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Extraction of Cu^{2+}, Ni^{2+} and Zn^{2+} Using 2-Aminophenol Modified Quecertin and Red Onion Skin Extract from Aqueous Medium

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Abstract

Red onion skin extract and quercetin dihydrate modified with 2-aminophenol were used as adsorbents to extract Cu^{2+}, Ni^{2+} and Zn^{2+} from their aqueous solutions. The unmodified and modified adsorbents were characterized using some physicochemical parameters such as melting point, solubility in different solvents, thin layer chromatography and FTIR. The FTIR revealed presence of various functional groups in the structure of modified and unmodified red onion skin extract and quercetin dihydrate. Extraction studies result showed that the maximum pH for metal removal is 3.30, 8.00 and 6.46 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively. The percentage removal and adsorption capacities of the metal ions increased with increasing contact time, dosage and metal ion concentration. Quercetin dihydrate-diazonium salt (QDDS) showed a higher percentage removal for Cu^{2+} (99.19 %) than Ni^{2+} and Zn^{2+} while Red onions skin extract- diazonium salt (ROSEDS) showed a similar percentage removal for Cu^{2+} (98.57%) > Ni^{2+} (84.51%) > Zn (66.86%). Heavy metal ions were removed in this order; Cu^{2+} (99.19%) > Ni^{2+} (87.64%) > Zn^{2+} (71.56%) using QDDS. The adsorption kinetic studies and isotherm studies indicated that Pseudo-second order kinetics and Freundlich isotherm model best describe the adsorption processes. Therefore, ROSEDS and QDDS have proven to be an effective adsorbent for heavy metal ions from waste waters and industrial effluents.

Keywords: Extraction, Red Onion Skin Extract, 2-aminophenol, Quercetin, Diazonium salt.

INTRODUCTION

The environmental quality is experiencing a steady decline and a continuous deterioration due to the rapid development of petrochemical and chemical industries. Inorganic and organic chemicals such as dyes, phenolic compounds and heavy metals are the major pollutant found in surface water, ground water and even treated wastewater (Selivanovskaya & Latypova, 2003). Heavy metal contamination is found in aqueous wastes of many industries such as radiator manufacturing, tanneries, smelting, metal plating, storage battery, mining operations, chloroalkali, ceramics and glass industries, pigment and paint industries and alloy industries Statistically it has been shown that 70% of industrial effluents in developing countries are discharged untreated into the water bodies polluting the consumable water supply (Igwe & Abia, 2006). The accumulation and magnification of heavy metals by living things reduces their balance and stability in the ecosystem. Therefore it is essential to treat heavy metal polluted water before discharging it into the environment. Conventional methods of treatment have been used in order to extract toxic metals. Such methods are chemical-precipitation, adsorption, solvent extraction, filtration, coagulation-flocculation, ion exchange, evaporation, flotation and membrane method (Cha *et al*., 1997; Momcilovic *et al*., 2011; Thanranitharan *et al*., 2014; Misihairabgwi *et al*., 2014). Adsorption is an efficient and powerful method of separation and purification using some new green agricultural adsorbent called red onion skin extract.

Onion (*Allium cepa*) also recognized as common onion or bulb onion is known to be among the world's oldest vegetable that are grown widely. Onion is known for their characteristics, medical properties and their pungent flavours. It differs in colour, size, flavour and shape. Onions are of three types, the yellow, white and red onion. They are known to contain large amount of dietary flavonoids especially quercetin (Slimestad *et al*., 2007), which are found in much higher concentrations in the onion skin than they are

found in the fleshy bulb (Akoh & Sellappan, 2002; Yao *et al.*, 2004: Kim *et al.*, 2006). Red onion skin also known as *Allium cepa* is one of the agricultural waste which can be used for adsorption. Some of these agro-waste adsorbents possess cellular structures with some functional groups (polyphenols) capable of binding metal complexes. Using agricultural waste products for metal removal not only possess the same advantage as other adsorption materials but it also uses what was once a waste product (Kumar, 2006).

The objective of this study is to extract polyphenols from red onion skin, modify commercial quercetin and red onion skin extract using 2-aminophenol, characterize red onion skin extract and quercetin compound using FTIR, TLC and other physical properties and to extract Cu^{2+}, Ni^{2+} and Zn^{2+} from their aqueous solutions using red onion skin extract and quercetin compounds.

MATERIALS AND METHODS

Collection and Preparation of Quercetin dihydrate and Red Onions Skin (*Allium cepa)*

Commercial Quercetin dihydrate was procured from central drug house (CDH) (p) Limited and used without further purification. The red onions skin used in this research were duly collected from slaughter central market, Trans Amadi Port Harcourt River State, Nigeria. They were put in a polythene bag and moved to the laboratory. The red-onion skin were sorted, thoroughly washed, properly rinsed with distilled water to remove soluble salt, dust particles and other available impurities. After that, it was properly and carefully air-dried for 10 days and afterwards was pulverized and was duly stored in an air – tight container under suitable laboratory conditions.

