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ORIGINAL ARTICLE

Chemical Characterization of Treated and Rejected Wastewater of Reverse Osmosis Treatment Plants in the Area of Allama Iqbal Town, Lahore

Naveed Aslam Dogar^{1,2,*}, Haroon Iftikhar², Noor-UI-Ain Khalid³, Muhammad Shahid⁴, Sajjad Ahmad²

¹Department of Chemistry, Government College University, Lahore, Pakistan. ²Department of Chemistry, Government College of Science, Wahdat Road Lahore, Pakistan. ³Department of Chemistry, Forman Christian College University, Lahore, Pakistan. ⁴Department of Chemistry, Lahore Garrison University, Lahore, Pakistan.

ABSTRACT

Background: Water is one of the most essential requirements of life. Life is not possible without water. Polluted water on the other hand can affect the health badly. Reverse Osmosis (RO) plants are used to remove dissolved solids including harmful and toxic materials from wastewater.

Objectives: To investigate the quality of 6 treated and rejected wastewater samples of RO plants water being consumed in the areas of College block, Hunza Block of Allama Iqbal Town, and Gulberg III Lahore, Pakistan.

Methodology: Both qualitative and quantitative analyses were done by using the parameters like Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Dissolved Solids (TDS), Cl⁻, pH, nitrate, nitrite, SO4²⁻, Na⁺, K⁺ and heavy metals like Cr³⁺, Fe³⁺, Cu²⁺, Zn²⁺ and Mn²⁺ through Flame emission spectroscopy, UV-Vis spectroscopy, Atomic absorption spectroscopy, and volumetric analysis.

Results: The sample analysis indicated that these parameters lie within the permissible limits with reference to National Environmental Quality Standards (NEQS) values with some exceptions. The pH of treated water of college block (sample A) was 9.219, which is slightly higher than normal pH value, which is between 6.5-8.5. The value of Cr^{3+} ion in rejected water of Gulberg III was 0.06ppm, which is also higher than the normal limit.

Conclusion: All the parameters of treated and rejected wastewater indicated the suitability of water samples for population of respective areas, but the values of rejected wastewater are towards an increase, and should therefore be treated before dumping.

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INTRODUCTION

When two moles of hydrogen and one mole of oxygen combine together, we get a colorless and odorless compound. This product is known as water. It is an essential requirement of every living cell without which life is impossible. Water is a universal solvent or solvent of life. A cell contains more than 70% of water. The human body contains almost 60% of water in which the brain and heart almost contain 73%, lungs contain 83%, skin has 64%,

muscles and kidneys contain 79% and the bones contain 31% water¹.

An average human body requires almost 2000ml to 2500ml of water but this may vary according to the temperature, pressure, and by other environmental conditions. Water is very essential for normal life, but polluted water can badly effect the human health and can cause deadly water borne diseases like vomiting, diarrhea, *E. coli* infections, typhoid, dysentery, Hepatitis A, B, C and E, etc².

Both natural and human activities are responsible for water pollution. Volcanic eruptions, earthquakes, tsunamis, etc. are natural sources but they are not as harmful as anthropogenic activities related to the generation of industrial domestic and commercial waste³.

The Government of Punjab has taken some serious actions in 2013 and installed many RO plants for the purification of drinking water in different areas of Lahore, Pakistan. This study was planned for the chemical characterization of treated and rejected wastewater of reverse osmosis treatment plants in the area of Allama Iqbal Town and Gulberg III, Lahore⁴. This research has extreme benefit in gaining a better understanding of the water quality in these areas.

MATERIALS AND METHODS

All the treated and rejected water samples were collected from reverse osmosis plants of College block and Hunza Block of Allama Iqbal Town and Gulberg III, Lahore, Pakistan.

Tests for Chloride (CI⁻) Determination

Apparatus and chemicals required for the determination included 20ml to 25ml burette graduated in 0.1ml, burette support, 100ml graduated cylinder, titrating flask, beakers, pipette, silver nitrate solution and potassium chromate as an indicator.

