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Evaluation of Co-adsorption Parameters for Arsenic, Fluoride and Nitrate using Copper Nanoparticles

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ABSTRACT: Water contamination with multiple contaminants at higher levels is a serious concern. These ions are individually toxic but their cumulative effects are even more complex and posing serious threats to human health. Nano-adsorbents have been widely developed and utilized for efficient removal of inorganic contaminants from aqueous environment. The present study has been carried out to evaluate efficiency of copper oxide nanoparticles for simultaneous removal of three naturally occurring inorganic contaminants: arsenic, fluoride and nitrate through co-adsorption. Fluoride and nitrate removal was best observed in the acidic pH whereas arsenic showed significant adsorption in alkaline pH. At optimized pH-6.0 and adsorbent dose 2g/L, the percent removals of arsenic, fluoride and nitrate were observed as 76%, 82% and 89% respectively. When the adsorbent dose was increased further upto 8 g/L, the adsorption of each adsorbate was increased reaching maximum to 98%, 90% and 94% for As, F and NO_3 respectively. Removal of each ion was rapid and completed in 3.5 hours. The classical Langmuir and Freundlich isotherms were applied to check the fitness of data. Also, co-adsorption data was found to be in good agreement with pseudo second order kinetic. No significant interference from carbonate, bicarbonate, chlorides and sulphate was observed during co-adsorption experiments performed with real water samples. Findings have suggested that copper oxide nanoparticles can be potentially used as an alternative to the high cost synthetic adsorbents where feed water has moderate concentrations of selected contaminants as mentioned in the study.

Keywords: Arsenic, Fluoride, Nitrate, Co-adsorption, copper oxide nanoparticles

I. INTRODUCTION

Co-contamination of natural water bodies with arsenic, fluoride and nitrate at elevated levels is of utmost importance due to their considerable impacts on human health. These contaminants have been found to co-exist in Indian subcontinent and many other places all over the globe [1-4]. These ions are individually toxic and their cumulative effects are even more complex and hazardous. Potential carcinogenicity and other multiple ailments associated with ingestion of these inorganic contaminants have made their removal essential from drinking water sources. Many conventional remediation methods have been developed to deal with the individual contaminant removal such as precipitation coagulation, electro-coagulation, adsorption on alumina and activated carbon, ion exchange and reverse osmosis. Many of these technologies are less efficient, require high chemical inputs, add by products to the treated water and thereby make it unfit for human consumption. Some of these generate large amount of toxic sludge disposal of which itself is a problem. Reverse osmosis is although an efficient and powerful technology for ion removal but its high installation and operational cost restricts its use at large scale particularly in developing countries. Moreover very few studies have been carried out to address the issue of their co-removal. The technologies available today for the co-removal of multiple contaminants are the integrated approaches that work on combination of two or more principles to remove contaminants in multiple stages.

The present study was undertaken to deal with the problem of multi-contaminant removal through adsorption with copper oxide nanoparticles. Various researchers have developed variety of nanoadsorbents with increased biocompatibility, reactivity and multi-functionality that are well suited towards specific contaminant removal. These offer the possibility of efficient removal of various inorganic contaminants such as arsenic, fluorides, nitrates and various toxic ions from drinking water. In the past decade, a wide variety of nanomaterials have been developed and investigated for the removal of arsenic, fluoride and nitrate from aqueous solution. Out of these, Nano based materials and composites have showed good potential for their removal from aquatic environments.

Several inorganic nanomaterials such as iron, alumina, titania, magnesia, silica, zirconium, cerium and calcium based metal oxide nanomaterials and composites have been widely employed for water decontamination [5-9]. The metal oxide based nano-adsorbents are being increasingly used due to their rapid kinetic and requirement in low doses. These exhibit higher removal capacities than their micron counterparts. This is because of their high surface to volume ratio [10-13].

Among various metal oxide nanomaterials, cupric oxide nanoparticles (CuO-NPs) offers certain advantages of being antimicrobial nature and capable of performing well in wider range of pH because of their high point of zero charge. Because of this unique property these can effectively remove both As(III) and As(V) without any pH adjustment [14]. Moreover, their removal performances are not affected by the presence of various salts or competing ions. In addition, these can also be easily regenerated with sodium hydroxide without causing any significant reduction in their removal efficiency. Studies on arsenic removal using copper oxide nanoparticles have proved their capabilities as potential adsorbents suitable for inorganic contaminants [15-17]. Overall, high adsorption capacities coupled to their non-toxic nature, good desorption potential and reported antimicrobial activity makes copper oxide nanoparticles an effective and economical material of choice [18].

II. MATERIALS AND METHODS

The simulated stock solutions of Arsenic (1000 µg/L), Fluoride (100 mg/L) and Nitrate (500 mg/L) were prepared by dissolving an appropriate amount of sodium arsenite, sodium Fluoride and sodium Nitrate in de-ionized water. The working solutions were prepared by making suitable dilutions of stock solutions. All the chemicals used were of analytical grade of make Merck, Germany. The concentration of Arsenic before and after adsorption was determined by AAS whereas Fluoride was measured by SPADNs method. The concentration of Nitrate was determined simply by measuring absorbance at 240 nm in UV region. The IR spectra were taken using instrument FTIR NXRFT Raman Spectroscope: Thermo Nicolet 6700. All statistical analysis was performed with help of software Origin 8.

A. Synthesis of Copper nanoparticles

In this approach copper Nanoparticles were synthesized in a microwave assisted process using Geraniol as reductant with water as the medium for reduction. The stabilization of copper Nanoparticles was studied with a wide variety of reagents such as starch, PEG and Gelatin. The reaction mixture was heated using a kitchen microwave for about 5 minutes to attain the required temperature for the reaction. The pH of the solution was adjusted to alkaline using 5% NaOH solution. Formation of Copper Nanoparticles was indicated by change in color of the solution from blue to yellowish black which is supported by the UV absorption at 540-570nm. The synthesized particles were washed several times with water and finally with alcohol. Synthesized particles were separated by ultracentrifugation and the dried powder was analyzed for their size and surface characteristics by the SEM, TEM and FTIR (Fig. 1) [19].

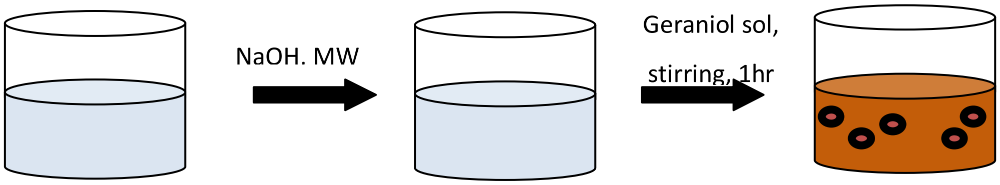


Fig. 1.

B. Adsorption experiments

The batch adsorption experiments were conducted in two phases. In the first phase, fifteen sets of experiments, five for each contaminant, were carried out for individual contaminant removal of each As, F and NO_3 from simulated solutions.

