	81.6	56.3
Cd	23.3	20	100	33.3	20	100	36.6	46.6	40	66.6
Cr	33.3	33.3	100	66	33.3	100	33.3	33.3	66.6	66.6
Cu	100	100	100	50	0.0	100	0.0	50	100	100
Sr	73.3	66.6	94	80	73.3	92	93.3	73.3	86	93
Mn	50	100	100	100	100	100	100	100	25	75
Zn	75	87.5	88	87.5	37.5	87	62.5	25	25	50

***I:** Treatment with aeration.* ***II:** Treatment with Alum.* *III: Treatment with kaolin* reduction in SiO_2 was observed. Sodium removal efficiency increased for the first 24 hours and then decreased due to adsorption of Na ions on the negatively precipitated charge. Due to the acidic action of the CO_2 in the air, pH dropped from 9.14 (the original wastewater concentration) to 6.89 after 120 hours of aeration (Soltan, 1991). The treatment efficiency of aeration for the heavy metals Fe, Cd, Cr, Cu, Sr, and Zn has not shown consistent trends, but virtually all of them reached maximum efficiency in the period of 48 to 120 hours.

These heavy metals might adhere to the solution-produced colloidal precipitate. In tropical settings, constructed wetlands were employed to treat certain toxic wastewater, removing more than 99% of the Cr and Ni contents (Polprasert et al., 1996 and Fazila et al., 2022). Nitrate was removed from wastewater using a single-stage and two-stage aerated systems (95% N2 efficiency removal) (Andreadakis et al., 1995 and Lixia Jia et al., 2021).

Table (1) displays the impact of contact time on alum-treated wastewater. The results showed that after 24 hours, OH, NO_3, Mn, and Cu were completely removed, but CO_3 took 120 hours. SiO_2 and Zn concentrations were lowered by the approach after 24 hours, but Na was reduced after 48 hours, and Cl, F, Cd, Sr, and Cr after 192 hours. The sample's initial phosphate concentration was 3.7 mg/l, and the alum approach showed faster elimination after 120 hours than the aeration method (after 192 hours) (Table 2). This decline was brought on by either the precipitation of calcium and aluminium phosphate or the phosphate's adsorption to hydrous aluminium oxide (Ngtez et al., 1999 and Alemu et al., 2022). After 24 hours, the original concentration of hydroxyl ion OH had totally disappeared. This removal was caused by the addition of alum, which produces the Al^{+3} ion in solution and releases the hydroxyl OH negative ion . Mn was removed as a result of microbes consuming it during the oxidation process. Because of the redissolved suspended or colloidal dehydrated oxide caused by pH reductions, Co, Cu, Cr, Cd, Fe, Pb, and Zn levels decreased (Ajmal et al, 1992 and Robert et al., 2022).

The influence of alum dose (50, 100, and 150 mg/l) on ion removal effectiveness is depicted in Figure 1 . The appropriate alum dose seen was 100 mg/l for CO_3, OH, Cl, PO_4, NO_3, SiO_2, Na, and Ca ions, while the appropriate alum dose for heavy metals was 50 mg/l. For the total elimination of CO_3, OH, and Mn, as well as for the reduction of the concentrations of Cl, PO_4, SiO_2, Na, and Ca, an alum dose of 100 mg/l for 120 hours was sufficient. The alum approach was less efficient than the aeration method in removing the evident heavy metals (30–50% efficiency removal). Al, Fi, Fe, and Mn oxides or hydroxides, which could make up the suspended particle matter (SPM), were found to have significantly differing binding affinities for metals (Ferreira et al., 1997). Trace metal binding to natural colloids and particles has been examined in relation to size and geochemical parameters, with Cd being more strongly bonded to the smallest fraction than Cu (Lead et al., 1999).

Applying kaolin method and studing the influence of initial metal concentrations. Table (3) illustrates that all initial element standards for Cr, Cd, Cu, and Pb completely adsorbed (100 %) on the surface of kaolin. Shaymaa & Seroor (2021) evaluated kaolin clay's capacity to remove lead from synthetic wastewater as an adsorbent material. They discovered The conditions of 2g adsorbent weight, 10 mg/L initial metal concentration, and pH 5 produced the highest removal effectiveness (85.1%). For the remaining elements, the greatest adsorption of Mn was found at 10 ppm Mn initial concentration, while the maximum adsorption of Zn, Sr, and Fe was

Table 2. Nutrient concentrations (ppm) in untreated and treated samples, and Egyptian standards.

