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Remediation of Heavy Metal Ions of Cadmium, Lead And Mercury From Its Salts Solution, By Precipitating Out Using Biological Fluid Indian Buffalo's (Bubalusarnee) Milk Subsequent Analysis of Filtrate By Icp-Aes And X Ray Fluorescence of White Flocculent Precipitate Containing Milk Protein and of Filtrate Solution.

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Abstract: *Boiled buffalos milk has been used to precipitate out metal ions of Cd,Pb and Hg from its salt solution of nitrates. The white flocculent containing metal ion and milk protein has been filtrated out the white flocculent after several wash was dried tested by Xray Fluroescence for the presence of these metals in the white flocculent. Xray Fluroescence results confirm the presence of these metal in the white flocculent .ICP-AES analysis for the filtrate solution have also been carried out for quantitative measurement of metal ion in the filtrate solutions ICP-AES results show for cadmium ion from conc of 450ppm in control solutions it becomes 95ppm,in case of Pb ion Control conc of 960ppm it becomes 15ppm and for Mercury control conc of 21660ppm it becomes 500ppm after addition of 20ml aliquot of boiled buffalo milk in 100ml of metal ions solution. The dilution effect taken in to account reduction in the metal ions conc from control solutions actually goes to the white Flocculent Milk protein by replacing Ca from the original Milk protein by toxic heavy metal ions a theory has been proposed based on the std reduction potential chart of metal ions. Thus biological fluid buffalos milk which is available in plenty in the world can be used for replacing synthetic reagents thus checking the environmental pollution thus can emerge as one of the best Green chemistry reagents and it may help in the metal processing industries of these toxic metals to ease pollution.*

I. INTRODUCTION.

Last 300 years with rapid growth of science and technology human race thought they have able to manipulate many things in the nature and make life better, however soon it has been realized the anthropogenic activities[1] leads different kind of environmental pollution it may be air pollution, water pollution , earth pollution or space pollution. Now we cannot go back to primitive stage nor we can advance in the same direction , so a middle path approach which can keep essence of modern science at the same time use natural substances which is easily available around us for utilization to protect the nature is being envisaged allover the world like for example currently the emergence of green chemistry concept [2] where the processes are being made more natural instead of final product recycling has been given top most thought. One such approach for remediation of toxic heavy metal ions Cd, Pb and Hg from its salt solution of nitrites using easily available Indian buffalos milk has been tried. In the last article of the author in the same journal cows urine have been utilized to precipitate out these toxic heavy metals has been reported[3]. The use of biological fluids such as cows urine or buffalos milk for remediation of toxic heavy metals has never been reported in internet search or else where , thus it opens new vistas for environmental pollution control. The reason of trying buffalos milk is not throwing stone in the dark which may hit the target but with proper scientific basis and understanding. Milk contains protein and Buffalos milk contain maximum protein as compared to cows , Goat and Camel milk . The protein has got natural affinities for these toxic heavy metals[4] especially because of sulfydryl groups – SH like in protein cysteine which is found in the milk[5]

II. Experimental.

Indian Buffalo (Bubalus ar nne) milk have been procured from local Buffalo shed. Milk was boiled to make it condense till the color changes to slightly reddish hue. The nitrate salts of Cadmium . Lead and Mercury was procured from local sd fine chemicals,Mumbai, India. The solutions of these heavy metal salts were made in nano pure water. The conc.of heavy metal ions in the solutions were of range 460ppm to 21000ppm. for Cd,Pb and Hg. In 100ml of the aliquot of these solutions 20ml of boiled buffalo milk were added. The addition of milk leads to precipitation of white flocculent protein material just like milk splitting phenomena but in this case white flocculent sinks at the bottom within 5-10 minutes. of addition of milk. The settling of white flocculent protein material was separated from the rest of the solution by filtrating out. The white flocculent