In each set of experiment, fixed amount of adsorbent (2g/L) was added to the 100 ml model solution of fixed concentration of Arsenic (100 µg/L), Fluoride (10 mg/L) and Nitrate (200 mg/L) in polyethylene flasks of 250 ml capacity. These were allowed to mix by placing on a shaker set at 180 rpm for 120 minutes. The pH of the solution of each set was adjusted as per requirement by adding small increments of 0.1N HCl and 0.1N NaOH. The adsorption of all the contaminants in each set was measured at regular intervals and recorded. The percent removal and adsorption capacity of specific adsorbate ion was calculated using following equations:

$$\text{Percent Removal} = \frac{C_i - C_e}{C_e} \times 100 \qquad (1)$$

where C_i and C_e are the initial and final concentrations of adsorbate in solution.

$$\text{Adsorption capacity } (Q_e) = \frac{C_i - C_e}{V} \times W \qquad (2)$$

where Q_e is the amount of adsorbate adsorbed, C_i and C_e are the initial and final concentrations of adsorbate in solution, V is the volume of solution and W is the weight of dry adsorbent in grams.

The studies were carried out by varying the process parameters such as pH, adsorbent dose, ion concentration and contact time, affecting the adsorption and were optimized. All the experiments were conducted in duplicates and the mean values are reported. The adsorption capacity of each contaminant (As, F and NO_3) was determined under optimized conditions.

In the second phase, similar set of adsorption experiments were performed with solutions containing all the three contaminants in a proportion of fixed concentration representing the characteristics of real water samples (drinking water). In this phase narrow range of all the process parameters (pH, dose, initial concentration and contact time) giving best removal efficiencies with individual contaminants in preliminary phase were selected and re-optimized.

Under optimized conditions, the removal efficiencies of each As, F and NO_3 by both adsorbents were calculated. Again the isotherms and kinetic models were applied to evaluate the fitness of data.

III. RESULTS AND DISCUSSION

A. Characterization of adsorbent with FTIR, SEM and EDX studies

Copper nanoparticles (CuNPs) prepared via green technology were first analyzed with UV-visible spectrum which gave characteristic absorption in the region 518-572 nm indicating that the synthesized copper nanoparticles are in colloidal form (Fig. 2).

The morphological, structural crystallographic and compositional characteristics were investigated with TEM, XRD and FTIR spectroscopy. The characteristic peaks observed at 3414, 1638 and 1030 cm^{-1} may be interpreted for O-H, C-O and Cu-O groups respectively which confirmed the formation of nanoparticles (Fig. 3).

Diffraction patterns of CuNPs were obtained with a drop casted on glass with XRD spectrometer operating at a 40 KV and 20 mA with Cu Kα line at 1.54Å (Fig. 4). The TEM analysis revealed that synthesized CuNPs are spherical in shape with size varied between 70-90 nm.

SEM and TEM images along with pore size distribution curve of copper nanoparticles are shown in Fig. 5 and 6 respectively. From figures, it was clear that synthesized particles are spherical in shape and were exhibited a wide range of sizes but major proportion of particles were found to have pore size between 80-90nm.

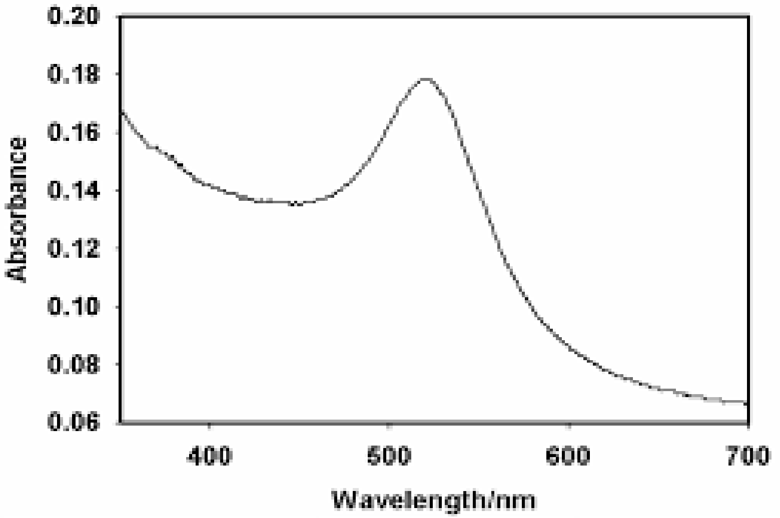


Fig. 2. UV-visible spectrum of colloidal copper nanoparticles.

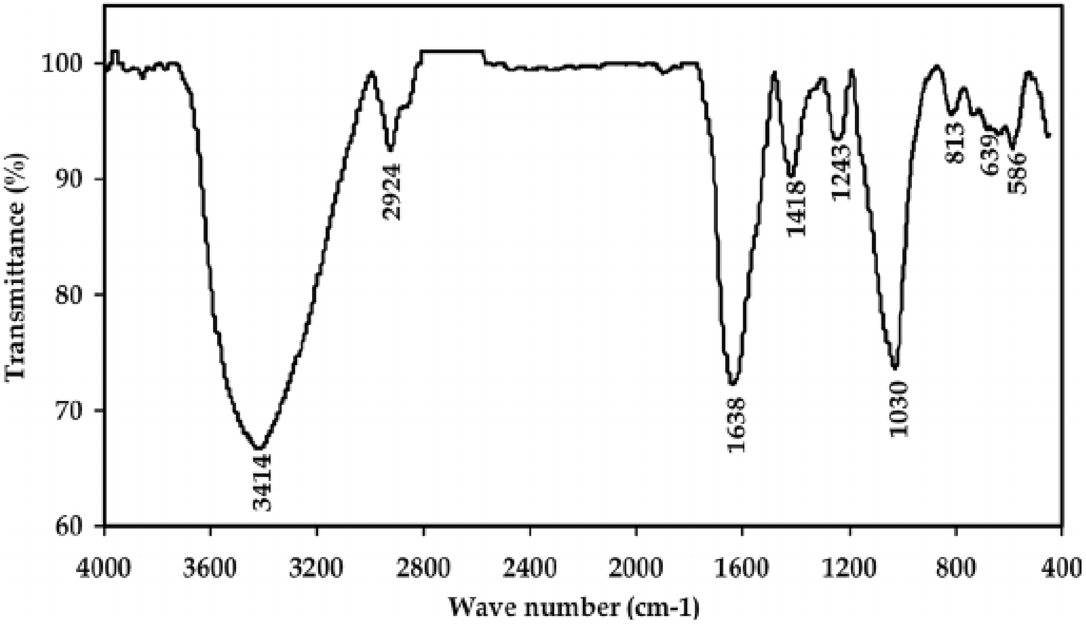


Fig. 3. FTIR spectrum of CuNPs.