Sample	pH	CO_3	OH	Cl	NO_3	PO_4	SiO_2	Ca	Na	F
Untreated sample	9.14	144	768	76.5	42	3.7	17	44.8	46	0.3
Aeration treatment	6.08	0.0	0.0	63	34	0.0	8.5	42.4	17	0.42
Alum treatment	6.92	0.0	0.0	63	0.0	0.0	8.8	43.2	15.5	0.06
Egyptian Standards	6-9	---	---	1.0	30	1.0	---	---	---	1.0

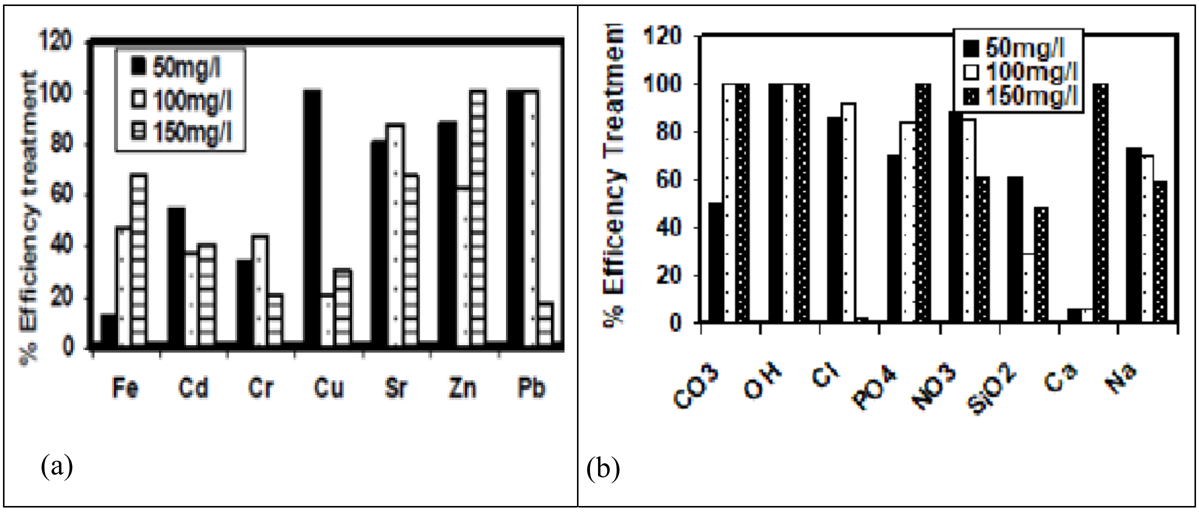

Fig. 1. (a). Effect of alum dose on heavy metal removal efficiency, (b). Effect of alum dose on nutrient removal efficien

Table 3. Influence of initial heavy metals concentration on efficiency of adsorption

Initial Metal Concentration (ppm)	Mn	Sr	Fe	Cr	Pb	Cd	Zn	Cu
	% Adsorption							
1	94	98	99	100	100	100	99	100
2	95.5	95	100	100	100	100	100	100
4	91.7	93	98.7	100	100	100	98.7	100
8	95.5	99	100	100	100	100	100	100
10	97	91	99.5	100	100	100	99.5	100

observed at 8 ppm. Parkman et al., (1998) reported that the highest initial Sr concentration had the greatest percent absorption on kaolinite.

To study the influence of pH, 10 ppm of the standard mixture's components used, Heavy metal adsorption on kaolin was investigated at various pH levels. The results in (Fig. 2) demonstrate that the examined heavy metals' adsorption increased as pH rose from 3 to 6.5, with the highest adsorption of the metals occurring at pH 7. This was explained that at the low pH value , hydrogen ions on the adsorbent surface which led to less attraction to metal ions , while with increase pH value the adsorbent surface became negatively charged and attract metal ions (Pandey et al., 2007). The precipitation of these metals causes a decrease in metal adsorption after pH 7.

Awwad et al., (2021) used a modified iron-kaolin clay as an adsorbent of Pb(II) and Cd(II) ions from aqueous solutions. They found that the removal percent of Pb(II) and Cd(II) ions increases with increasing pH from 1.0 to 5.5 and then decreases to reach pH 7.0. Rashed et al.(2020) reported the maximum adsorption of Pb and Cd on Muscovite were at pH 6 for Pb and pH7 for Cd.