Extraction of Polyphenols from Red Onion Skin

Fifty grams (50 g) of the pulverized ROS were subjected to extraction using 500 ml of methanol in a soxhlet extractor for seven hours. The onion extract-solvent mixture was subjected to evaporation to recover the onion extract. The concentrated onion extract was washed with boiled water. The aqueous layer was decanted and allowed to cool. Futhermore the residue was dissolved in 50 ml of methanol containing about 2 ml of conc. hydrochloric acid (HCl) to strip adhering oil and methanol; this was allowed to stand uninterruptedly for air – drying. A yellowish-brown compound was obtained after 48 hours. The percentage yield of the onion-extract was determined. The same sample extraction procedure above was carried out using 500 ml of acetone as solvent under the same conditions which yielded a brown coloured compound. The percentage yield of the extract was determined.

Again, fifty grams (50 g) of pulverized red onion skin were subjected to batch extraction by utilizing hot-water and a simple apparatus (beaker). The pulverized red onions skin was soaked in hot water (H_2O) (100 ^oC) for 3 hours with a continuous stirring, after which the mixture was filtered. The extract was recovered from solution by distillation using water bath.

Modification and Coupling Procedures

This procedure of modification of Quercetin dihydrate and red onion extract was adopted from Akaranta & Efanga (1997).

Preparation of Alkaline Quercetin Solution

Ten percent (10 %) sodium hydroxide (NaOH) solution was prepared by dissolving 3 g of sodium hydroxide (NaOH) pellets in 27 ml of water in a 250 ml capacity conical flask.

A measured amount of 1.2685 g of quercetindihydrate (0.005 mol) was dissolved in 11cm^3 of the prepared NaOH solution, the mixture was stirred until complete dissociation occurred. The solution was cooled further in an ice bath.

Preparation of Alkaline Red-Onion Skin Extract Solution

Ten percent (10 %) sodium hydroxide solution was prepared by dissolving 3 g of soduim hydroxide pellets in 27 ml of water in a 250 ml capacity conical flask. 3.6 g of the pulverized/milled onions skin-extract were weighed and dissolved in the prepared soduim hydroxide solution with continues stirring. The solution was cooled in an ice-bath.

Preparation of Benezenediazonium Salt Solution (diazotization) and its Coupling with Quercetin Dihdrate Solution

Dry sodium nitrite (0.2587 g, 0.005 mol) was dissolved in 2 cm^3 of cold water (0-5 ^oC) and the solution was cooled in an ice–bath. A measured amount of 0.45015 g (0.005 mol) of 2-aminophenol was dissolved with 17 cm^3 of cold distilled water in a 100 ml conical flask. Specifically, 4.5 ml of concentrated Hydrochloric acid was slowly added into the mixture as the stirring continues until the mixture was practically and fully dissolved. The solution was then stirred in an ice-bath and cold solution of sodium nitrite was added dropwise into the acidified solution of 2-aminophenol with a continuous stirring in an ice-bath which spanned for 3-5 minutes.

Coupling

The benzenediazonium salt solution was added slowly into the alkaline quercetin dihydrate solution for 3-5 minutes.The reaction mixture was stirred effectively under ice-bath during addition. The mixture was stirred at 0^oC for 30 minutes for reaction completion. The mixture was filtered by suction filteration. The solid product on the buchner funnel was washed with a small amount of cold distilled water and dried with the suction turned on for few minutes. The product was tranfered to a watch-glass and allowed to dry for 2 days.

The product was weighed and percentage yield for the reactions was determined.

Preparation of Benezenediazonium Salt Solution (diazotization) and its Coupling with ROSE Solution

A measured amount of 0.6898 gram of sodium nitrite (0.005 mol) was dissolved in 5 ml of cold water and the solution was cooled in an ice-bath. A measurement of 2-aminophenol (1.2004 g, 0.005 mol) was dissolved with 45 ml of cold distilled water in a 150 ml conical flask. 12 ml of concentrated HCl was added into the mixture slowly as the stirring was continuous until it dissolved completely; the solution was stirred in an ice-bath. The cold solution of sodium nitrite was added drop wise into the acidified solution of 2-aminophenol with continuous stirring in an ice-bath for 3-5 minutes.

Coupling

The 2-aminophenoldiazonium salt solution was added slowly into the alkaline solution of red onion-skin extract for 5 minutes and afterwards, the mixture was stirred at 0 ^{o}C for 30 minutes to complete the reaction. The mixture was filtered by suction filteration. The solid product on the buchner funnel was washed with a small amount of cold water and dried with the suction turned on for a few minutes. The product was tranfered to a watch-glass and allowed to dry for 2 days after which it was weighed and percentage yield for the reactions was determined.

Characterization of Azo-Dye

Quercetin dehydrate (QD), Quercetin dihydrate-diazonium salt (QDDS), Red onions skin-extract (ROSE) and Red onions skin extract-diazonium salt (ROSEDS) were characterized using Fourier transform infra-red spectroscopy, solubility, thin layer chromatogaphy, colour and melting point.

Preparation of the Extractant

Specifically (0.5279 g, 0.005 M) of the azo-dye was weighed, dissolved in a beaker using ethyl acetate and transferred to 250 ml volumetric flask and diluted up to the mark using ethyl acetate.

Extraction of the Selected Heavy Metals

A measured amount of 0.2 ml of Cu^{2+}, Ni^{2+} and Zn^{2+} solutions were poured into different sample bottles, secondly, 1.8 ml of the buffer solution of different pH were added to the sample bottles and lastly, 2 ml of the azo-dye ligand solution (extractant) were added to the mixtures in the sample bottles with the aid of a micro-pipette. The mixture was shaked for 45 minutes with the aid of a mechanical shaker, allowed to stand and separate into two phases. 1ml of the aqueous phase was taken from each mixture and placed in different sample bottles after which it was diluted with 2 ml distilled water to reduce its concentration from 50 ppm to 16.6667 ppm. Each sample was analyzed using atomic absorption spectrophotometer (AAS). The amount of the metal ion extracted at its optimal pH was obtained by the difference between the initial metal ion concentration and the supernatant solution.