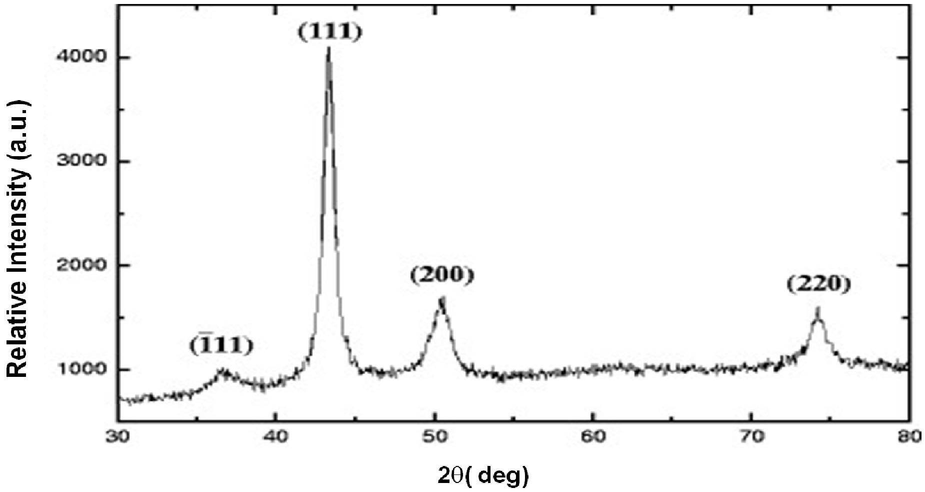


Fig. 4. XRD spectrum of CuNPs.

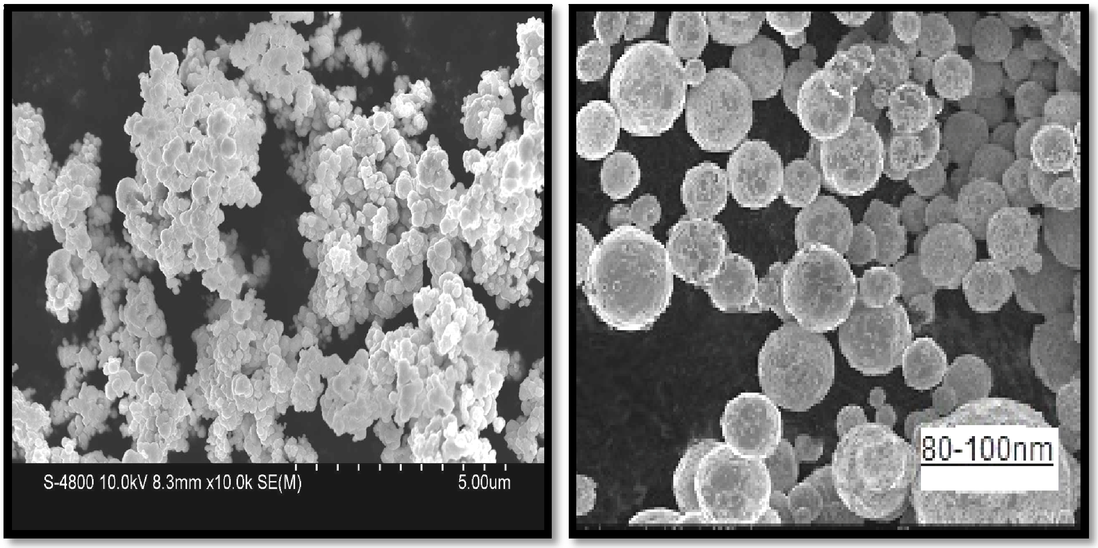


Fig. 5. SEM and TEM images of synthesized CuNPs.

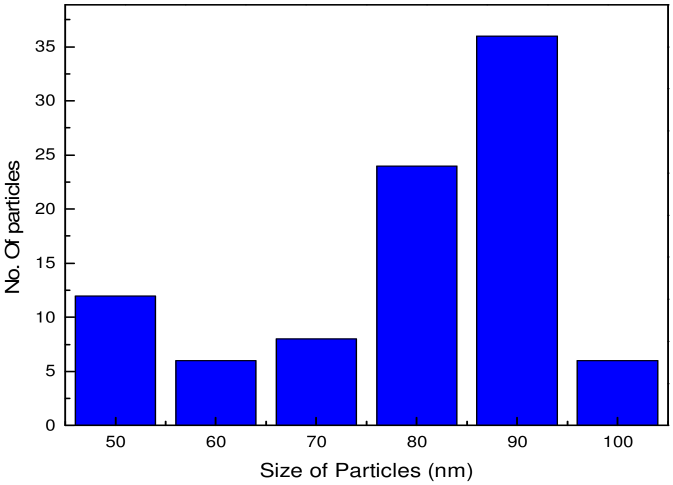


Fig. 6. Pore size distribution of synthesized CuNPs.

B. Arsenic removal by Copper Nanoparticles

Studies of arsenic adsorption on copper nanoparticles were carried out at room temperature with arsenic concentration 200 µg/L. Arsenic solution (100 ml) was mixed with 0.2g of adsorbent and kept at orbital shaker stirring at 180 rpm for 2 hours. The pH of solution was varied between 1.5-11.5 and the adsorption was recorded. Results of experiments for investigating effect of pH revealed that arsenic adsorption occurred in selected pH range (1.5–11.5) but maximum percent adsorption (96.5%) was achieved in alkaline medium at pH 11.5. The poor adsorption in acidic medium is because of neutral status of As_2O_3. It occurs in ionic form in alkaline medium only and therefore cannot be removed at pH below 7.

The standardization studies for copper nanoparticle dosage were carried out by varying the copper nanoparticle doses from 0.5 to 3.5 g/L. It was found that percent adsorption was increased from 51% to 98% with increase in adsorbent dosage from 0.5-3.5 g/L. This was due to increased surface area available for adsorption of arsenite ions present in fixed concentration. More than 90% adsorption was observed with 2g adsorbent dose of CuNPs, therefore rest of experiments were performed with 2g of adsorbent dose.

To see the effect of arsenite ion concentration and contact time on adsorption, experiments were performed by varying the ion concentration from 25-200 µg/L and 10-200 minutes with optimized adsorbent dosage and pH. Significant adsorption upto 88% was observed with 100 µg/L arsenite concentrations and thereafter it was slightly reduced with further rise in ion concentration.

More than 90% adsorption was occurred in 3 hrs of duration. In initial time period, adsorption was increased rapidly and then took longer time to reach equilibrium.

Equilibrium studies conducted for arsenic adsorption by copper nanoparticles have revealed that adsorption experimental data followed both Langmuir and Freundlich isotherms with high value of correlation coefficient.

C. Adsorption of Fluoride on Copper Nanoparticles

Fluoride adsorption experiments were carried out with 10 mg/L fluoride concentration. Fluoride adsorption on copper nanoparticles is highly pH dependent phenomenon. Maximum adsorption (83.6%) was achieved at pH 5.0 and reduced greatly above and below this pH.