AgNO₃ (0.16M) solution was prepared by adding 2.73g of AgNO₃ in 100ml of distilled water in a burette. Water (10ml) was pipetted out, which was to be tested in the titrating flask. Two to 3 drops of potassium chromate were added to the flask as an indicator. It was titrated against the standard solution till AgNO₃ turned red. The volume of AgNO₃ used was recorded till the end point⁵.

Biological Oxygen Demand (BOD) Analysis

The apparatus required for BOD were 20ml to 25ml burette, burette support, 100ml graduated cylinder, titrating flask, beakers, pipette, reagents, silver nitrate solution, potassium chromate as an indicator, 500ml conical flask, pipette bulb, pipette with elongated tips and 250ml graduated cylinders and washed bottles. Chemicals required were calcium chloride, magnesium sulphate, ferric chloride, di-sodium hydrogen phosphate, potassium di-hydrogen phosphate di-sodium hydrogen phosphate, ammonium chloride, magnese sulphate, potassium hydroxide, potassium iodide, sodium azide, conc. sulphuric acid, starch indicator, sodium thiosulphate and distilled water.

Four (300ml) BOD bottles were taken and 10ml of sample was added in two of them while the remaining two were filled with diluted water alone for blank. Glass stoppers were placed to preserve one blank and one sample in the BOD incubator at 20°C. The other two bottles containing one sample and one blank were investigated immediately. Then, 2ml of alkali iodide azide reagent was added. Sufficient time was required for complete reaction with oxygen. Next, 2ml of conc. H₂SO₄ was added and 10ml of the solution was pipetted out from the bottle and transferred to the Erlenmeyer flask, which was then standardized with sodium thiosulphate solution. When the solution became pale yellow, starch indicator was added to it which turned the solution blue. Titration was continued till blue color turned to colorless (endpoint). The titration process was repeated for concordant readings. After 5 days, the incubated sample and blank bottles were titrated to find Dissolved Oxygen (DO) value in mg/l. The titration process was repeated for concordant readings^{6,7}.

Chemical Oxygen Demand (COD) Determination

The apparatus included COD Digester, burette and burette stand, COD vials with stand, 250ml Erlenmeyer flask, pipette & pipette bulb, tissue paper, and wash bottles. The chemicals required were potassium dichromate, Conc. sulfuric acid, ferrous ammonium sulphate (Mohar Salt), silver sulphate, ferroin indicator, and organic free distilled water.

Reagents required included 0.25N solution of potassium dichromate, 0.1N ferrous ammonium sulphate solution,

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and ferroin indicator. Concentrated sulphuric acid was also required.

 H_2SO_4 and the sample were taken in a reflux flask and 10ml of 0.25N K₂Cr₂O₇, H_2SO_4 and AgNO₃ were added reagent in it, mixed and refluxed for two hours. Then, 150ml distilled water was added to dilute it. The indicator was added till the color changed from green to wine red, which is the end point. The experiment was performed against blank⁸.

Total Alkalinity Determination

Alkalinity is due to the presence of CO_2 , HCO_3^{1-} , CO_3^{2-} , and OH etc. It may come in water form acid rain and earths' natural buffering system etc. It can be determined easily by using methyl-orange as an indicator and N/50 sulphuric acid solution titration⁹.

pH Determination

pH meter is used for the determination of pH. Standard buffer solution was used for the calibration of glass electrode and then pH of the sample was measured¹⁰.

Determination of Total Hardness

Buffer solution of pH 10 was used along with Erichrome Black-T indicator and EDTA as a standard solution (0.01M). Value of $CaCO_3$ in ppm expressed the total hardness of water¹¹.

Determination of Calcium Ions

Standard EDTA solution of 0.01M was used along with EBT and buffer of pH 10. The sample was taken and boiled to remove bicarbonates. Then, it was titrated against EDTA solution using EBT as an indicator¹².