Effect of Variation in Adsorbent – Adsorbate Contact/Agitation Time

The effect of contact/agitation time on heavy metal ion extraction using QDDS and ROSEDS was performed by shaking the mixture of the extractant (2 ml), 0.2 ml of each metal ion solution and 1.8 ml of the optimal pH of water for each metal for 10, 20, 30, 40 and 50 minutes. At the end of each contact time, 1ml of the aqueous solution was collected using a pipette and dilluted with 2 ml distilled water into a sample bottle which was analyzed using AAS.

Effect of Variation of Dosage

The effect of dosage on the extraction of heavy metals was studied by shaking the mixture of 0.2 ml of each metal solution and 1.8 ml of the optimal value of pH of buffer and the solution of the extractant at different weights (0.0251 g, 0.055 g, 0.1146 g, 0.1655 g and 0.2020 g). Afterward 1ml of the aqueous solution was diluted using 2 ml distilled water and sent for further AAS analysis.

Effect of Initial Metal Concentration

The effect of metal ion concentration on the extraction of heavy metals was studied by agitating the mixtures of 0.2 ml of metal ion concentration, 1.8 ml of each optimal pH of each of the metal and 2 ml of extract for 45 minutes, after which 1ml of aqueous solution was taken out using pipette, diluted to various concentration of 5 mg/l, 10 mg/l, 16.6667 mg/l, 20mg/l and 25 mg/l and afterwards sent for AAS analysis.

RESULT AND DISCUSSION

The solubility of the ROSE and ROSEDS in different solvents are presented in Table 1. These adsorbents are highly insoluble in water and hexane both at room temperature and at increased temperature (80 ^{o}C and 35 ^{o}C), sparingly soluble in acetone both at room temperature and at elevated temperature (40 ^{o}C) but soluble in ethanol, DMSO, ethyl acetate and methanol.

Table 1 Solubility of the adsorbent in varying solvents

Compound	Water		Acetone		Ethanol		DMSO		Methanol		Hexane		Ethyl Acetate	
Temperature		80°C	RT	40°C	RT	60°C	RT	80°C	RT	55°C	RT	35°C	RT	50°C
ROSE	HI	HI	SS	VS	VS	VS	VS	VS	VS	VS	I	I	S	S
ROSEDS	HI	HI	SS	SS	VS	VS	VS	VS	VS	VS	I	I	S	S

Key: RT- Room Temperature, I – Insoluble, HI – Highly insoluble, S – Soluble, SS – Sparingly soluble, VS – Very soluble.

Melting point Determination and other Physical Properties of the Samples

The melting points and other physical properties of ROSE and ROSEDS are presented in Table 2. The melting points of the ROSE and ROSEDS were not certain; this could be attributed to the fact that they are impure compounds. Below 300^0C all the adsorbents did not melt. This observation emanated from the presence of some flavonoids (polyphenolic mixtures) within the structure of the ROS (*Allium cepa*) extract. These flavonoids are highly capable of reacting with diazonium salts. Similar observation was reported recently by Akaranta and Efanga, 1997.

Extraction of polyphenols from ROS using methanol as a solvent produced a greater percentage yield of 14.8512% than using acetone (11.4525%) and water (6.9519%) as a solvent.

The colour of red onion skin extract from methanol solvent is yellowish brown while the extract from acetone and water are brown in colour. The yellowish colour observed from the methanol extract could be attributed to a much higher concentration of quercetin (which is yellow in colour) found in the polyphenols extracted using methanol as solvent.

The Rf value (Retention value) of the thin layer chromatography for ROSE and ROSEDS are 0.6429 and 0.9285 respectively, the difference in these values show that the modification process was feasible.

Table 2: Physical properties of adsorbents before and after modification

Compound	Colour	Percentage yield (%)	Melting point	Retention value (Rf)
ROSE from methanol	Yellowish brown	14.8512	NS	0.6429
ROSE from acetone	Brown	11.4525	NS	0.6429
ROSE from water	Brown	6.9519	NS	0.6429
QDDS	Reddish-brown	201.3165	NS	0.7250
ROSEDS	Reddish-brown	121.2861	NS	0.9285

NS – Not Sharp

FTIR Results

Both the unmodified adsorbents (Quecertin dehydrate (QD) and ROSE) and the modified adsorbents (QDDS and ROSEDS) undergo adsorption characterization using FTIR spectrophotometer. The spectra results shown in Tables 3 and 4, present some prominent functional groups such as C=O, -CH, -OH, -COOH, -NH, S=O and C-N which are responsible for metal chelatng.