To evaluate the effect of adsorbent dose, the experiments were performed with varied amounts of copper nanoparticles (0.5-3.5 g/L) with fixed fluoride concentration (10 mg/L) at optimized pH (5.0) for 90 minutes. The results showed that for initial doses (0.5-1.5 g/L) the adsorption was increased rapidly and afterwards became constant when the adsorbent dosage was increased from 1.5-3.5 g/L.

The effect of fluoride concentration on adsorption has revealed that when it was increased from 10-60 mg/L, the percent adsorption did not suffer at all but reduced the adsorption drastically from 72.66 to 33.75% when it was increased beyond 60 mg/L to 120mg/L. The results of experimental run measuring effect of fluoride ion concentration on adsorption has clearly indicated that CuNPs are highly efficient in removing fluoride ions from the water containing fluoride content upto 60 mg/L which has been normally present in the groundwater samples collected from many places.

The similar trends of results were observed with the experiments performed for standardization of contact time. Initially upto 80 minutes the adsorption occurred at faster rate and did not show any significant increase further with time.

The fluoride adsorption data obtained under standardized conditions of pH -5.5, adsorbent dose – 2 g/L for 2 hours with fluoride concentration 10 mg/L followed the Langmuir model with high R^2 value = 0.97.

D. Adsorption of Nitrate on Copper Nanoparticles

To study nitrate adsorption characteristics on copper nanoparticles, batch adsorption experiments were performed with 100 mg/L sodium nitrate as model contaminant. The effects of various parameters were investigated by similar methodology described in the previous section. The pH optimization studies were done by varying pH from 1.5-11.5 keeping all other parameters constant. Nitrate removal efficiency was higher in the acidic pH than in alkaline.

It has been observed that adsorption was increased with increasing an adsorbent dose which may be due to increased adsorption sites. Maximum 99.25% nitrate removal was achieved with 3.5g adsorbent dosage. There was very little rise in adsorption observed when dosage was increased from 2g/L, therefore this dosage was taken as standard to conduct further adsorption experiments.

To study the influence of nitrate concentration on adsorption, it was varied from 50 – 350 mg/L. Significant adsorption (more than 80%) was attained with 200 mg/L nitrate concentration. Thereafter, great fall in percent removal was observed reaching to 63% with further rise in concentration upto 350 mg/L.

About 94% nitrate was removed under predefined conditions of pH (6.0), adsorbent dose (2g/L) and contact time (90 mins). The nitrate adsorption was quiet rapid and reached equilibrium in 90 minutes.

Analysis of equilibrium studies performed and high correlation coefficient (R^2) values obtained indicated that the data obeys the both Langmuir and Freundlich isotherms but linear fit of nitrate adsorption data was better described by the Langmuir isotherm with R^2 = 0.99.

E. Studies for Arsenic, Fluoride and Nitrate Co-removal

To evaluate the efficacy of copper nanoparticles for simultaneous removal of As, F and NO_3, experiments were conducted with their initial concentration 100 µg/L, 10 mg/L and 200 mg/L respectively, at selected pH range (3-7) and adsorbent dose (1-5 g/L) for fixed time span (90 mins). All the parameters were standardized as per methodology mentioned in the previous sections.

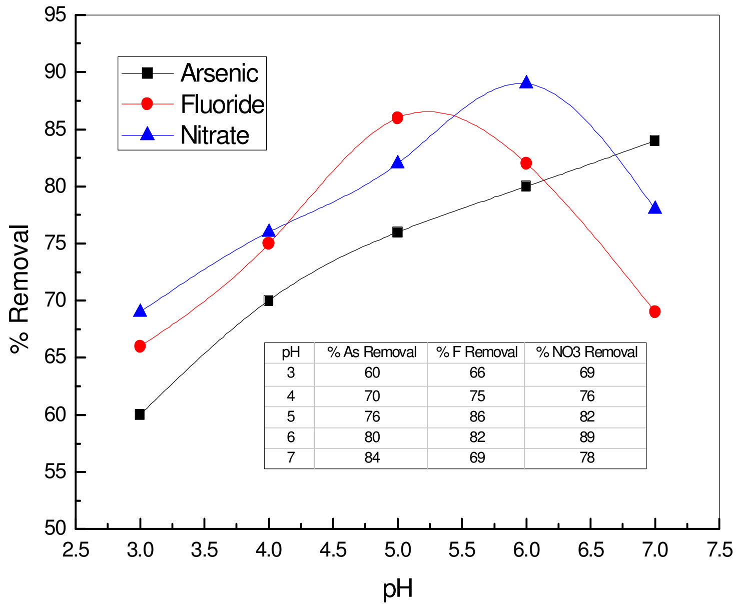
Table 1: Summary of results of adsorption process parameters standardized for Single contaminant (Arsenic, Fluoride and Nitrate) removal by CuNPs.

Parameters Studied	Arsenic Removal	Fluoride removal	Nitrate removal
pH (1.5 – 11.5)	11.5	5.0	5.5-6.0
Adsorbent dose (0.5–3.5 g/L)	3.5 g/L	2 g/L	2 g/L
Contact Time (20 – 240 mins)	3 hrs	90 mins	90 mins
Initial ion concentration	100 µg/L	10 mg/L	100 mg/L
Stirring speed	180 rpm	180 rpm	180 rpm
% Removal	88 %	83.6 %	96 %
Isotherm model	Both Langmuir & Freundlich with R^2= 0.991 & 0.998	Freundlich R^2 = 0.98	Freundlich R^2 = 0.99

Trends of As, F and NO_3 Co-adsorption with pH. Results of pH standardization are shown in Fig. 7. Initially the percent removal of all contaminants was increased with pH and reached maximum at different pH values. Fluoride and nitrate showed similar trends with pH optima at 5.5 and 6.0 and thereafter the adsorption declined drastically. On the other hand, arsenic adsorption was observed highest at pH-7. Optimum uptake of arsenic (80%), fluoride (82%) and nitrate (89%) was observed at pH-6 in 90 minutes.

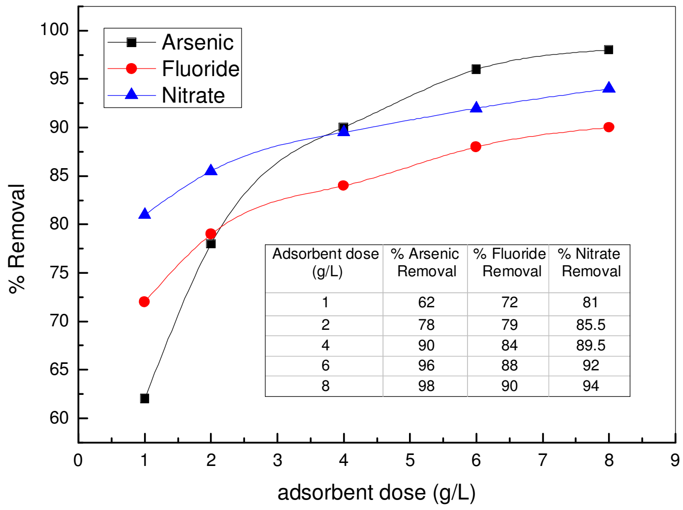
Trends of Co-adsorption with Adsorbent Dose. Arsenic showed positive relationship with adsorbent dosage and maximum adsorption of 98% was attained with 8g adsorbent dosage whereas both fluoride and nitrate adsorption was only slightly increased with the adsorbent dosage (Fig. 8). The adsorption capacities (Q_e) of As, F and NO_3 with differential adsorbent dosage are given in Table 2 Significant percent removal of each As(78%), F(79%) and NO_3(85.5%) was observed with adsorbent dosage of 2g and therefore it was taken as standard for further experimental runs.