Another investigation on the heavy metals adsorption on Phormidium sp biomass showed that Pb, Cu, Cd, Zn, and Ni were acceptable at pH 5 (Wang et al., 1998), the maximum adsorption was 13.6 g/kg for Pb; 10.1 g/kg for Cu; 9.6 g/kg for Cd; 9.4 g/kg for Zn and 5.7 g/kg for Ni. Ajmal et al., (1995) reported the greatest Pb, Zn, and Cd adsorption on pyrolusite at pH 7. For Cd, Cu, and Mo removal using carbonaceous material created from waste slurry from a fertiliser factory, the ideal pH was about pH 6, for Cr and Hg it was at pH 2, and for Pb it was almost in the range of 6-7 (Srivestava et al., 1989). Oladipo and Mustafa (2016) studied

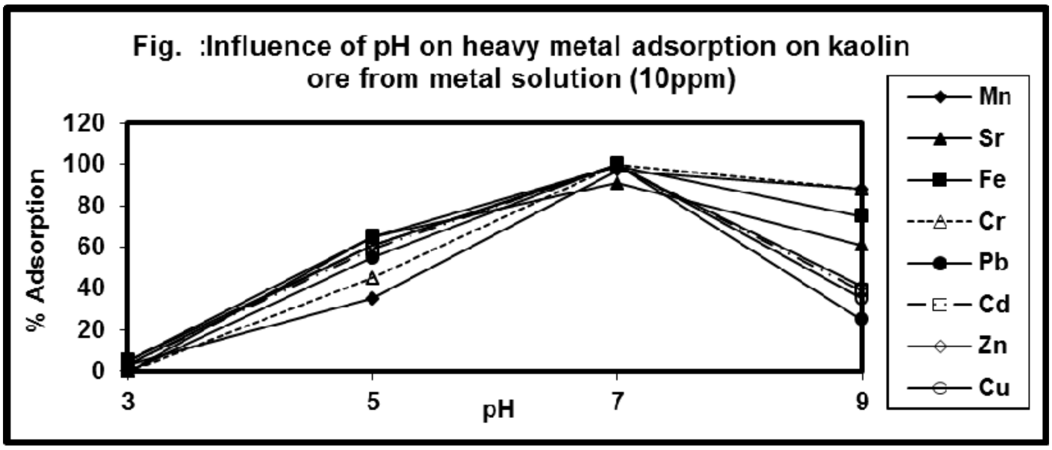

Fig. 2. Effect of pH on the adsorption of heavy metals

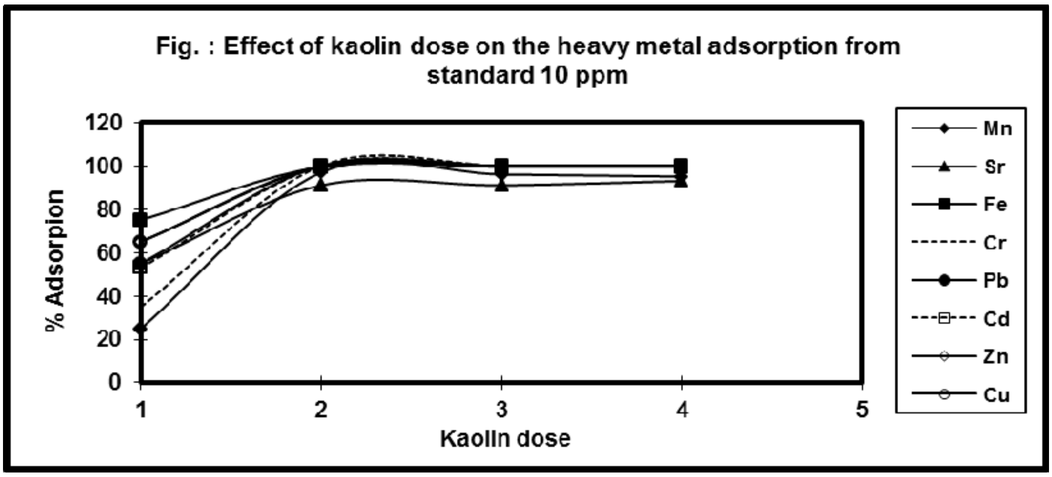

Fig. 3. Effect of kaolin dose (gm) on the adsorption of heavy metals

the removal of boron by functionalized magnesium ferrite nanopowders and found the maximum adsorption was at pH 7.

For the adsorption approach and investigation of kaolin dose influence, different kaolin doses (0.5, 1, 1.5, and 2 gm) were used. The optimal kaolin dose for the greatest adsorption of the examined heavy metals was achieved (Fig.3). It was demonstrated that the adsorption of Co, Cu, Fe, Cd, Cr, Sr, Pb, and Mn increased with increasing kaolin doses and peaked at 2 g, this increased as a result of an increase in the active sites on the surface of kaolin, which leads to the generation of active radical species on the surface of the composite (Abdelwahab and Helaly, 2017). Rui et al. (2022) used biogenic FeS–kaolin composite (KL–FeS) as a green adsorbent and concluded that the KL–FeS synthesized at a concentration of 2 g/L kaolin performed a better removal effect on heavy metal(loid)s.