Table 3: FTIR of unmodified adsorbents (QD and ROSE)

Type of vibration/group	Frequency/Band (cm^{-1}) for QD	Frequency/Band (cm^{-1}) for ROSE	Remark
O-H	3416.12	3418.998 – 3223.319	Stretching vibration attributed to O-H groups present in polyphenol group and carboxylic acid
C-H	2903.137 – 2721.084	2864.809	Probably due to saturated C-H stretching vibration of the aromatic ring.
C=O	1675.997	1852.966	Most likely due carbonyl(C=O) group stretch of cyclic ketone
C=C	1545.16	1619.045	May probably be the presence of C=C bond in benzene ring.
C-C	1394.024	1410.887	May be due to the stretching movement of C=C bond in benzene ring.
C-O and C-O-C	1073.843	1273.899	Probably because of stetch vibration of C-O-C or C-O present in the ring C
S=O	-	941.2308	May be due to the presence of sulfoxide group.
Benzene ring	-	757.9616	Most likely the presence disudstitution meta, para or ortho on benzene ring.

Table 3 shows the characteristics adsorption frequency of QD and ROSE. The strong-band of 3416.1 cm^{-1} and 3418.9-3223.3 cm^{-1} of QD and ROSE respectively may be because of the stretching and bending vibrations of 5-OH groups (polyphenol) present in the flavanol (Avisha *et al.,* 2012). The peak at 2903.1 - 2721.1cm^{-1} and 2864.8 cm^{-1} for QD and ROSE respectively are most likely to be the C-H stretching (saturated) vibration of the ring (aromatic) (Avisha *et al.,* 2012). The band at 1675.9 cm^{-1} is probably because of the presence of carbonyl group stretching of cyclic-ketone (Torres *et al.,* 2003). The stretching movement of C=C non-conjugated bond of the ring shown in peak 1675.9 cm^{-1} and 1619.0 cm^{-1} while the peak at 1394 cm^{-1} and 1410 cm^{-1} of QD and ROSE may be due to the vibration of C-C bond in the compound. The appearance of 1073.8 cm^{-1} band is most-likely due to the presence of alkoxy group C-O-C and C-O of ring C and presence of S=O group found in ROSE.

Table 4: FTIR of modified adsorbents (QDDS and ROSEDS)

Type of vibration/group	Frequency/Band (cm^{-1}) for QDDS	Frequency/Band (cm^{-1}) for ROSEDS	Remark
O-H	3506.439 3257.173	3460.331 3358.899	Stretching vibration attributed to O-H probably due to the presence of water, alcohol and carboxylic acid.
C-H	2798.058	2843.5 – 2961.6	Probably due to saturated C-H stretching vibration of the aromatic ring.
C=O	1749.522	1767.4	Most likely due carbonyl(C=O) group stretch of cyclic ketone
C=C	1574.302	1567.6	May probably be the presence of C=C bond in benzene ring.
N=N	1410.169	1567.6/1438.7	Could probably be attributed to the presence of azo compound
C-N	1212.171	1297.563	Could indicate the presence of C-N bond.
C-C	1394.024	1438.7	May be due to the strectching movement of C-C bond in the benzene ring.
C-O and C-O-C	1035.721	1179.0	Probably because of stretch vibration of C-O of carboxylic acid and C-O-C of ring C.
C-OH	-	1021.3	May be due to the presence of C-OH group.
Benzene ring	883.5241	729.2	Most likely the presence disudstitution meta, para or ortho on benzene ring.

The FTIR-spectra result of QDDS and ROSEDS presented in table 4 reports that the strong/sharp band between 3506.44 - 3139.0 cm^{-1} and 3460 - 3229.3 cm^{-1} for QDDS and ROSEDS respectively shown the presence of -OH stretch of water and alcohol, -COOH in ROSEDS and –NH (Avisha *et al.,* 2012) but the sharpness of the peak indicate that its probably due to the stretch and bending movement of polyphenol (OH) groups present in flavonoids. The 2798.0cm^{-1} band for QDDS and 2843.7cm^{-1} -2961.7$cm^{-1}$and for ROSEDS may be attributed to –CH stretching (saturated) vibration of the ring (aromatic) (Avisha *et al.,* 2012). The peak which appear at 1767 cm^{-1} most probably may be due to carbonyl group present (Torres *et al*., 2003). Mostly likely the stretching movement/vibration of C=C aromatic ring form a peak at 1574.3 cm^{-1} – 1410 cm^{-1} for QDDS and 1567.6 cm^{-1} for ROSEDS. The peak at 1410.2 cm^{-1} - 1574.3 cm^{-1} and 1438.7 cm^{-1} – 1567 cm^{-1} for QDDS and ROSEDS respectively may be attributed to the presence of azo functional group N=N while 1297.5 cm^{-1} and 1212.2 cm^{-1} may indicate the presence of C-N groups (Nasreen, Rana & Yasmeen, 2011; Ahmed, Dewani, Pervez, Mahboobo & Soomro, 2016). The appearance of the peak at 1035.7 cm^{-1} for QDDS and 1021-1179 cm^{-1} for ROSEDS may indicate the presence C-O-C and C-OH stretching movement.

Previous literatures of Waweru *et al.,* 2016 and Uzoukwu, 2009 were also used to compare the presence of these functional group.

Extraction Studies

Effect of pH Variation

Varying the pH for the adsorbate – adsorbent emulsion demonstrated an effect on the percentage removal of the metal ions. The percentage removal of the metal ions were observed to increase as the pH of the mixture increased from 1.12 to 3.3, 1.12 to 8.00 and 1.42 to 6.46 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively. The percentage removal (%R) increased from 72.71 % to 97.42 %, 79.05 % to 98.26 % and 96.35 % to 97.46 % for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively. Increasing the pH of the metal ion solution beyond 3.3, 8.00 and 6.46 showed a decrease in the percentage removal of the ions. This revealed that optimum pH for the metal ion removal occured at 3.3, 8.00 and 6.46 fo Cu^{2+}, Ni^{2+} and Zn^{2+} respectively. Beyond this optimum pH, a gradual decrease was observed at the percentage removal (% removal) emanating from the precipitation of the metal ions from the solution. The process of metal ion

adsorption kinetically occured faster than the chemical precipitation at lesser pH whereas at the optimum pH and beyond precipitation kinetically occured faster than metal adsorption (Appel & Lena, 2002). Similar findings was observed and reporterd by Avisha *et al.* (2012); Ibezim-Ezeani & Okon, 2016.