Trends of Co-adsorption with Contact Time. In order to study the effect of contact time on co-adsorption, the adsorption experiments were run with varied time intervals ranged from 50–250 minutes. Removal of all the three contaminants was rapid and reached equilibrium in 3.5 Hrs. Rate of arsenic removal was faster followed by nitrate and fluoride (Fig. 9). More than 75% removal of As, F and NO_3 was observed in first 90 minutes, therefore, optimum contact time (90 mins) was selected for further optimization experiments.



pH	% As Removal	% F Removal	% NO3 Removal
3	60	66	69
4	70	75	76
5	76	86	82
6	80	82	89
7	84	69	78

Fig. 7. Trends of As, F and NO_3 Co-adsorption with pH.

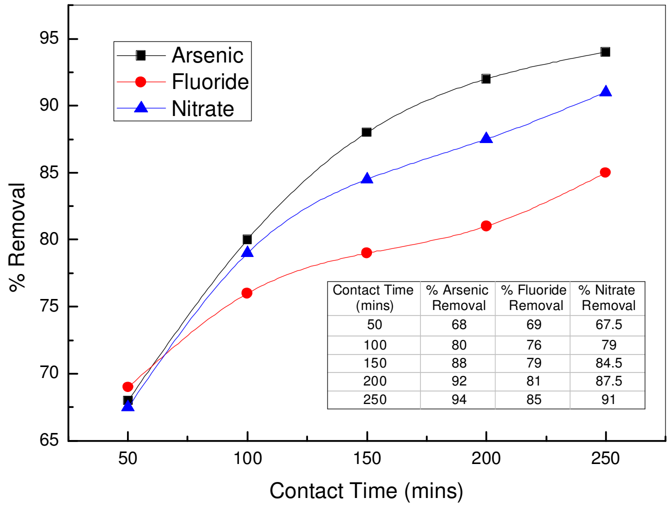


Adsorbent dose (g/L)	% Arsenic Removal	% Fluoride Removal	% Nitrate Removal
1	62	72	81
2	78	79	85.5
4	90	84	89.5
6	96	88	92
8	98	90	94

Fig. 8. Trends of As, F and NO_3 Co-adsorption with varied CuNPs dosage.

Table 2: Adsorption capacities of As, F and NO_3 obtained with varied adsorbent doses of CuNPs.

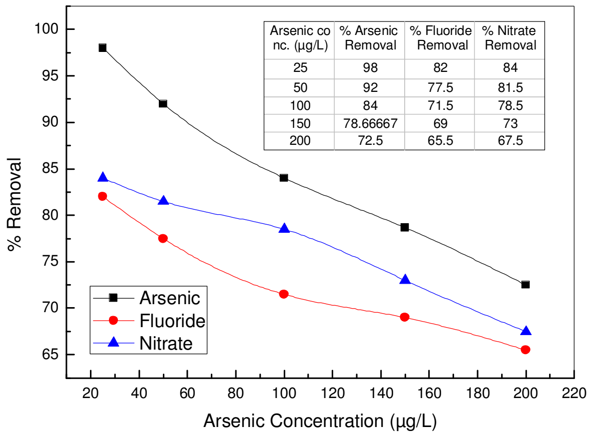
Adsorbent Dose (g/L)	Arsenic (Qe, µg/g)	Fluoride (Qe, mg/g)	Nitrate (Qe, mg/g)
1	6.2	0.72	16.2
2	3.9	0.395	8.55
4	2.25	0.21	4.475
6	1.6	0.146667	3.066667
8	1.225	0.1125	2.35



Contact Time (mins)	% Arsenic Removal	% Fluoride Removal	% Nitrate Removal
50	68	69	67.5
100	80	76	79
150	88	79	84.5
200	92	81	87.5
250	94	85	91

Fig. 9. Trends of As, F and NO_3 Co-adsorption with Time.

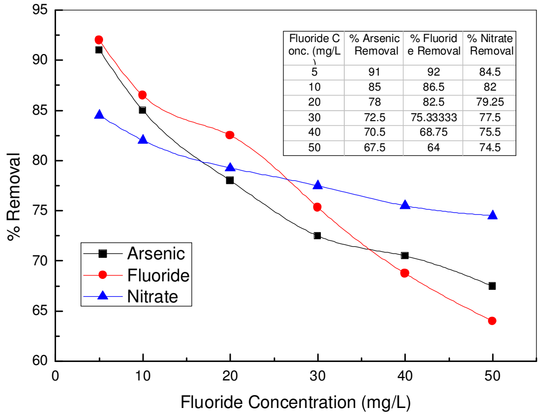
Trends of Co-adsorption with Arsenic Concentration. The influence of arsenic concentration on co-adsorption of other contaminants; fluoride and nitrate is shown in Fig. 10. The results have showed that increasing arsenic concentration from 50–250 µg/L in solution greatly reduced the removal of both fluoride and nitrate. It has been further observed that reduction in percent fluoride removal was greater than nitrate removal. With optimum As conc. = 100 µg/L, significant removal efficiencies were observed as percent removal of As (84 %), F (71.5 %) and NO_3 (78.5 %) respectively.



Arsenic conc. (µg/L)	% Arsenic Removal	% Fluoride Removal	% Nitrate Removal
25	98	82	84
50	92	77.5	81.5
100	84	71.5	78.5
150	78.66667	69	73
200	72.5	65.5	67.5

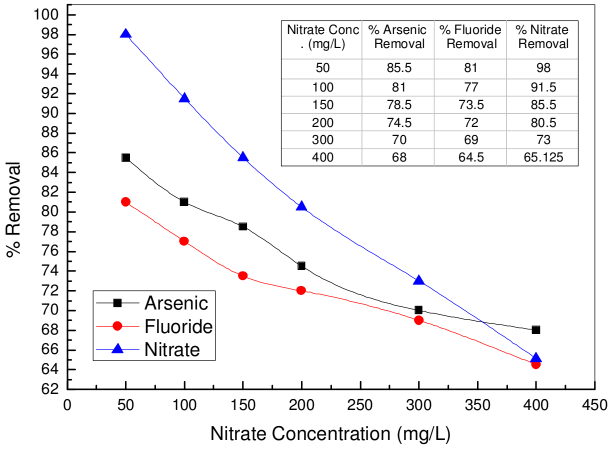
Fig. 10. Trends of As, F and NO_3 Co-adsorption with As concentration.