According to the results of experimental work, the efficiency of using kaolin in wastewater treatment has been observed. After the proper conditions for heavy metal adsorption were met, sample from Kima drain wastewater was used to study the removal of heavy metals from wastewater. Cu, Sr, Mn, Fe, Pb, Cr, Co, and Cd were measured after adsorption on kaolin using a standard metal solution. Treatment with kaolin ore (size of 63 µm) shown high efficacy for full heavy metal removal. For Cd, Pb, Cu, Cr, and Mn, the adsorption percentage that indicated in Table (4) was 100 percent. Fe, Sr, and Zn concentrations are all decreased by

Table 4. Levels of heavy metals (ppb) in Alum treatment samples and Egyptian standard.

Sample	Fe	Cd	Cu	Cr	Sr	Mn	Pb	Zn
Original sample	430	30	22	32	150	40	32	80
Alum treatment	30	0.0	0.0	0.0	10	0.0	0.0	10
Kaolin treatment	1	0.0	0.0	0.0	0.80	0.0	0.0	0.9
Egyptian Standard*	$\rightarrow$ $\sum \leq 1000$ ppb $\leftarrow$							

**Egyptian limits for treating wastewater discharge to surface water, law 48 of the year 1982 for the protection of the Nile river.*

Table 5. parameters of Langmuir for the adsorption of heavy metal on kaolin

Ions	Adsorption maximum a (mg/kg)	Binding energy b (mg/kg)	R^2 for Langmuir equation
Mn	2.62	0.557	0.224
Fe	1666	1.007	0.999
Zn	1000	1.006	0.999
Sr	90.9	1.003	0.999

kaolin (adsorption percentages of 92%, 94%, and 88%, respectively). In comparison to aeration and alum techniques, the treatment by kaolin method was particularly effective at removing the heavy metals Fe, Cd, Cr, Co, Cu, Sr, Mn, and Pb (Table 4). The wastewater treatment process results shown in Table (4) were within the limits set by the Egyptian Standard Code for disposing into surface water or reuse for irrigation field.

Among the low-cost adsorbents reported to be effective for heavy metal removal from wastewater, Fe (III) hydroxide was used to remove Ni, Cu, Cr, Zn, and Cd from electroplating wastewater (Ajmal et al.,1992). Jia-Boon et al., (2020) reported natural kaolinite clay of Malaysian origin was tested and found to be an effective and low-cost adsorbent for the removal of heavy metal ions such as Cu(II) and Ni(II) in low concentrations in aqueous solution.

Isotherm of Langmiur Adsorption being very important to confirm the results of experimental work that related to adsorption process. The updated Langmuir equation was utilised as the adsorption model, and it was expressed in its linear form (Bohn et al, 1985)

$$1/(x/m) = 1/c\ b + 1/a \qquad (1)$$

where c (mg/kg), is the concentration of adsorbate left in solution at equilibrium. x/m(mg/kg), is the amount of adsorbate adsorbed per unit mass of adsorbent. a , and b (mg/kg) are Langmuir binding energy coefficient and the adsorption maximum, respectively. The equation can be used to get parameters (a) and (b) as shown in Table (5).

It was demonstrated that the highest value of the adsorption maximum parameter employing kaolin (a) was for Fe, while the lowest value was for Mn. Maximum zinc adsorption was lower than for Fe and Sr. Fe, Zn, and Sr had approximately identical kaolin binding energies (b), but Mn had the lowest. This indicates that Mn and Sr were less tightly linked to kaolin than Fe and Zn. From Langmuir isotherms, correlation coefficients (R^2) were shown to be positive and highly significant.

Another research on the binding and removal of heavy metals by Phormidium sp biomass found that the greatest adsorption, as determined by the Langmuir isotherm, was for Pb (13.6 g/kg), Cu (10.1 g/kg), and almost the same amounts for Cd (9.6 g/kg) and Zn (9.4 g/kg) (Wang et al., 1998). The following figures show Langmuir adsorption isotherm of Mn, Fe, Zn, and Sr. Figure (4) show the Langmuir adsorption isotherm of Mn, Fe, Zn, and Sr respectively.