Determination of Nitrate and Nitrite Ions in Water

Nitrate ion can be measured spectroscopically. Salicylic acid under basic conditions forms a stable complex with nitrate ion, which can be estimated by a spectrophotometer at 410nm. Chromophore absorption is directly proportional to amount of nitrate present. Blank is prepared using distilled water with simple normal reagent.

For the determination of nitrite ion, spectrometer, pipette, glass stopper flask, beaker and distilled water were required. Colored reagents were produced by adding 100ml of 85% phosphoric acid and 10ml sulphanilamide mixed in 800ml of water. N-1-naphthylethylene diamine di-hydrochloride (1g) was added and diluted up to 1000ml by distilled water. This coloring agent was then stored in the

dark. Further, 0.05N sodium oxalate was prepared, followed by the preparation of a stock nitrite solution of 0.018N. This solution required 1ml of CHCl₃ for its preservation. Standard 0.05N KMnO₄ was also used in this analysis.

Further, 50ml of sample was taken and 2ml of coloring reagent was added to it as a chromophoric reagent. The absorbance was measured at 543nm, followed by a waiting period of 10min to 120min after addition of the coloring agent. Standard curve was used to estimate the sample nitrite concentration¹³.

Measurement of Total Dissolved Solids (TDS)

First, 100ml of filtered water was taken using the Whatmann filter paper. The water was evaporated in an electric oven at 110°C. The amount of solid residue in the sample was then weighed¹⁴. Formula used was:

TDS (mg/L) = [(A-B)*1000*1000] / Sample volume (ml)

Where, A = Weight of dried residue + dish (g)

B = Weight of dish (g)

Determination of Heavy Metals

Atomic Absorption Spectroscopy (AAS) is used for the determination of heavy metals. Standard solution (5ppm, 10ppm, 15ppm and 20ppm) of Fe, Cr, Pb, Cd and Mn were prepared and tested by AAS. Comparison was used between the standard and unknown sample to determine heavy metals in water¹⁵.

Estimation of Na⁺ and K⁺ Ion by the Help of Flame Photometric Method

After calibration of the instrument with the help of standard and adjusting the reading between 0-10mg/l and 0-100mg/l, distilled water was aspirated to bring zero mark reading and the sample was applied to the flamephotometer. The readings were accordingly noted¹⁶.

Determination of Sulphate Concentration in Water Sample

For this determination, magnetic stirrer, physical balance, measuring cylinder along with spectrophotometer etc. were used. Then, 50ml of the sample was taken along with buffer and 2ml conditioning agent. A pinch of BaCl₂ was added and stirred for 1min at a defined speed. Its absorbance was measured at 420nm. Afterwards, 5mg to 40mg of standard curve was used for the determination of sulphate ions¹⁷.

Iron Determination

Porcelain dish, measuring cylinder, glass rod, wash bottles, iron wire and spectrometer etc. were the apparatus used for iron determination. Glacial acetic acid, HCI, ammonium acetate buffer, hydroxyl amine hydrochloride solution 1,10-phenenthroline solution, ammonium ferrous sulphate solution and 0.1N KMnO₄ were the reagents required for this estimation.

Water sample (50ml) was taken and 2ml HCl was added in it. The solution was heated till its volume reached to 20ml. 10ml of ammonium acetate buffer and 4ml of 1,10-phenenthroline were added in it. The solution was then incubated in the dark for 20min and then absorbance was measured at 510nm. The sample value was compared with the calibration curve obtained from known concentration¹⁸.

RESULTS

Samples A and A* represent the treated and rejected water of College block, respectively. Samples B and B* represent the treated and rejected water of Hunza block, respectively. Similarly, samples C and C* represent the treated and rejected water of Gulberg III block, respectively.

The parameters like pH, TDS, total hardness, Ca²⁺ ions, Cl¹⁻ ions, total alkalinity, BOD, COD¹⁹ values are given in Table **1**. All these values were compared with National Environmental Quality Standards.

Table **1** shows that the treated sample A (collected from the college block RO plant) has a pH value greater than NEQS, therefore it is not much suitable for drinking. All other parameters of all the samples lie within the permissible limits.