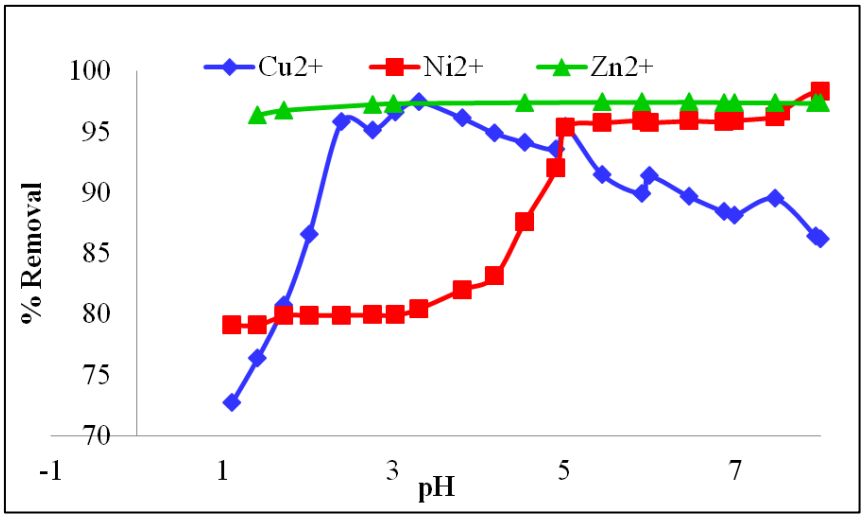

Figure 1: Effect of pH on percentage removal of metal ions using red onion skin extract diazonium salt (ROSEDS)

Adsorption Kinetics

Three adsorption kinetics utilized for this study are Lagergren pseudo-first order, pseudo-second order and intra-particle diffusion. The correlation coefficient /factor, R^2 obtained from Lagergren pseudo-first as presented in Figure 2 are 0.6438, 0.9226 and 0.8695 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using ROSEDS and 0.8137, 0.9702 and 0.9712 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using QDDS respectively.

The correlation coefficient/factor, R^2 obtained from the pseudo-second order as presented in figure 3 are 1, 1, 1 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using ROSEDS whereas the R^2 obtained for the Cu^{2+}, Ni^{2+} and Zn^{2+} removal using QDDS are 1, 0.9999 and 0.9999 respectively.

The correlation coefficient/factor, R^2 obtained from the intra-particle diffusion as presented in figure 4 are 0.8939, 0.9659 and 0.8966 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using ROSEDS and 0.9827, 0.8797 and 0.9164 for Cu^{2+}, Ni^{2+} and Zn^2 respectively.

The data obtained are well fitted with pseudo-second order adsorption kinetics because their correlation coefficient/factors are closer and equal to unity. This implies that pseudo-second order kinetics best describe the Cu^{2+}, Ni^{2+} and Zn^{2+} removal from aqueous solution using ROSEDS and QDDS. Similar observation was reported by Ho & Mckay, 1999.

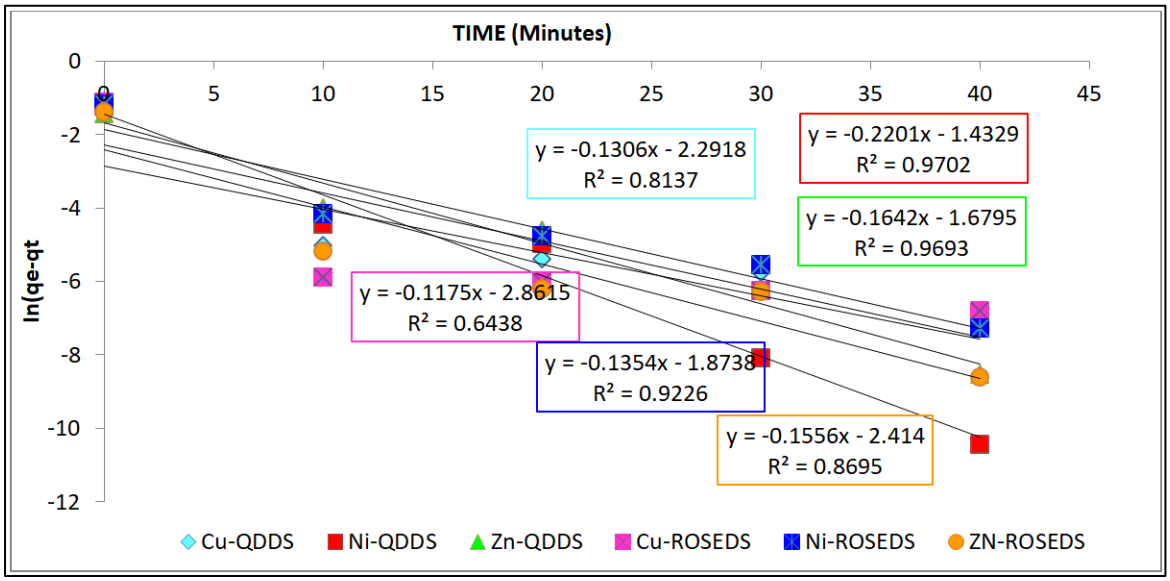

Figure 2: Lagergren pseudo-first order kinetics for metal ions removal using ROSEDS and QDDS