material was given several wash and dried. Energy Dispersion X ray Fluroescence experiments were carried out for the white flocculent materials for all the three metals Cd,Pb and Hg. as well as for the solutions which was left out after the filtration using Jordan Valley XRF instruments . ICP_AES analysis were also carried out for the metal Cd.Pb and Hg in filtrate solutions, using JY238Jobin Yohn instrument French based company. The color of the solutions of Cadmium nitrate and Lead nitrate are shown in the Figure1 before addition of buffalo milk and in Fig2 after addition of Buffalo milk. Fig.3,Fig.4 and Fig.5 are Xray Fluroescence Spectra of Metal Cd,Pb and Hg in white Flocculent of Milk Protein (shown in Redlines) with overlap presence of these of Metals in the filtrate solution.(shown in Blue lines) Table-1 Shows the chart of Std Reduction Potential of ions and Table-2 Shows the ICP-AES results of the Filtrate Metal (Cd,Pb,Hg)Solutions.

IV. Results and Discussion.

Milk is a Colloidal aqueous suspension consisting of 85 % water and rest as many components which includes carbohydrates, lipids Protein and Fats. Buffalo Milk contains about 4% protein highest among the mammals. The boiled buffalo milk contains even more protein as water gets evaporated. The main milk protein casein contains Ca and it is this element which plays a vital role to reduce other metallic ion in the solution as per Std Reduction Potential Chart shown belowTable-1. The std reduction potential chart as shown below table-1 suggests that the element as down the chart will be strong reducing agent as compare to those who are at the top of the chart. Thus Ca is the strongest reducing agent as compared to Cd, Pb and Hg. The potential values with respect to hydrogen electrode.Ca^{+2} +2e-→$Ca_{(S)}$ is -2.87 which is more negative as compare to Cd^{+2} +2e-→Cd(s), -0.40 , Pb^{+2e} +2e→Pb(s) -0.13 and Hg^{+2}+2e →Hg.(s) +0.85. Thus addition of boiled buffalos milk to salt solutions of Cadmium nitrate , Lead Nitrate and Mercury Nitrate leads to decrease of pH below isoelectric point of Milk thus proteins separate out and Ca+2 ion in protein gets replaced by Cd+2, Pb+2 and Hg+2 ions respectively in the white flocculent as per the position in the reduction potential chart and Ca^{+2} comes in the solution. This proposition has been confirmed by the results of Xray fluorescence of white flocculent protein material of milk and ICP-AES of the filtrate solutions. The ICP –AES results confirms that in case of Cadmium initial 460ppm conc of Cd ion becomes 95 ppm in the filtrate solution after addition of 20 ml of boiled buffalo Milk . Thus almost 360 ppm of Cd ion has gone to the white Flocculent of Milk Protein by replacing Calcium from Milk protein. Thus in XRF spectra of the White Flocculent the presence of Cd has been found more shown by Redlines in white Flocculent solid Material of Milk protein as compared to the filtrate Solution as shown by Blue Lines , also presence of Calcium has been found in the solution as well as in the white Flocculent of Milk protein. Since Cd std reduction potential is not far above from Ca std potential chart it is not able to replace entire calcium from white Flocculent Milk protein as compared to Pb and Hg as shown in Fig4 and Fig.5 and in Table-2 Conclusion part Column extreme right this has been shown. As per chart Table-1 since Hg is at the top as compare to Pb so the % displacement in Table-2 for Hg should have more to that of Pb.but 97% for Hg and 98% for Pb is almost same . Since there can be 2% +- error in ICP-AES measurement. and at the same time at higher % displacement the values approach to a constant asymptotically.The main Protein in milk is casein.Casein is a phosphoprotein which has phosphate group .Casein exists in milk as a calcium salt , Calcium caseinate and has an isoelectric point ofpH 4.6.,this means it is insoluble in solutions with a pH less than4.6 The pH of Milk is 6.6 when milk is added to solutions of Metalic salts the reaction which takes place are accordingly Ca-Caesinate (Milk Protein) + Solutions of Cd Nitrate or Pb Nitrate or Mercury Nitrate (which are highly acidic) thus leads to go below iso electric point of Calcium caseinate of pH 4.6 thus white flocculent protein precipitates in that process Ca^{+2} ion gets replaced by Cd+2, Pb+2 and Hg+2 metal ions .