Table 1. Sample Parameters Measured for	r Treated Sample A (Collected from	the College Block RO Plant).

PARAMETERS	Α	A *	В	B *	C	C*	NEQS
рН	9.239	7.965	8.262	7.940	7.715	7.619	6.5-8.5
TDS	120	180	100	110	200	230	<1000
Total Hardness	25	93	26	37	33	86	<500
Ca ²⁺	40	65	18	88	40	93	<500
Total Alkalinity	80	130	94	128	102	288	<300
CI ¹⁻	13	20	15	25	30	85	<250
COD	56	74	33	55	10	69	150mg/l
BOD	26	58	12	18	28	60	80mg/l



Figure 1. pH values of all the samples.

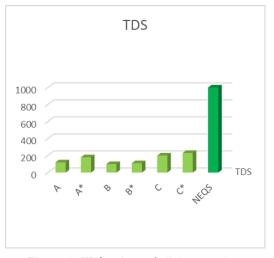


Figure 2. TDS values of all the samples.



Figure 3. Total Hardness of all the samples.

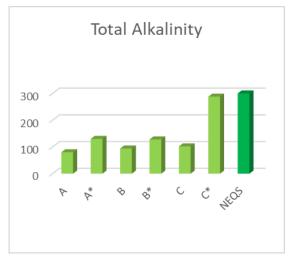
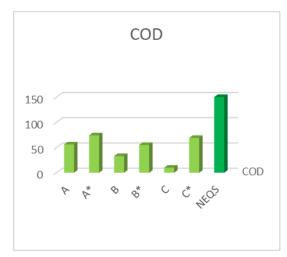
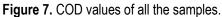


Figure 5. Total alkalinity of all the samples.





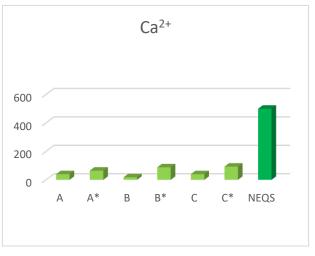


Figure 4. Total Ca+2 ions in all the samples

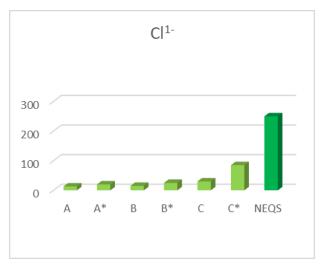
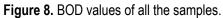


Figure 6. Total Cl⁻¹ ions in all the samples.





METAL	Α	A *	В	B*	С	C*	NEQS (ppm)
Fe ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	2.0
Zn ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Cu ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	<0.05
Mn ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	<0.05
K⁺	1.4567	3.5674	1.05	2.7768	1.4612	3.4013	12
Na⁺	0.00	0.00	0.00	0.00	0.00	0.00	250

Table 2. Measurement of lons in all the RO Plant Samples.

Table 3. Measurement of Na⁺ / K⁺ Levels in all the RO Plant Samples.

	۸	۸*	D	D*	C	C*	NEQS
PARAMETERS (ppm)	A	A	D	D	C	C.	(mg/l)
Na⁺	30	65	40	88	21	22	250mg/l
K⁺	2	5	4	7	5	6	12mg/l

Figure **1** represented that the pH value of treated water from the college block is not within the NEQS permissible limit, while Fig. **2** to Fig. **8** showed that all other parameters such as total alkalinity, total hardness, TDS, Ca⁺² and Cl⁻¹ ions concentration, BOD and COD values are within the permissible limits, and the treated water sample can be used and is safe for drinking purposes.

By using atomic absorption spectroscopy, the metals like Fe^{3+} , Zn^{2+} , Cu^{2+} , Mn^{2+} , K^+ and Na^+ were estimated and their values are given in Table **2**. It shows that only K^+ ions are present in all the RO plant samples. The concentration of K^+ ions lies within the safety limit of NEQS values.

Na⁺ and K⁺ ions were estimated by flame photometric method (Table **3**). The values lie within the safety limits.