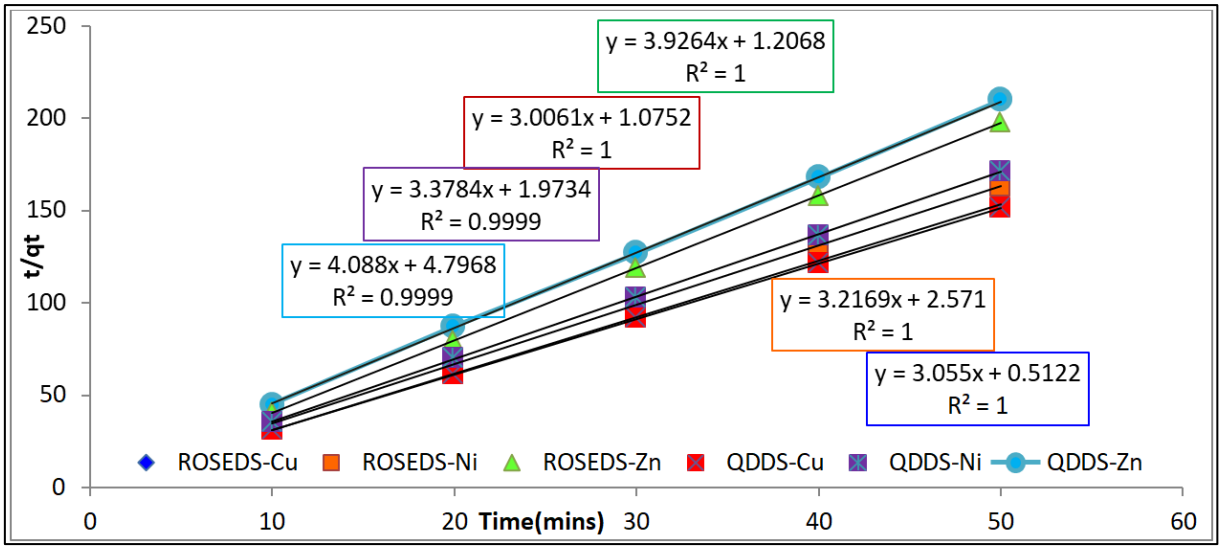

Figure 3: Pseudo-Second order kinetics for metal ions removal using ROSEDS and QDDS

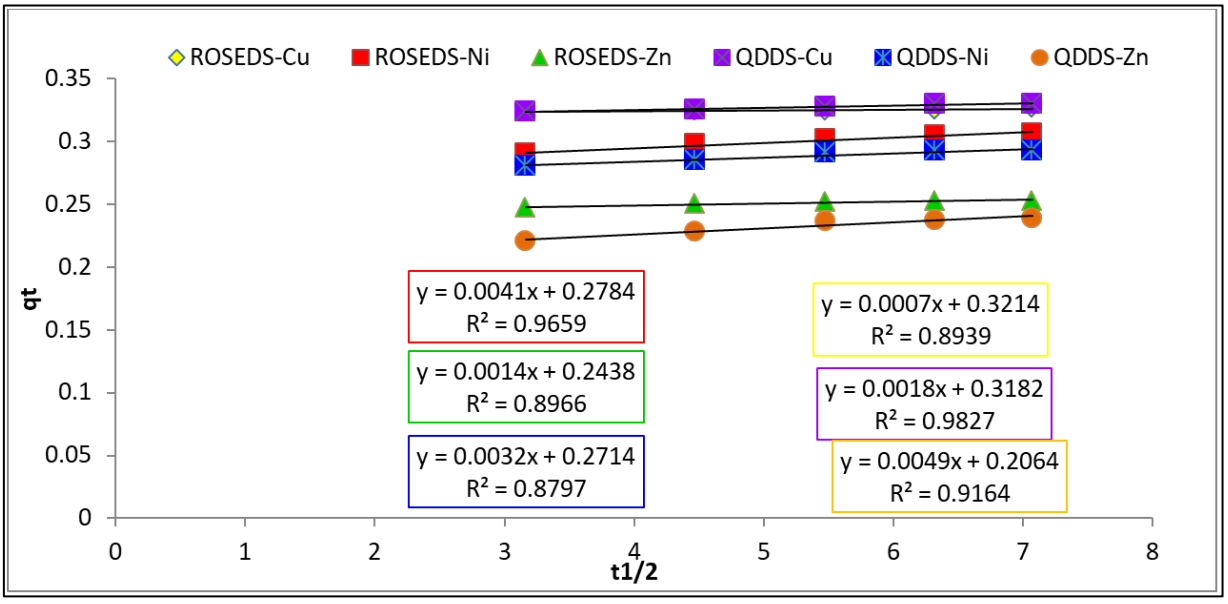

Figure 4: Intra particle diffusion kinetics for metal ions removal using ROSEDS and QDDS

Effect of Adsorbent Dosage Variation

Variation in adsorbent dosage affected the metal ions removal. Increment in the adsorbent dosage resulted to increased percentage removal as presented in Figure 5. The percentage removal increased from 71.81 % to 98.57 %, 76.71 % to 84.51 % and 50.34 % to 66.86 % for the removal of Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using ROSEDS. The percentage removal (%R) increased from 80.56 % to 99.19 %, 73.04 % to 87.64 % and 48.69 % to 71.56 % for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using QDDS as the adsorbent dosage increased from 0.0281 gram to 0.2020 gram. QDDS removed more of Cu^{2+} from the solution relative to Ni^{2+} and Zn^{2+} while ROSEDS removed Ni^{2+} and Zn^{2+} from solution more than Cu^{2+}.

