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Posted by Anonymous on Fri, 2016-08-12 13:42

Can potassium permanganate waste be neutralised? I noticed in a previous question you mentioned the importance of ensuring potassium permanganate does not go down the sink because it is toxic to aquatic organisms. Your recommendation was for potassium permanganate waste to go to a chemical waste treatment facility. I was wondering if in fact the potassium permanganate can be neutralised by first acidifying it then reacting it with a non-hazardous, non-dangerous oxalate (eg potassium oxalate). Correct me if I am wrong, but from what I gather the products from this reaction are all non-hazardous and are able to be disposed of down the sink (manganese, salt and water from acid reacting with the oxygen, carbon dioxide gas).

Looking forward to your response.

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Can Potassium Permanganate waste be neutralised?

Submitted by on 31 August 2016

Answer reviewed 27 February 2023

Permanganate waste can be treated by reducing the permanganate ions, MnO_4^-, to manganese (II), Mn^{2+}. The manganese is then in a form which is soluble and does not have the strong oxidising properties of permanganate. Nevertheless, manganese in any form can potentially be harmful for the aquatic environment. In general, water authorities in Australia have low acceptance limits for manganese ions. However, as schools mostly use only low concentrations of permanganate in solution (< 0.1M), reducing the permanganate to manganese (II) and flushing the solution down the sink with dilution may be acceptable for small quantities on an infrequent basis (e.g. once per year).

The ‘standard’ method for treating permanganate waste is to use either sodium bisulfite ($NaHSO_3$) or sodium metabisulfite ($Na_2S_2O_5$) as the reducing agent to reduce permanganate to manganese (II).[1,2] Oxalic acid will also reduce permanganate to manganese (II), however the reduction may not be so efficient, as the reaction is slower than with other reagents and may require warming.[3,4] Alternatively,[5] the reduction can be carried out under conditions which will reduce permanganate to manganese (IV) as manganese dioxide, MnO_2, which is also less reactive than permanganate. As manganese dioxide is insoluble, it will form a precipitate, which should be collected and stored for disposal via by a licenced chemical waste contractor.

For larger quantities of surplus permanganate solutions, we recommend either arranging for its collection by a licensed waste contractor or, if time and resources allow, by reducing the permanganate to manganese dioxide which should then be stored for collection.

Additional information

Manganese is ubiquitous in the environment and is an essential nutrient for plants, animals and microorganisms. While there is a wide range in tolerance to manganese, it can be significantly bioconcentrated by aquatic organisms[6] and some terrestrial plants such as members of the Ericaceae family,[6] and toxic effects have been observed in sensitive species even at manganese concentrations as low as 1mg/L.[6]

Manganese is in the +7 oxidation state in the permanganate ion, making it a powerful oxidising agent. As well as the hazard associated with manganese itself, permanganate is a very reactive chemical, and therefore its release to the environment should be avoided. Treatment of waste permanganate by its reaction with a reducing agent generates a less hazardous form of manganese.

In general, water authorities in Australia accept manganese at the concentration of 10 mg/L or less. Taking into consideration the low concentrations and quantities of permanganate used in schools, we suggest that disposing of small quantities of manganese (II) solutions down the drain on an infrequent basis, such as once per year, would be acceptable. However, trade waste acceptance limits and policies vary between water catchment regions, and your local water authority should be consulted for advice specific to your region.

The pathway taken in the reaction of permanganate with a reducing agent is dependent on the pH.[7,8]

Under near neutral to slightly alkaline conditions, permanganate is reduced to manganese (IV), which precipitates from solution as black manganese dioxide, MnO_2.[7,8]

$2MnO_4^- + 3HSO_3^- ? 2MnO_2 + 2SO_4^{2-} + HSO_4^- + H_2O$

Under acidic conditions, permanganate is reduced to manganese (II), giving a colourless to faint pink solution. [1,7,8]

$2MnO_4^- + 5HSO_3^- + H^+ ? 2Mn^{2+} + 5SO_4^- + 3H_2O$

Unlike permanganate and manganese dioxide, manganese (II) is not regarded as an oxidant, and is the most stable of the manganese oxidation states in neutral solution and under environmental conditions.[6,7]

Using oxalic acid as the reducing agent under acidic conditions, manganese (II) and carbon dioxide are produced.[3,4]

$2MnO_4^- + 6H_3O^+ + 5H_2C_2O_4 ? 2Mn^{2+} + 14H_2O + 10CO_2$

We have not found any reference to the use of oxalic acid as a reducing agent for treating permanganate waste, however, nor can we find any strong argument against doing so. Both reagents are fairly inexpensive. Compared with bisulfite, oxalic acid is more hazardous to health, but less so for the environment, as it will biodegrade. The reaction of permanganate with sulfite is fast, whereas the reaction with oxalic acid may take up to 20 minutes and may require warming.[3,4]

For small quantities, we suggest the following procedure:[1,2]

To treat 500mL of 0.1M $KMnO_4$ solution:

1. Acidify the permanganate solution by addition of dilute sulfuric acid (e.g for the given quantity, add 10 mL of 2M sulfuric acid).
2. Prepare a solution of ~10% sodium bisulfite ($NaHSO_3$) by dissolving 10 g of the salt per 100mL of water. (Alternatively, prepare the solution using sodium metabisulfite ($Na_2S_2O_5$), also from 10 g of the salt per 100mL). 300 mL of bisulfite solution should be sufficient to treat the given quantity of permanganate solution.
3. Working in a fume cupboard, slowly, and with stirring, add the bisulfite solution to the permanganate solution. The resulting solution should become colourless. If permanganate still remains, add a further portion of bisulfite solution. Flush the solution down the sink with further dilution.

In the procedure of Lunn and Sansone,[5] the permanganate ion is reduced under basic conditions. The reduced manganese ions are allowed to air-oxidise to give manganese dioxide, which is then collected by filtration and stored.

To treat 100 mL of 5% permanganate solution:[9]

1. Add the permanganate solution to 100 mL of 2M sodium hydroxide solution.
2. To this solution add 10 g of sodium metabisulfite.
3. If, after stirring, the permanganate colour remains, add a further small portion of sodium metabisulfite.
4. Stir the mixture for 30 minutes, then collect the precipitated manganese dioxide by filtration. Allow the filter cake to dry, place into a suitable labelled container and store for collection.
5. Neutralise the filtrate to within pH 6–8, then dilute with an equal volume of water and flush down the sink.

Related questions that we have previously answered: Potassium permanganate

References

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[8] Pearson, R. S. 1988. ‘*Manganese Color Reactions’*, Journal of Chemical Education*,* 1988, 65(5), 451-452.

[9] Adapted from Lunn and Sansone’s procedure, reference 5.

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