UV-Visible spectrophotometer studies were conducted to find the ppm percentage of NO_2^{1-} , NO_3^{1-} , Fe^{3+} , Cr^{3+} , and SO_4^{1-} . From the data in Table **4**, it can be concluded that the rejected water of Gulberg III contained 0.06ppm of Cr^{3+} , which exceeds the safety limits of NEQS. The sample of rejected water (sample B*) of Hunza block had 42.20ppm of NO_2^{1-} which is very high as compared to NEQS, which is 12ppm only.

Variations of different parameters like pH, TDS, total Hardness, Ca²⁺, total alkalinity, and Cl⁻ ion for the treated and rejected water of Hunza block, College block and Gulberg III were investigated for seven days as shown in Tables **5-10**.

PARAMETERS (ppm)	Α	A *	В	B*	С	C*	NEQS (ppm)
NO ₃ 1-	0.000	0.085	0.004	0.000	0.000	0.000	12
NO ₂ ²⁻	0.00	0.002	5.747	42.20	0.044	0.110	12
SO 4 ²⁻	1.321	92.62	23.34	27.46	29.62	27.26	1000
Fe ³⁺	0.151	0.108	0.744	0.02	0.173	0.220	2.0
Cr³⁺	0.00	0.001	0.010	0.00	0.003	0.06	<0.05

Table 4. Measurement of Specific Cations and Anions Level in all the RO Plant Samples.

Sample	Parameters	1 st Day	2 nd Day	3 rd Day	4 th Day	5 th Day	6 th Day	7 th Day
HunzaBlock	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
01	рН	6.9	7.2	7.95	7.75	7.8	7.95	7.81
02	TDS	1.5	2.0	8.0	4.01	3.04	1.80	2.00
03	Total Hardness	50	56	33	76	31	53	61
04	Ca ²⁺	85	88	88	90	85	89	86
05	Total Alkalinity	92	101	79	83	105	36	45
06	CI ¹⁻	25	28	21	18	17	24	19

Table 5. Measurement of Different Parameters in Hunza Block (Treated Water) Sample.

 Table 6. Measurement of Different Parameters in Hunza Block (Rejected Water) Sample.

Sample	Parameters	1 st Day	2 nd Day	3 rd Day	4 th Day	5 th Day	6 th Day	7 th Day
HunzaBlock	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
01	рН	6.95	7.26	7.05	7.65	7.88	7.95	8.01
02	TDS	257	230	150	311	324	180	200
03	Total Hardness	101	177	303	116	201	153	101
04	Ca ²⁺	115	168	88	260	115	275	111
05	Total Alkalinity	92	110	119	88	155	163	155
06	CI ¹⁻	115	98	141	37	111	204	19

Table 7. Measurement of Different Parameters in College Block (Treated Waste Water) Sample.

Sample	Parameters	1 st Day	2 nd Day	3 rd Day	4 th Day	5 th Day	6 th Day	7 th Day
College Block	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
01	рН	7.5	7.35	7.45	7.25	7.86	7.68	7.50
02	TDS	125	126	110	120	118	125	127
03	Total Hardness	98	102	92	97	90	97	91
04	Ca ²⁺	60	65	70	65	70	68	72
05	Total Alkalinity	88	81	94	87	80	85	88
06	Cl ¹⁻	14	22	29	36	31	20	13

Table 8. Measurement of Different Parameters in College Block (Rejected Waste Water) Sample.