Utilizing both the ROSEDS and the QDDS for the heavy metal ion removal from aqueous solution denoted that Cu had the highest percentage removal (%R) while Zn had the least percentage removal (%R). The metals were removed in the order; $Zn^{2+} < Ni^{2+} < Cu^{2+}$

Similar results were obtained recently by Waweru *et al*., 2016; Avisha *et al*., 2016; Salehzadeh, 2013. The result revealed that the optimum weight of the adsorbents (ROSEDS and QDDS) is 0.1655 for Cu and Ni, hence beyond these maximum weight, no further increase was observed in the percentage removal (% R), although zinc showed an exception to this. The corresponding rise in percentage removal with the adsorbent weight increase is as a result of more adsorption site on the surface of the adsorbent. Hence beyond the optimum weight a point of saturation is said to be attained by the adsorbent. Therefore adsorbent – dosage is a factor which must be considered during the extraction of heavy – metal(s).

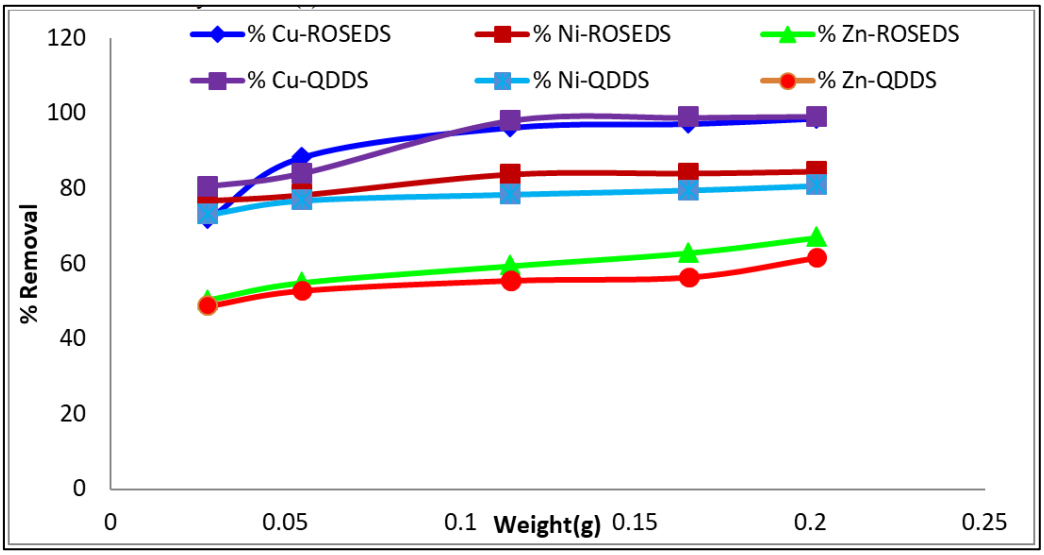

Figure 5: Variation effect of adsorbent-dosage on percentage removal of metal ions using red onion skin extract diazonium salt (ROSEDS) and quecertin dihydrate diazonium salt (QDDS)

Adsorption Isotherm

Two adsorption isotherms (Freundlich adsorption isotherm model and Langmuir adsorption isotherm model) were explored for this study. The correlation coefficient/factor, R^2 obtained from the freundlich isotherm model as presented in Figure 6 are 0.9711, 0.9825 and 0.8402 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using ROSEDS and 0.9316, 0.9054 and 0.8580 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using QDDS. The values obtained from Freundlich constant with respect to heterogenous surface, 1/n are less than unity (<1), which clearly demonstrated that adsorption is high favourable using ROSEDS and QDDS.

The correlation coefficient/factor, R^2 obtained from Langumir adsorption isotherm model are shown in figure 4.23 for ROSEDS and figure 7 for QDDS. The R^2 values are 0.9635, 0.9751 and 0.6385 for Cu^{2+}, Ni^{2+} and Zn^{2+} respectively using ROSEDS whereas the R^2 obtained for Cu^{2+}, Ni^{2+} and Zn^{2+} using QDDS are 0.9269, 0.7960 and 0.6785 respectively.

The values obtained from the Langmiur separation factor R_L are within the range of 0 and 1. These implies that adsorption of Cu^{2+}, Ni^{2+} and Zn^{2+} using ROSEDS and QDDS are highly favourable.

Freundlich adsorption isotherm model best describe the metal ions (Cu^{2+}, Ni^{2+} and Zn^{2+}) removal because the correlation coefficient/factor, R^2 obtained from it are higher and quite closer to unity (1) than those of Langumir adsorption model. Similar observation was reported by Mona *et al.*, 2014.