Trends of Co-adsorption with Fluoride Concentration. Increasing fluoride concentration also affected the adsorption of arsenic and nitrate (Fig. 11). It reduced the percent arsenic removal to a greater extent whereas percent removal of nitrate was only slightly affected indicated that fluoride and nitrate adsorption sites are unique and adsorbent can effectively removes both fluoride and nitrate simultaneously.



Fluoride Conc. (mg/L)	% Arsenic Removal	% Fluoride Removal	% Nitrate Removal
5	91	92	84.5
10	85	86.5	82
20	78	82.5	79.25
30	72.5	75.33333	77.5
40	70.5	68.75	75.5
50	67.5	64	74.5

Fig. 11. Trends of As, F and NO_3 Co-adsorption with F concentration.



Nitrate Conc. (mg/L)	% Arsenic Removal	% Fluoride Removal	% Nitrate Removal
50	85.5	81	98
100	81	77	91.5
150	78.5	73.5	85.5
200	74.5	72	80.5
300	70	69	73
400	68	64.5	65.125

Fig. 12. Trends of As, F and NO_3 Co-adsorption with NO_3 concentration.

Trends of Co-adsorption with Nitrate concentration. Following similar methodology, influence of nitrate concentration on co-adsorption was studied. Increase in nitrate concentration resulted great reduction in percent removal of all the selected contaminants. With NO_3 conc. = 200 mg/L, significant removal efficiencies were observed as 74.5% (As), 72% (F) and 80.5% (NO_3) respectively (Fig. 12).

F. Equilibrium Analysis: Isotherms

Equilibrium studies using adsorption isotherm models are important for designing an adsorption system. Two popularly used classical models; Langmuir and Freundlich were employed to the co-adsorption data. Langmuir and Freundlich graphs of arsenic, fluoride and nitrate adsorption are presented in Fig. 13, 14 and 15. The results revealed that arsenic adsorption data was in good agreement with Freundlich model and is suggestive of heterogeneous adsorption of arsenic on this adsorbent.

Fluoride adsorption followed both Langmuir and Freundlich model with high regression coefficient, R^2 = 0.981 and 0.989 and was better fitted to the Freundlich model (Fig. 13), indicating mixed type of fluoride adsorption.

Nitrate adsorption data followed Freundlich isotherm with high regression coefficient, R^2 = 0.992. Linear fit to the Freundlich isotherm suggested that nitrate adsorption is heterogeneous multilayer i.e through multiple adsorption sites.

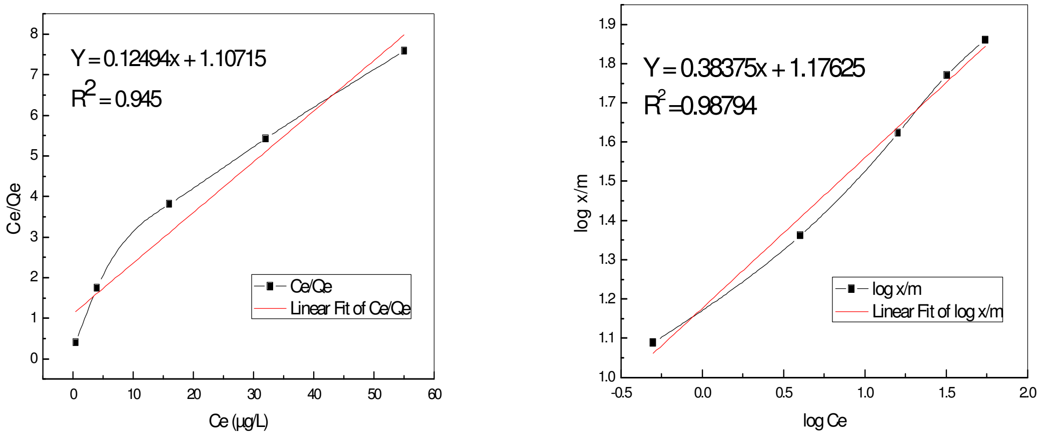


Fig. 13. Langmuir and Freundlich plot of As adsorption on CuNPs.

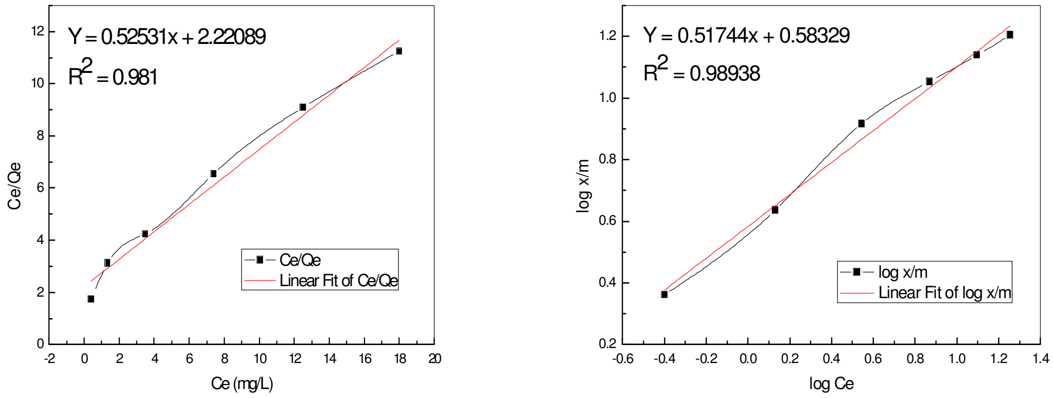


Fig. 14. Langmuir and Freundlich plot of F adsorption on CuNPs.

The Langmuir and Freundlich constants of each arsenic, fluoride and nitrate adsorption were determined under predefined conditions of pH- 6.0, adsorbent dose – 2g/L, contact time – 90 mins and are given in Table 3.

The affinity of each contaminant taken under study for CuNPs was also predicted from equilibrium parameter, R_L which was derived from following expression:

$$R_L = \frac{1}{(1+bCi)} \tag{3}$$

The R_L values calculated for all contaminant ions were below 1 which was suggestive of their favorable adsorption onto CuNPs.

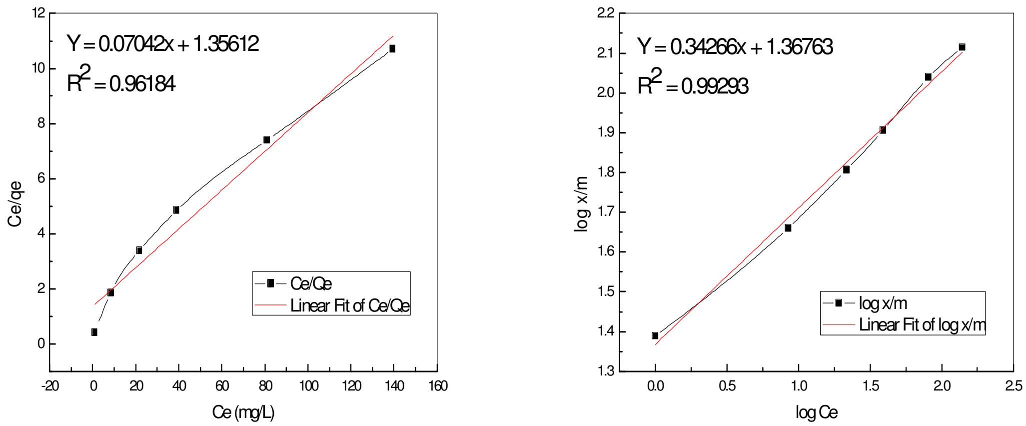


Fig. 15. Langmuir and Freundlich plot of NO_3 adsorption on CuNPs.