Sample College Block	Parameters (ppm)	1 st Day (ppm)	2 nd Day (ppm)	3 rd Day (ppm)	4 th Day (ppm)	5 th Day (ppm)	6 th Day (ppm)	7 th Day (ppm)
01	рН	6.5	7.15	7.45	6.25	8.86	7.08	7.04
02	TDS	448	156	350	430	128	445	527
03	Total Hardness	228	132	302	207	210	307	411
04	Ca ²⁺	104	225	110	215	118	182	372
05	Total Alkalinity	266	319	401	213	120	115	88
06	CI ¹⁻	133	221	194	200	103	119	103

Sample	Parameters	1 st Day	2 nd Day	3 rd Day	4 th Day	5 th Day	6 th Day	7 th Day
Gulberg III	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
01	рН	7.65	6.28	7.05	7.51	7.11	8.00	7.65
02	TDS	100	103	110	204	107	309	102
03	Total Hardness	304	302	166	117	136	66	133
04	Ca ²⁺	270	282	168	76	117	101	109
05	Total Alkalinity	119	104	137	198	165	274	196
06	CI ¹⁻	111	135	121	119	112	106	105

 Table 9. Measurement of Different Parameters in Gulberg III (Rejected Water) Sample.

Sample	Parameters	1 st Day	2 nd Day	3 rd Day	4 th Day	5 th Day	6 th Day	7 th Day
Gulberg III	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
01	рН	7.1	6.13	6.0	7.11	7.9	6.95	8.0
02	TDS	1.00	1.03	1.10	2.04	1.07	3.09	1.02
03	Total Hardness	30	32	66	47	36	49	34
04	Ca ²⁺	70	82	68	76	67	60	86
05	Total Alkalinity	99	104	107	98	96.5	97.4	96
06	CI ¹⁻	15	11	18	19	12	16	15

DISCUSSION

This work was planned to evaluate the quality of treated and rejected wastewater used in the vicinity of Allama Iqbal Town and Gulberg III in Lahore, Pakistan. Table 1 shows the parameters like pH, TDS, hardness, chloride ion, alkalinity, COD, and BOD are within the permissible limits of treated wastewater samples. As reported by Elorm and Sudesh, the parameters are very important for understanding how to make it re-useable, as the improvement in waste can make it re-useable for this growing population²⁰. Tables 2 and 3 revealed that the heavy metals like Zn2+, Cu2+ and Mn2+ are not detected in the treated or rejected wastewater of all the samples, and the concentration of Na⁺ and K⁺ was within acceptable limits in all samples. If these metals are present, then removal of these heavy metals is very important because heavy metals are carcinogenic and even in rejected water, they must be removed before disposal²¹. The presence of sulphate, phosphate and other nitrate ions does not make the water safe for drinking because they can precipitate the calcium and magnesium present in the human body,

resulting in the weakening of bones and loss of minerals in the human body. The kidney stones are composed of oxides and phosphates of calcium, and their presence can be a dangerous threat to humans as well as animals²². These acidic radicals can also create boiler scales in industry and can be very harmful to machine life²³. Table 4 showed that the concentrations of nitrite, nitrate, sulphate, ferric, and chromium lie within safe limits, which are considered to be safe for domestic life. The pH of all the treated wastewater samples increased because the concentrations of sulphates, nitrates and other acidic radicals decreased in these, while they increased in rejected wastewater samples. Chromium is very harmful and has many side effects, such as irregular heartbeats, sleep disturbances, headaches, mood changes, and allergic reactions. Chromium may also increase the risk of kidney or liver damage²⁴. The value of chromium in rejected wastewater from Gulberg III (sample C*) exceeded the safety limit and should be treated properly before dumping. Tables 5-10 showed the collection of treated and rejected wastewater for consecutive seven days, and study of their parameters reveals that the water meets standard drinking values with some variations among each other during consecutive 7-day studies.

CONCLUSION

Conclusively, the RO plants seem to be efficient in treating water and enabling it suitable for the population of these areas. This treated and rejected wastewater is within permissible limits but in rejected wastewater, values of some parameters increased, which can be threatening to human health due to the accumulation of the elements in the environment.

CONFLICT OF INTEREST

No conflicts of interest have been declared by the authors.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
EBT	Erichrome Black-T
EDTA	Ethylenediaminetetraacetic acid
Μ	Molar Solution
Ν	Normal Solution
NEQS	National Environmental Quality Standards
pН	Potential of Hydrogen
RO	Reverse Osmosis
TDS	Total Dissolved solids

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