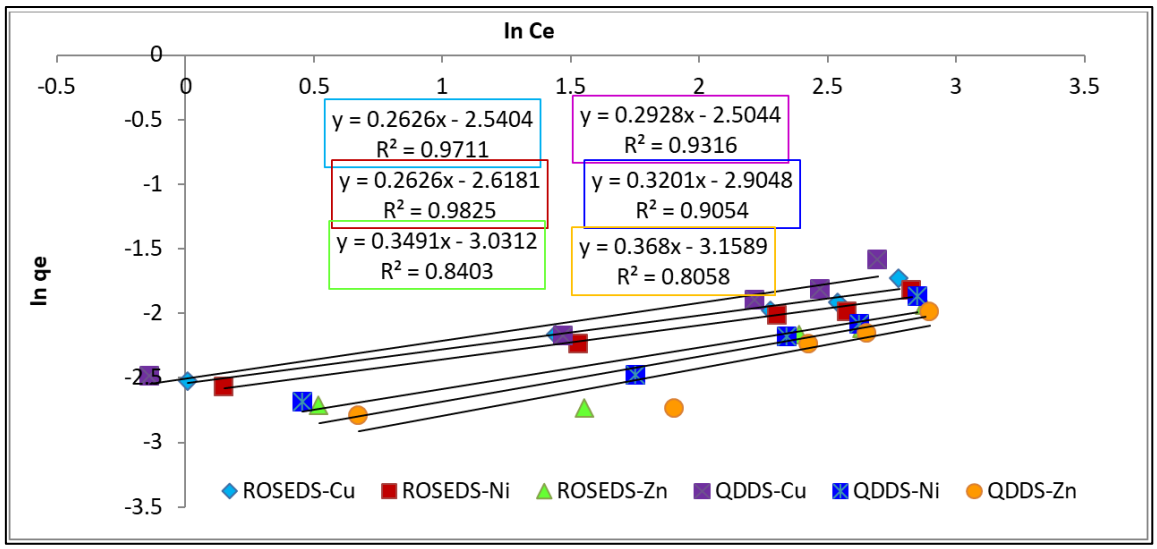

Figure 6: Freundlich adsorption isotherm for metal ions removal using ROSEDS and QDDS

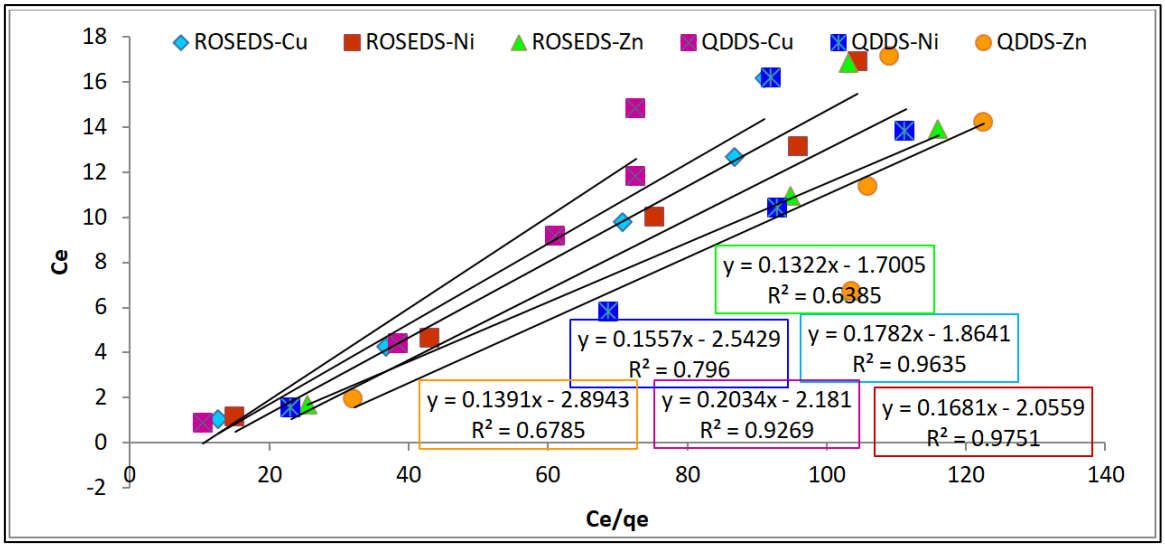

Figure 7: Langmuir adsorption isotherm for metal ions removal using ROSEDS and QDDS

CONCLUSION

Modification of quercetin dihydrate and red onion skin extract was successfully carried out by coupling 2- aminophenol diazonium compound within the structure of the adsorbents. This enhanced it's adsorption capacity and also increased the surface area. QDDS and ROSEDS are both water insoluble adsorbents that have affinity for heavy metals ions (Cu^{2+}, Ni^{2+} and Zn^{2+}) in aqueous solution**.** The Quercetin dihydrate and red onion skin extract are good adsorbents for the removal of Cu^{2+}, Ni^{2+} and Zn^{2+} in aqueous solution, in comparison they are relatively effective but red onion skin is preferred to quercetin because of its availability and low-cost. The variation in some factors such as pH, contact/agitation time, concentration of ions and adsobent dosage/weight vividly demonstrated that each of the factors is highly important in extraction processes.

Freundlich adsorption isotherm model and pseudo-second order kinetics best described Cu^{2+}, Ni^{2+} and Zn^{2+} removal from aqueous solution.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

Data Availability Statement

The authors declare that the manuscript has no associated data.

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