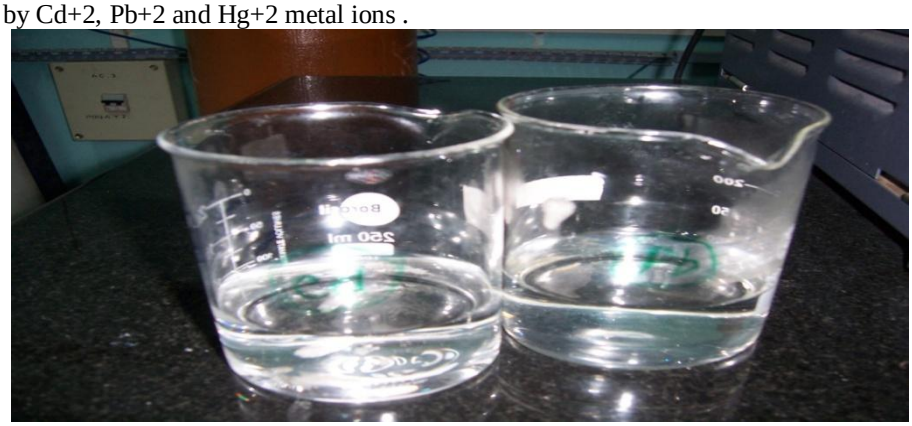

Fig.1 Solutions of Cadmium Nitrate and Lead nitrate before addition of Buffalos Milk. Note Mercury Solution has not been shown in the figure but it is exactly like that of Cd and Pb

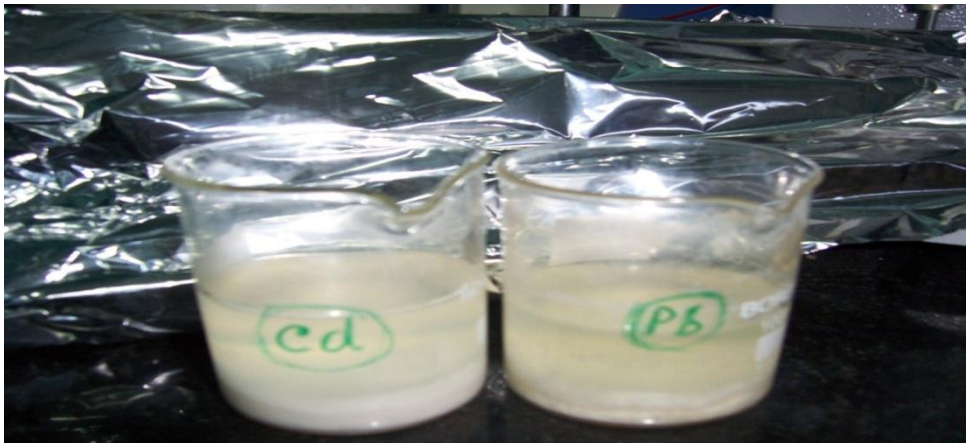

Fig.2 Solutions of Cadmium Nitrate and Lead nitrate after addition of Buffalos Milk. Unlike milk splitting by acid or rennin the white flocculent swims in whey water but here metal gets hooked with white flocculentmilk protein thus makes it to sink. Note Mercury Solution has not been shown in the figure but it is exactly like that of Cd and Pb.