Table 3: Summary of adsorption isotherm parameters.

Parameter	**Copper Nanoparticles**		
Langmuir Isotherm	**Arsenic***	**Fluoride**	**Nitrate**
Q_0 (mg/g)	8.0038	1.9036	14.2005
b (mg^{-1})	0.1383	0.2365	0.0519
R^2	0.945	0.981	0.9618
R_L	0.0674	0.2972	0.0879
Freundlich Isotherm	**Arsenic**	**Fluoride**	**Nitrate**
K_f	15.0055	3.8308	23.3147
N	2.6058	1.9327	2.9183
R^2	0.9879	0.9894	0.9929

* units of arsenic adsorption capacity is µg/g.

G. Kinetic Studies

Kinetic pertaining to co-adsorption of arsenic, fluoride and nitrate on copper nanoparticles was studied by employing most common pseudo-first order and pseudo-second order models. To check validity of both models, graphs of ln (q_e - q_t) versus time and t/q_t versus time were plotted that are presented in Fig. 16 and 17. Linear fit to the models were assessed. The present co-adsorption system was found to be in good agreement with pseudo-second order model with high R^2 value for As = 0.998, F = 0.999 and NO_3 = 1.0. The values of constants k_1 and k_2 and q_e were calculated from slope and intercept values of the graphs and has been summarized in Table 4.

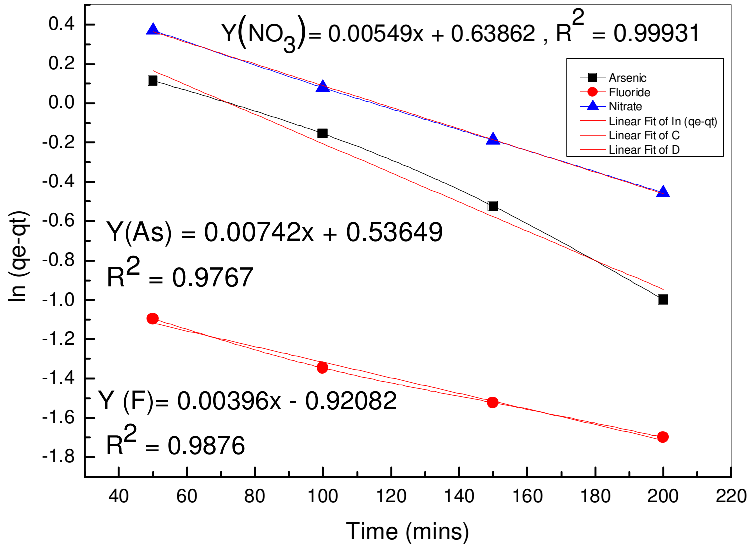


Fig. 16. Pseudo-first order kinetic plot of As, F and NO_3 co-adsorption on CuNPs.

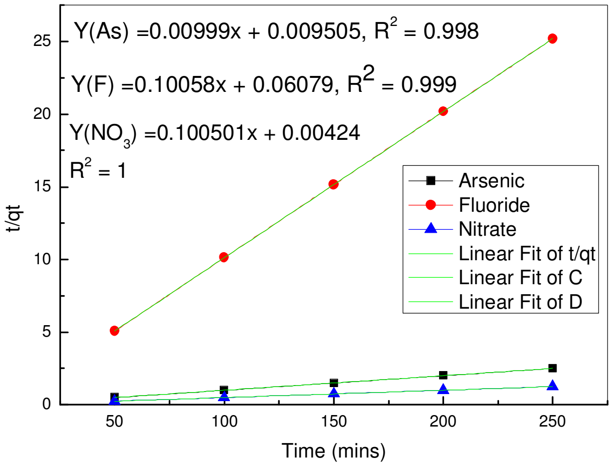


Fig. 17. Pseudo-second order kinetic plot of As, F and NO_3 co-adsorption on CuNPs.

Table 4: Summary of adsorption kinetic parameters.

Parameter	**Copper Nanoparticles**		
Pseudo-first order	**Arsenic**	**Fluoride**	**Nitrate**
K_1 (min^{-1})	0.01708	0.00911	0.01264
q_e (mg.g^{-1})	3.4395	8.3334	4.3513
R^2	0.9767	0.9876	0.9993
Pseudo-second order			
K_2 (g.mg^{-1}min^{-1})	0.0010	0.1664	0.2382
q_e (mg.g^{-1})	101.01	9.9423	9.9501
R^2	0.998	0.999	1.0

H. Co-Removal of Arsenic, Fluoride and Nitrate from Real Water Samples

Efficiency of copper nanoparticles as adsorbent for co-removal of arsenic, fluoride and nitrate was further assessed by carrying out adsorption experiments with real groundwater samples containing varied concentrations of interfering ions as well as the contaminants to be removed. The physical and hydrochemical characteristics of samples taken are presented in Table 5 and 6.

Table 5: Physical characteristics of groundwater samples studied for co-adsorption.

Sample No.	**Location**	**pH**	**TDS (mg/L)**	**EC (µS/cm)**	**Depth (ft)**
1	30˚43’49’’N 74˚43’51’’ E	6.7	1002	1814	110
2	30˚41’24’’N 74˚39’53’ E	6.9	956	1020	90
3	30˚41’10’’N 74˚44’59’’E	7.1	845	1187	40
4	30˚43’52’’N 74˚ 42’33’’E	7.3	982	1088	35
5	30˚43’31’’N 74˚42’9’’ E	6.8	794	881	45
6	30˚43’32’’N 74˚42’9’E	7.2	678	996	35
7	30˚41’31’’N 74˚ 47’48’’E	7.1	871	1224	90
8	30˚25’19’’N 74˚50’26’’E	7.7	843	664	100
9	30˚25’14’’N 74˚ 50’30’’E	7.5	966	1532	25
10	30˚25’18.52’’N 74˚50’25.45’’E	7.9	588	882	40
11	30˚43’31’’N 74˚42’8.68’’E	6.9	922	792	33
12	30˚34’9.61’’N 74˚55’20.42’’E	7.4	887	766	100
13	30˚57’8’’N 74˚37’9.12’’E	8.1	996	1246	60
14	30˚57’23’’N 74˚37’29’’E	7.2	891	1027	50
15	30˚41’33’’N 74˚47’55’’E	7.4	901	756	40
Mean Value		7.28	874.8	1058.33	
Max. Permissible limits		6.5-8.5	2000		

Table 6: Hydro chemical characteristics of groundwater samples selected for co-adsorption.