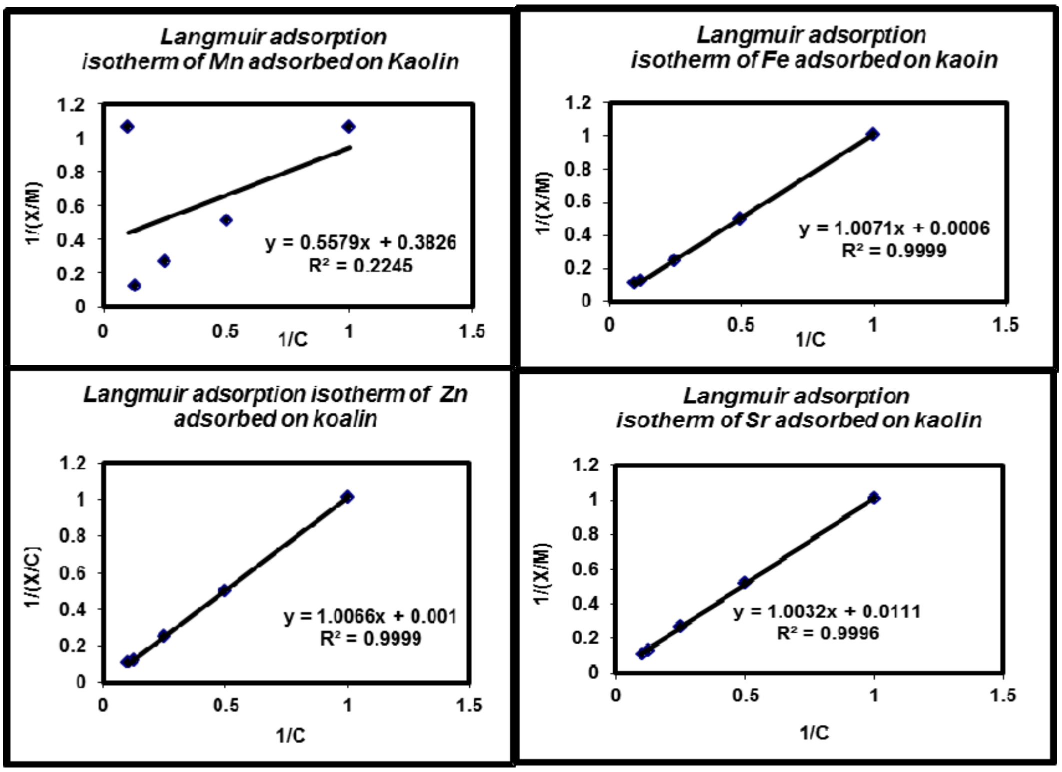

Fig. 4. Langmuir adsorption Isotherm for Mn, Fe, Zn, and Sr

CONCLUSIONS

For the continuous removal of nutrients and heavy metals, techniques such as aeration, alum addition, and adsorption at kaolin surfaces were developed, conclusions can be summarized in the following points:

- The results showed that optimum removal efficiency % by applying aeration method for; CO_3, OH, Cl, PO_4, NO_3, SiO_2, Ca, Na, Fe, Cd, Cr, Sr, Mn, and Zn were, 100, 100, 91.6, 100, 100, 50, 100, 63, 82.7, 40, 60, 93.3, 100, and 87.5 % after contact time equals; 120, 24, 24, 192, 24, 120, 120, 48, 120, 192, 48, 120, 48, and 48 hours, respectively.
- Applaying Alum treatment method can remove completely; CO_3, OH, PO_4, NO_3, and Mn, after contact time; 120, 24, 120, 24, and 24 hours respectively, whever reduce the concentration of Cl, SiO_2, Ca, Na, Fe, Cd, Cr, Sr, and Zn by efficiencies; 91.6, 58.8, 96.4, 66.3, 69.9, 66.6, 66.6, 93, and 87.5 % , respectively.
- When Kaolin ore used as adsorbent the removal efficiency of ; Fe, Cd, Cr, Cu, Sr, Mn, and Zn were; 92, 100, 100, 100, 94, 100, and 88 %, respectively in 24 hours contact time
- The adsorption of Co, Cu, Fe, Cd, Cr, Sr, Pb, and Mn increased with increasing kaolin doses that recorded 2 g, and optimum pH 7.
- For Alum dose and its effect on heavy metals removal 50 mg/L was observed as a reasonable dose, whever 100 mg/L was accepted for neturient removal.

The effluent treatment techniques produced results within the parameters specified by Egyptian standard code for reuse in irrigation or discharge into surface water.

GRANT SUPPORT DETAILS

The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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