Table-1

Standard Reduction Potentials at 298K, 1M, 1atm

strong oxidizing agents

HALF-REACTION	E° (V)
$F_{2(g)} + 2\,e^- \rightarrow 2\,F^-_{(aq)}$	+2.87
$O_{3(g)} + 2\,H^+_{(aq)} + 2\,e^- \rightarrow O_{2(g)} + H_2O_{(l)}$	+2.07
$Co^{3+}_{(aq)} + e^- \rightarrow Co^{2+}_{(aq)}$	+1.82
$H_2O_{2(aq)} + 2\,H^+_{(aq)} + 2\,e^- \rightarrow 2\,H_2O_{(l)}$	+1.77
$PbO_{2(s)} + 4\,H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2\,e^- \rightarrow PbSO_{4(s)} + 2\,H_2O_{(l)}$	+1.70
$Ce^{4+}_{(aq)} + e^- \rightarrow Ce^{3+}_{(aq)}$	+1.61
$MnO_4^-{}_{(aq)} + 8\,H^+_{(aq)} + 5\,e^- \rightarrow Mn^{2+}_{(aq)} + 4\,H_2O_{(l)}$	+1.51
$Au^{3+}_{(aq)} + 3\,e^- \rightarrow Au_{(s)}$	+1.50
$Cl_{2(g)} + 2\,e^- \rightarrow 2\,Cl^-_{(aq)}$	+1.36
$Cr_2O_7^{2-}{}_{(aq)} + 14\,H^+_{(aq)} + 6\,e^- \rightarrow 2\,Cr^{3+}_{(aq)} + 7\,H_2O_{(l)}$	+1.33
$MnO_{2(s)} + 4\,H^+_{(aq)} + 2\,e^- \rightarrow Mn^{2+}_{(aq)} + 2\,H_2O_{(l)}$	+1.23
$O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^- \rightarrow 2\,H_2O_{(l)}$	+1.23
$Br_{2(l)} + 2\,e^- \rightarrow 2\,Br^-_{(aq)}$	+1.07
$NO_3^-{}_{(aq)} + 4\,H^+_{(aq)} + 3\,e^- \rightarrow NO_{(g)} + 2\,H_2O_{(l)}$	+0.96
$2\,Hg^{2+}_{(aq)} + 2\,e^- \rightarrow Hg_2^{2+}{}_{(aq)}$	+0.92
$Hg_2^{2+} + 2\,e^- \rightarrow 2\,Hg_{(l)}$	+0.85
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	+0.80
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 2\,H^+_{(aq)}\,2\,e^- \rightarrow H_2O_{2(aq)}$	+0.68
$MnO_4^-{}_{(aq)} + 2\,H_2O_{(l)} + 3\,e^- \rightarrow MnO_{2(s)} + 4\,OH^-_{(aq)}$	+0.59
$I_{2(s)} + 2\,e^- \rightarrow 2\,I^-_{(aq)}$	+0.53
$O_{2(g)} + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-_{(aq)}$	+0.40
$Cu^{2+}_{(aq)} + 2\,e^- \rightarrow Cu_{(s)}$	+0.34
$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$	+0.22
$SO_4^{2-}{}_{(aq)} + 4\,H^+_{(aq)} + 2\,e^- \rightarrow SO_{2(g)} + 2\,H_2O_{(l)}$	+0.20
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$	+0.15
$Sn^{4+}_{(aq)} + 2\,e^- \rightarrow Sn^{2+}_{(aq)}$	+0.13
$2\,H^+_{(aq)} + 2\,e^- \rightarrow H_{2(g)}$	0.00
$Pb^{2+}_{(aq)} + 2\,e^- \rightarrow Pb_{(s)}$	-0.13
$Sn^{2+}_{(aq)} + 2\,e^- \rightarrow Sn_{(s)}$	-0.14
$Ni^{2+}_{(aq)} + 2\,e^- \rightarrow Ni_{(s)}$	-0.25
$Co^{2+}_{(aq)} + 2\,e^- \rightarrow Co_{(s)}$	-0.28
$PbSO_{4(s)} + 2\,e^- \rightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$	-0.31
$Cd^{2+}_{(aq)} + 2\,e^- \rightarrow Cd_{(s)}$	-0.40
$Fe^{2+}_{(aq)} + 2\,e^- \rightarrow Fe_{(s)}$	-0.44
$Cr^{3+}_{(aq)} + 3\,e^- \rightarrow Cr_{(s)}$	-0.74
$Zn^{2+}_{(aq)} + 2\,e^- \rightarrow Zn_{(s)}$	-0.76
$2\,H_2O_{(l)} + 2\,e^- \rightarrow H_{2(g)} + 2\,OH^-_{(aq)}$	-0.83
$Mn^{2+}_{(aq)} + 2\,e^- \rightarrow Mn_{(s)}$	-1.18
$Al^{3+}_{(aq)} + 3\,e^- \rightarrow Al_{(s)}$	-1.66
$Be^{2+}_{(aq)} + 2\,e^- \rightarrow Be_{(s)}$	-1.85
$Mg^{2+}_{(aq)} + 2\,e^- \rightarrow Mg_{(s)}$	-2.37
$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$	-2.71
$Ca^{2+}_{(aq)} + 2\,e^- \rightarrow Ca_{(s)}$	-2.87
$Sr^{2+}_{(aq)} + 2\,e^- \rightarrow Sr_{(s)}$	-2.89
$Ba^{2+}_{(aq)} + 2\,e^- \rightarrow Ba_{(s)}$	-2.90
$K^+_{(aq)} + e^- \rightarrow K_{(s)}$	-2.93
$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$	-3.05