S No.	**HCO_3^-**	**CO_3^{2-}**	**Cl^-**	**SO_4^{2-}**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**As**	**F^-**	**NO_3^-**
MCL (mg/L)			500	500	200	10	200	150	10	1.5	10
1	304	29	502	159	166.4	16.7	51	26	12.22	7.82	12.74
2	344	35	562	153	147.6	11.5	72	32	25.12	5.46	24.68
3	309	30	474	139	94.5	14.8	79	43	17.08	3.23	40.64
4	350	34	446	113	159.8	13.6	112	52	17.52	2.88	55.50
5	209	28	451	119	166.7	21.9	121	47	10.88	1.94	62.38
6	221	31	412	123	161.2	18.7	119	38	8.66	4.66	37.82
7	264	32	463	106	138.8	19.4	126	39	25.36	6.42	48.68
8	235	28	482	129	124.9	22.5	69	33	23.48	7.55	64.85
9	199	30	540	117	171.5	19.3	137	51	49.56	4.22	28.54
10	232	29	467	136	157.8	25.1	74	32	17.82	3.96	36.66
11	192	25	506	142	147.4	15.6	109	27	12.54	2.98	54.83
12	181	26	476	127	118.3	18.8	123	36	11.20	10.60	67.42
13	187	29	458	120	104.9	21.4	158	41	27.42	9.24	82.22
14	203	32	477	144	129.8	20.7	123	36	13.98	5.68	49.56
15	228	33	464	149	88.2	19.3	156	46	22.66	7.26	62.81
Mean value	243.87	30.07	478.67	131.73	138.52	18.62	108.6	38.6	19.7	5.59	48.62

Besides the arsenic, fluoride and nitrate (major inorganic contaminants of GW), the common anions and cations of the collected groundwater samples were carbonate, bicarbonate, chlorides, sulphates, sodium, potassium, calcium and magnesium. Among anions, carbonates and chlorides were of major occurrence whereas potassium and calcium were the major cations observed in these samples. Sulphates were also present but majority of the samples were having sulphate ions well within the maximum permissible limits i.e 150 mg/L. Chlorides were also within the prescribed limits with the exception of four samples that were observed with marginally higher concentration i.e beyond 500 mg/L. All samples were highly contaminated with fluoride while maximum arsenic concentration observed was 49.6µg/L. To evaluate the efficacy of adsorbent under realistic conditions i.e in the presence of other natural ions, the co-adsorption experiments were performed with the real water samples having varied concentrations of ions. The experiments were conducted at all standardized conditions of pH-6.0, adsorbent dose-2 g/L for contact time- 90 minutes.

The results of co-adsorption experiments with groundwater samples are presented in table 7. The concentration of arsenic and fluoride in all samples treated with CuNPs was reduced to well below their WHO permissible limits in drinking water. 100% fluoride reduction in the groundwater samples below to its permissible level may be attributed to its highest affinity for the adsorbent as compared to arsenic and nitrate. Though arsenic has least affinity for adsorbent, maximum percent arsenic removal was due to its lesser concentrations in natural waters than the studied concentration of 200µg/L under optimized conditions. There was only one sample with initial arsenic, fluoride and nitrate concentration of 27.42, 9.24 and 82.22 mg/L (Sample 13) respectively, found to have final nitrate concentration (12.48 mg/L) slightly above the permissible limit of 10 mg/L. The probable reason for lesser percent nitrate removal may be due to high arsenic and fluoride in the sample. No significant interference from carbonate, bicarbonate, chlorides and sulphates has been observed on co-adsorption.

Table 7: Summary of results obtained for co-adsorption of As, F and NO_3 with CuNPs.

S. No	Initial arsenic conc.	Initial fluoride conc.	initial Nitrate conc.	Final arsenic conc.	Final Fluoride Conc.	Final Nitrate conc.	As	F	NO_3	% adsorption (As)	% adsorption (F)	% adsorption (NO_3)
							I - F	I - F	I - F			
	µg/L	mg/L	mg/L	µg/L	mg/L	mg/L	µg/L	mg/L	mg/L			
1	12.22	7.82	12.74	0.98	1.31	0.98	11.24	6.51	11.76	91.98036	83.24808	92.30769
2	25.12	5.46	24.68	2.16	0.73	2.94	22.96	4.73	21.74	91.40127	86.63004	88.08752
3	17.08	3.23	40.64	1.41	0.47	5.55	15.67	2.76	35.09	91.74473	85.44892	86.3435
4	17.52	2.88	55.5	1.49	0.16	6.83	16.03	2.72	48.67	91.49543	94.44444	87.69369
5	10.88	1.94	62.38	0.49	0	8.54	10.39	1.94	53.84	95.49632	100	86.30971
6	8.66	4.66	37.82	0.29	0.7	4.91	8.37	3.96	32.91	96.65127	84.97854	87.01745
7	25.36	6.42	48.68	3.84	1.3	7.82	21.52	5.12	40.86	84.85804	79.75078	83.93591
8	23.48	7.55	64.85	3.79	1.48	9.24	19.69	6.07	55.61	83.8586	80.39735	85.75173
9	49.56	4.22	28.54	5.87	0.69	4.12	43.69	3.53	24.42	88.15577	83.64929	85.56412
10	17.82	3.96	36.66	1.68	0.52	3.72	16.14	3.44	32.94	90.57239	86.86869	89.8527
11	12.54	2.98	54.83	0.83	0.19	8.26	11.71	2.79	46.57	93.38118	93.62416	84.93525
12	11.2	10.6	67.42	0.65	1.38	9.87	10.55	9.22	57.55	94.19643	86.98113	85.36043
13	27.42	9.24	82.22	3.12	1.41	12.48	24.3	7.83	69.74	88.62144	84.74026	84.82121
14	13.98	5.68	49.56	1.74	0.85	8.32	12.24	4.83	41.24	87.55365	85.03521	83.21227
15	22.66	7.26	62.81	3.58	1.21	9.77	19.08	6.05	53.04	84.20124	83.33333	84.44515

CONCLUSION AND PERSPECTIVES

Treatment of real water samples with CuNPs has reduced the levels of As, F and NO_3 below their permissible limits in drinking water under standard conditions of adsorption parameters. The adsorbent showed greater affinity for fluoride than nitrate and arsenic. Further, the adsorption did not suffer any significant interference from common ions existing naturally in groundwater. Moreover, reported antimicrobial activity of copper oxide nanoparticles coupled to their potentially high removal efficiencies for multiple contaminant removal makes them more promising material for treatment where feed water has concentrations of selected contaminants as mentioned in the study.

Also, removal efficiency of CuNPs can be further improved by controlling its size which in turn relies on optimal synthesis processes. Studies can be further extended to investigate column characteristics essential to design water treatment units. Findings of the present study can therefore be utilized to design inexpensive small household water treatment units to be employed as point of use system.

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