strong reducing agents

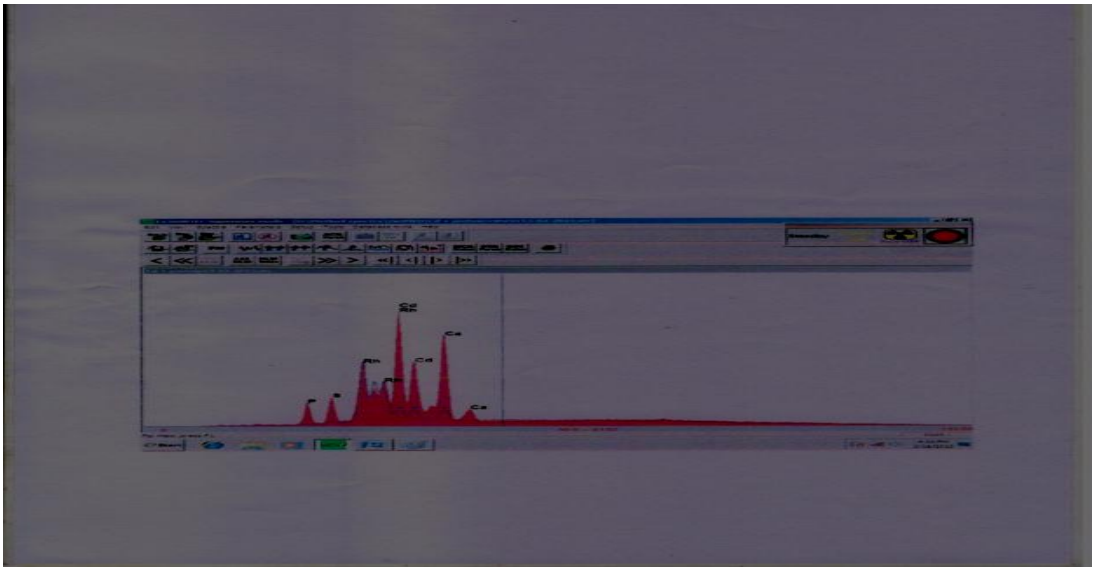

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Fig.3 Overlap Photograph of X Ray Fluroescence of Cadmium Cd in MilkwhiteFlocculent protein(Redline) And in solution after filtration (Blue line)

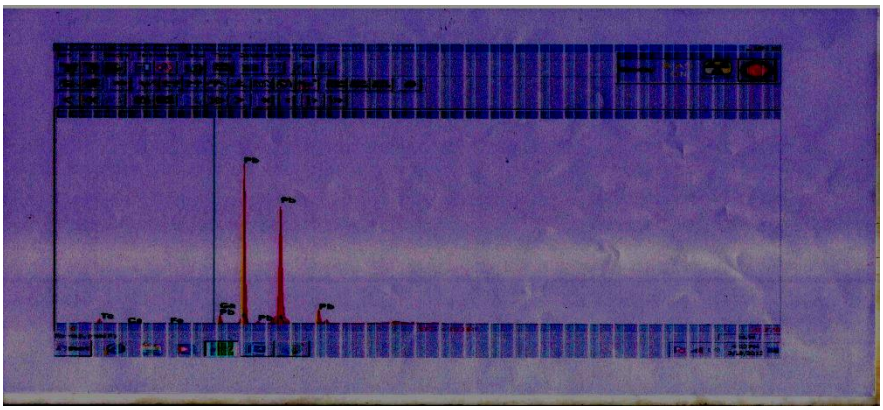

Fig.4 Overlap Photograph of XRayFluroescence of Lead Pb in Milk white Flocculent Protein(Redline) and in solution after filtration (Blue line)

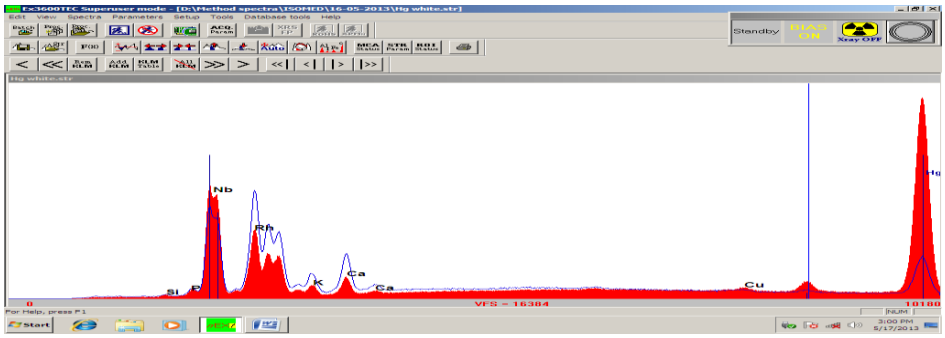

Fig.5 Overlap Photograph of XRayFluroescence of Mercury Hg in Milk white Flocculent Protein (Redline) Hg is shown extreme right in red color and in solution after filtration (Blue line)

Table-2 ICP-AES Results For the Filtrate solution of Metal ions after Addition of Buffalo Milk

Table-2 ICP-AES Results For the Filtrate solution of Metal ions after addition of Buffalo Milk.

Serial nos.	Control solutions metalion conc in ppm	After adding BuffalosMilkConc.of Metalions in solution in ppm	% of Metal ions Remained in control solutions	Conclusion % Metal ions gone towhiteFlocculent Milk protein
1	**Cd 450**	**Cd 95**	**Cd25%**	Cd 75%
2	**Pb 960**	**Pb15**	**Pb1.8%**	Pb 98%
3	**Hg 21660**	**Hg500**	Hg 2.7%	Hg 97%

V. Conclusion

I am thankful to Supreme Lord Sri Krishna the cowherd God playing flute and always surrounded by celestial cows and the Holy Mother cow as described in vedic literatures the ancient Indian texts whose causeless mercy inspired me to do such kind of findings. Iam also thankful to shri Sujoy Biswas and Shri Vijay Rupawate of UED division of BARC for helping me to carry out XRF and Icp-Aes in their division. Thus the value of cows urine and Buffalos Milk carries immense importance even in the days of Modern Science and Technology. The innocent valuable cattles should not be sent to slaughterhouses in so called advance human civilization of 21st century.

Biological Fluid Buffalo's Milk is available plenty in the world since the huge population of Buffalo around the world. Even a Buffalo gives 20 litres of Milk with huge population of buffalos in the world it is enough for environmental.requirements. India is one of the top producer milk.in the world.The milk is cheap , biodegradable and the product white flocculent which holds the toxic heavy metals after the reaction with it is also biodegradable thus easy to dispose off in the barren field or can be used as insect poison or rat poison. The metal can be recovered by burning the white flocculent material. Biological fluid like Cows urine and Buffalo's milk are used for the precipitation of Toxic heavy Metal ions like Cd,Pb and Hg are the new discoveries which hitherto nobody has ever mentioned in internet search. The biological fluid like cows urine or Buffalos milk can be used for testing the water samples in village areas where there is lack of synthetic reagents availability if it gives precipitate then water may be contaminated. Thus based on above findings the same experiments can be given trial for Arsenic, Cesium and other elements of the Periodic table particularly lanthanides and actinides series of elements.

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